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THE SYNTHESIS AND CHARACTERISATION OF AROMATIC HYPERBRANCHED POLYESTERS

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A thesis submitted for the degree of Doctor of Philosophy at the University of Durham

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Abstract

The Synthesis and Characterisation of Aromatic Hyperbranched Polyesters

Angela Keeney PhD Thesis October 1998

We report here a synthetic strategy used to prepare the AB_2 dimethyl 5-(ω-hydroxyalkoxy)isophthalate monomers containing between 3 and 6 methylene units in the alkylene chain. The hyperbranched polyesters derived from these monomers have been made in a simple one step condensation reaction, and materials with a range of molecular weights have been produced.

The influence of the alkylene chain length on the physical properties of these hyperbranched polymers has been investigated. Structural and physical characterisation of these materials has been carried out using a variety of analytical techniques including SEC, MALDI-TOF MS, DSC, quantitative ^{13}C nmr spectroscopy, and dilution viscometry. Results arising from this work, such as evidence for cyclisation products, will be discussed.

In order to investigate differences observed in the growth of molecular weight for the hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalates), a range of hyperbranched copolyesters and polymer blends have been prepared. Results obtained from characterisation of these materials using the techniques described above will be discussed.

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Finally, I would like to thank <u>all</u> my family, especially my parents for all their love and support throughout my life, I am eternally grateful.

Memorandum

The work reported in this thesis has been carried out at the Durham site of the Interdisciplinary Research Centre in Polymer Science and Technology between October 1995 and September 1998. This work has not been submitted for any other degree either in Durham or elsewhere and is the original work of the author except where acknowledged by means of appropriate reference.

Statement of Copyright

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CHAPTER ONE

AN INTRODUCTION TO HYPERBRANCHED POLYMERS

1.0 Introduction

The increasing use of synthetic polymers in all aspects of our life has stimulated the search by industry for more versatile polymeric materials covering a range of properties. Consequently, the control of macromolecular structure and the realisation that this can lead to the development of new polymeric materials with improved and/or new mechanical and physical properties has recently become an important feature of research in polymer science. The properties of a polymer depend on its chemical structure (i.e. the type, sequential and stereochemical organisation of the monomer repeat units in the polymer chain), its spacial organisation (i.e. the chain conformation and crystalline organisation), the distribution of chain lengths, and whether the polymer is linear, branched or cross-linked. Until recently the quest for materials with new or enhanced properties had focussed on variation of molecular architecture of conventional polymers (i.e. linear and branched), whose syntheses were well established. However, over the past decade the syntheses of polymers with novel topologies, (i.e. dendrimers, hyperbranched polymers, rods, cantenanes and rotaxanes), has been an area of intensive research in both academia and industry. The novel topologies and architectures presented by such materials are expected to generate properties which are significantly different from those of conventional polymers, the hope being that these different properties may prove technologically useful.

Dendritic macromolecules, encompassing both dendrimers and hyperbranched polymers, are one example of such novel topology polymers. Their extensively branched structures, and the consequently large number of end groups, are anticipated to induce new and intriguing properties in such materials. The work reported in this thesis is related specifically to hyperbranched polymers, therefore the following sections are intended to explain what hyperbranched polymers are, how such materials may be synthesised, what properties they possess and some of their potential applications.

However, since work in this area of polymer science began with dendrimers, it is useful to describe first what dendrimers are and how these materials are constructed, before discussing hyperbranched polymers in detail. Finally the background and aim of the research reported in this thesis will be described.

1.1 Dendrimers

Dendrimers are highly branched, monodisperse polymers which have well defined molecular weight, structure, size and organisation. Typically, a dendrimer contains three basic units, the core moiety C, the interior building blocks B, and the terminal or surface groups, S, see Figure 1.1. The interior building blocks B are arranged into layers, or generations, around the core moiety resulting in a highly symmetrical cascade structure.

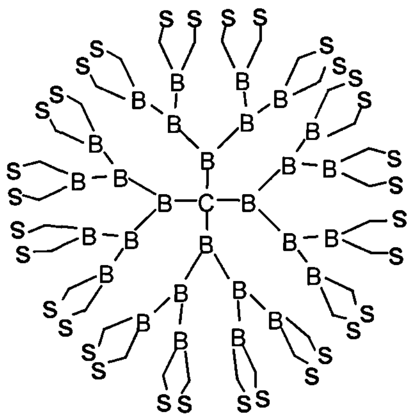


Figure 1.1: Idealised diagram of a dendrimer

The branching geometry of the various internal building blocks, coupled with steric constraints, means that the dendrimers are three-dimensional objects rather than the two dimensional structure shown in Figure 1.1. The dendrimer fills space adopting a globular form and above a certain size can be considered to be spherical.

Dendrimer precursors, described as 'cascade' molecules, were first reported in

1978 by Vogtle and co-workers[1] These workers reported the synthesis of 'cascade' molecules as part of a programme of study directed to constructing compounds with large molecular cavities for the study of Host-Guest interactions (see Figure 1.2); they were not primarily concerned with dendrimer synthesis.

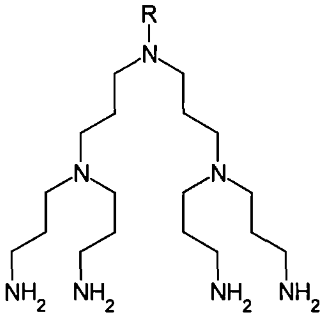


Figure 1.2: The Vögtle Cascade Structure.

Extensive work on the synthesis and characterisation of dendrimers was not reported until 1985 by Tomalia[2] with the synthesis of regularly branched poly(amidoamine)s, which he called Starburst (PAMAM) Dendrimers. At the same time Newkome[3] reported the synthesis of highly branched molecules called 'arborols' where each layer or generation had a different constitution. It became apparent that these unique macromolecules exhibited unusual physical properties generating much interest in this area of polymer science. Consequently the number of groups designing dendrimer syntheses and the variety of dendrimers made has grown immensely, with notable contributions made from research groups led by Fréchet[4] and Meijer.[5]

1.1.1 Construction of dendrimers

Dendrimers are essentially prepared through either a divergent or convergent approach, the fundamental difference between these synthetic routes being the direction of growth. Dendrimers were originally prepared via the divergent method[2,3] where construction of the dendrimer begins with the core molecule and proceeds outwards, as shown schematically in Figure 1.3. A central core molecule is reacted with two or more protected branching units, whose protecting groups are subsequently removed to give reactive terminal functionalities. These can be coupled with further protected branching units, with repetition of these steps to yield dendrimers. However, at higher generations the surface of the dendrimer becomes increasingly congested which can lead to incomplete reactions, appearing as defects in the dendrimer structure.

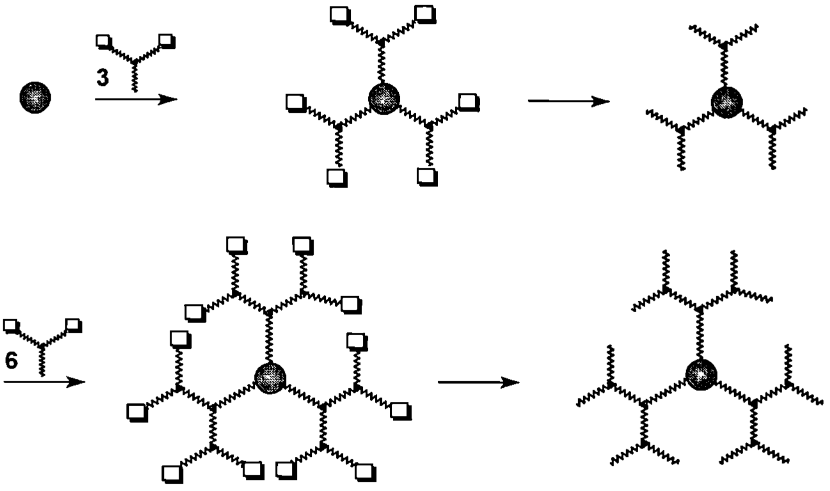


Figure 1.3: A schematic representation of the divergent route

In the convergent route, developed later by Hawker and Fréchet,[4] construction begins at what will eventually be the outer surface of the dendrimer and proceeds inwards. A series of dendritic wedges are constructed which are protected at the focus. Removal of these protected groups allows the wedge to be attached to a central core molecule (see Figure 1.4).

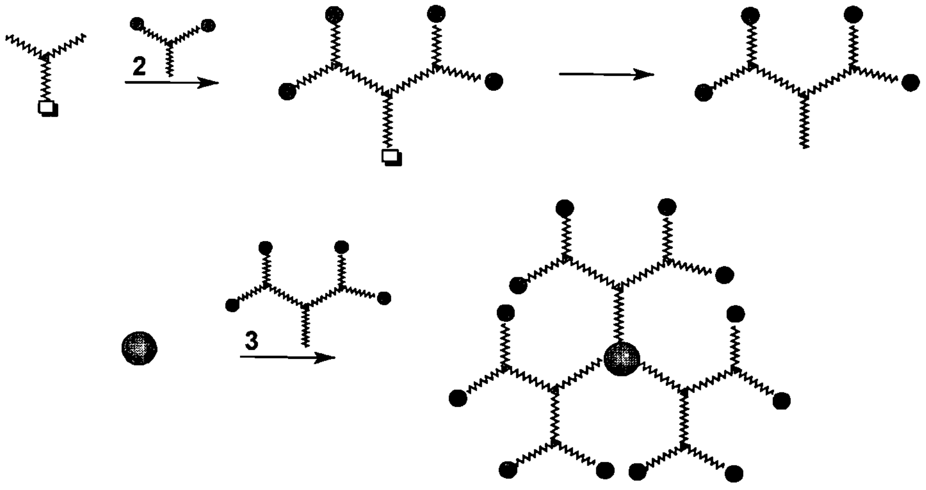


Figure 1.4: A schematic representation of the convergent route

This synthetic approach is more versatile, allowing different dendritic wedges or core molecules to be incorporated in the dendrimer. However, difficulties can arise when attaching several large dendritic wedges to a central core molecule due to steric hindrance.

Both these synthetic routes involve numerous protection, deprotection and purification steps which are in most cases costly and time-consuming. Generally dendrimer preparations are restricted to relatively small scale operations, a significant exception being the poly(propylene imine) dendrimers introduced by DSM.[5]

Recently Rannard and Davies[6] reported the preparation of a variety of highly functionalised dendritic structures on a moderate scale using reactions of 1,1'-carbonyldiimidazole (CDI) with amines, alcohols and carboxylic acids (see Figure1.5).

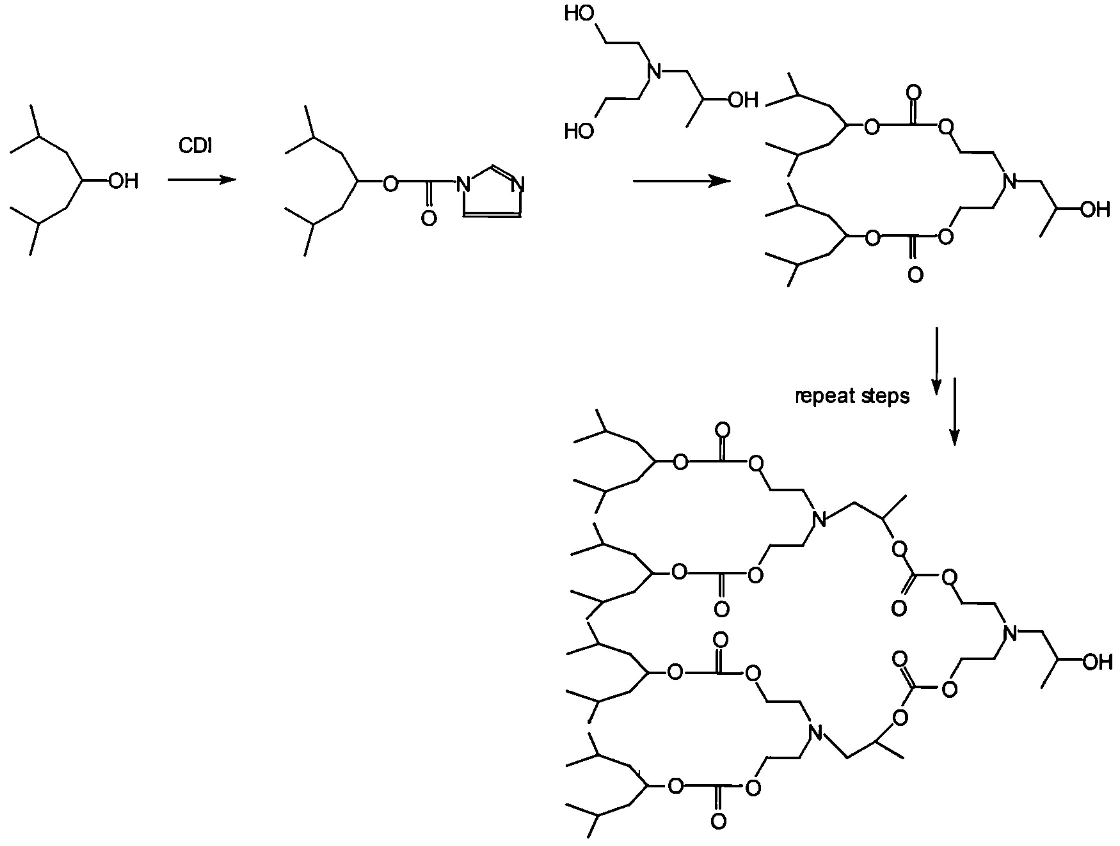


Figure 1.5: Highly selective CDI chemistry used to prepare dendrimers

The intermediate imidazole derivatives were shown to have high selectivity between primary and secondary functionality in subsequent reactions with amines and alcohols. Consequently, syntheses where protection-deprotection chemistry was not required could be designed and the synthesis of large dendritic wedges and dendrimers was achieved via significantly fewer steps than earlier procedures. This chemistry shows considerable flexibility and gives access to a variety of structures.

Due to the rigorous procedures required to construct dendrimers using the divergent or convergent routes, very few commercial dendrimers are currently available. Although there have been extensive claims of the potential uses of dendrimers, to the best of the author's knowledge none have been found to date.

1.2 Hyperbranched polymers

The fundamental concepts underlying the synthesis of highly branched macromolecules were first discussed by Flory[7] in 1952. In his theoretical treatment, Flory discussed the preparation of polymers from $AB_{f\text{-}1}$ type monomers, containing one A functional group and f-1 B functional groups, where f represents the number of functional groups in the monomer. In order to simplify his statistical analysis Flory made the following assumptions:

1. The only reaction which can occur is between the A and B functionality in the polymerisation step.
2. No intramolecular cyclisation reactions can occur.
3. The reactivity of A and B are assumed to be independent of their location in the molecule.

Flory predicted that for the polymeristion of x $AB_{f\text{-}1}$ monomers this would produce highly branched, three-dimensional structures free from cross-links, therefore creating a novel branched polymeric material. The resulting molecule contains 1 A functionality and (fx–2x+1) unreacted B functionalities (see Figure 1.6).

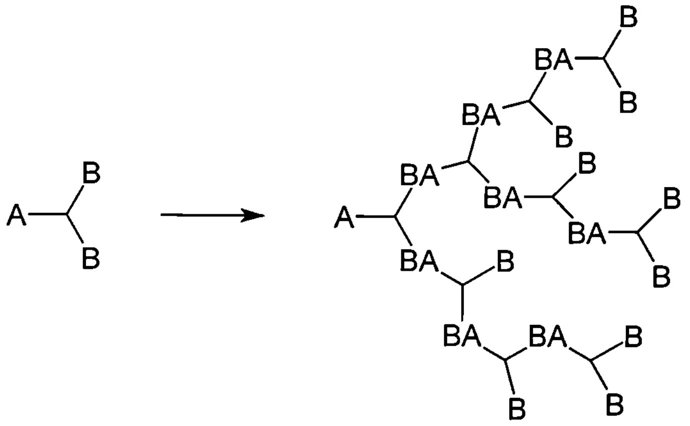


Figure 1.6: A schematic view of the polymerisation of an AB_2 monomer.

As the highly branched polymers proposed by Flory were predicted to be non-entangled and noncrystalline (i.e. possessing poor material properties) this area of research was not pursued. Interest remerged in the early 1990's when Kim and Webster presented hyperbranched poly(phenylene)s with intriguing properties and coined the term 'hyperbranched'.[8]

Although dendrimers and hyperbranched polymers are both derived from AB_{f-1} monomers, their structural differences originate from the synthetic strategies used to prepare them. This is shown schematically in Figure 1.7, which highlights the differences between hyperbranched and dendritic structures derived from AB_2 monomers. Hyperbranched polymers are prepared via a one step polymerisation of AB_{f-1} monomers, since the addition of each monomer takes place randomly, the growth of the polymer is uncontrolled. Consequently as the polymer grows steric constraints will become an important factor giving rise to incomplete reaction of the all the B groups in each monomer repeat unit.

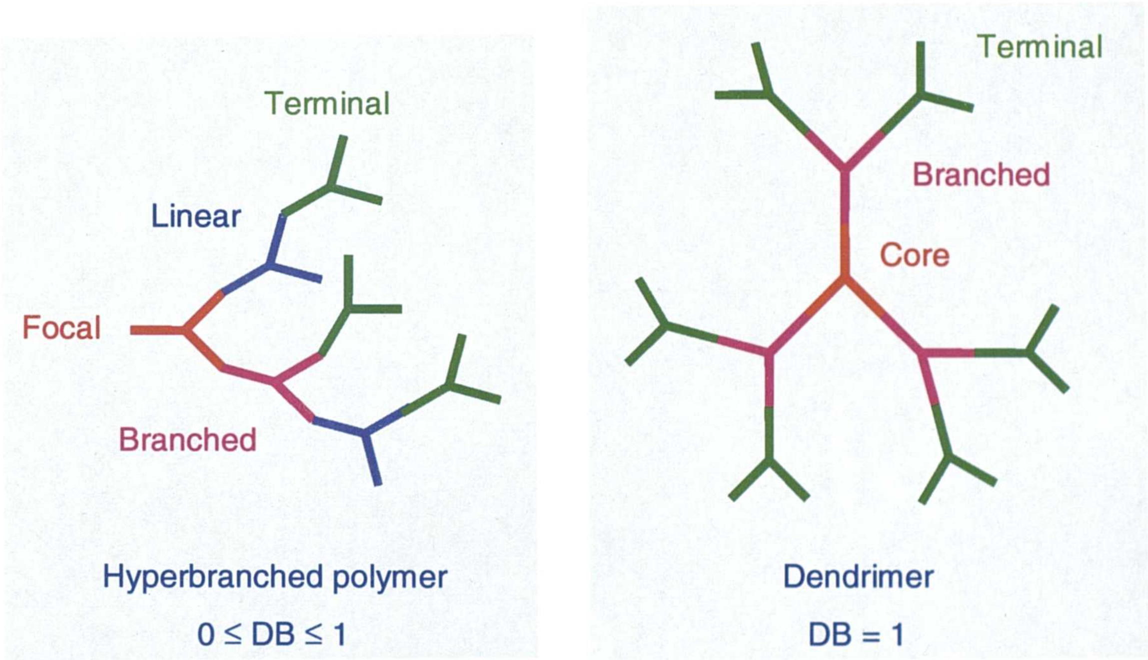


Figure 1.7: Schematic representation of a hyperbranched polymer and a dendrimer (DB = degree of branching, see text)

The resulting hyperbranched structure contains four different types of monomer residue units namely the focal, linear, branched and terminal units. Providing an intramolecular cyclisation reaction has not occurred, the focal unit contains an A functionality. Where only one of the B functionalities in the AB_2 monomer has reacted there is a linear unit, similarly, where both B groups have reacted there is a branched unit, and where neither B groups have reacted there is a terminal unit. The unreacted B groups are referred to as terminal functional groups regardless of the unit they originate from (i.e. terminal or linear).

Dendrimers however contain a core molecule from which the polymer grows and only two monomer residue units, namely branched and terminal. The rigorous synthetic methods used to prepare dendrimers ensure that no linear units are formed and, in principle, perfectly branched, monodisperse polymers result. This is in sharp contrast to hyperbranched polymers where the uncontrollable nature of the one step polymerisation results in polymers which are usually polydisperse in both molecular weight and structure. The existence of linear units within the polymer structure account for the imperfect branching found in hyperbranched polymers when compared with dendrimers. However, by allowing the formation of linear units their synthesis is much more straightforward to perform with the hyperbranched polymers being cheaper and easier to produce, making their preparation on a large scale more feasible than that of dendrimers. Since the hyperbranched polymers retain some of the structural features and properties of dendrimers this has made them commercially attractive generating much interest from both academia and industry in recent years.

In order to describe the proportion of the different units (branched, linear and terminal) present within a hyperbranhced polymer the concept of degree of branching was first introduced by Frechet[9] (Equation 1.1).

$$DB = \frac{N_B + N_T}{N_B + N_L + N_T} \qquad \text{Equation 1.1}$$

Where N_B, N_L and N_T refer to the number of branched, linear and terminal units located in the hyperbranched polymer respectively.

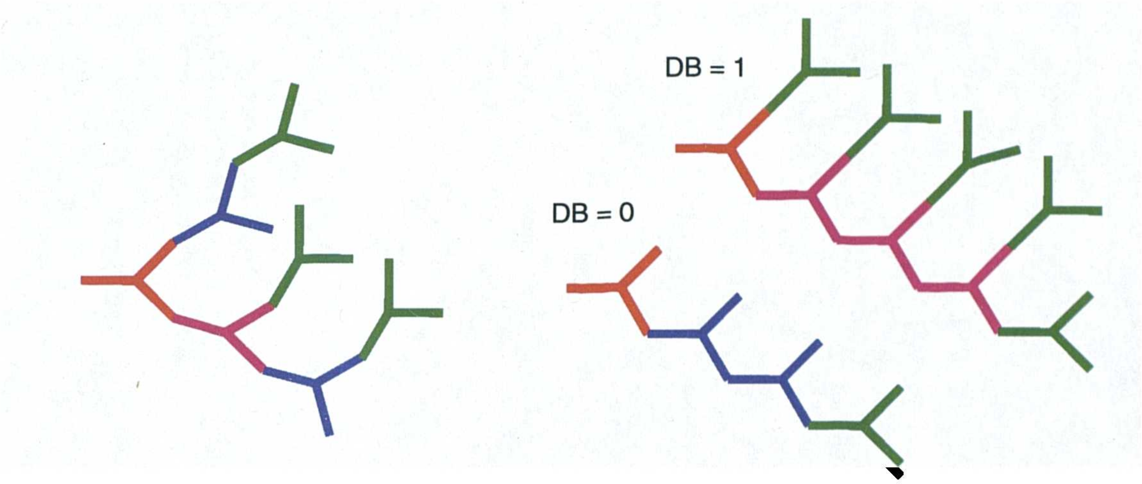
In Frechet's expression unreacted monomers contributed towards number of terminal groups in a polymer and thus contributed to the degree of branching resulting in misleading values of DB, particularly for low conversion products. However, recently this equation has been modified by Frey[10] (equation 1.2), in Frey's expression terminal groups are not counted and the expression is valid for both low and high molecular weight hyperbranched polymers. For high conversion products, both expressions give the same values of DB.

$$DB = \frac{2N_B}{2N_B + N_L} \qquad \text{Equation 1.2}$$

Where N_B and N_L refer to the number of branched and linear units located in the hyperbranched polymer.

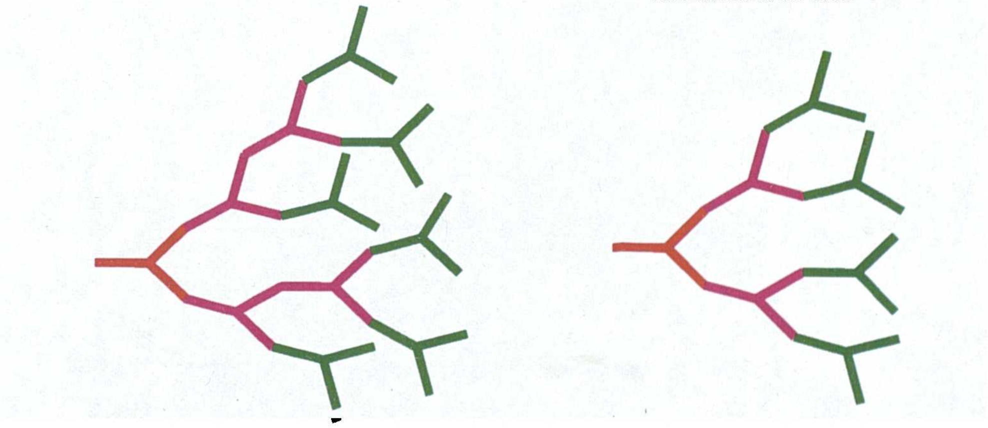
Using this expression (equation 1.2) a degree of branching equal to zero is obtained for a linear polymer (containing no branched units), whilst a perfectly branched dendrimer (containing no linear units) would have a degree of branching equal to one. Hyperbranched polymers are expected to have a degree of branching between zero and one depending on the proportion of linear units present in the polymer structure. Although it is theoretically possible to form hyperbranched structures which resemble those of linear polymers or of dendrimers (see Figure 1.8), Frey and co-workers[10] have shown in their theoretical treatment of an AB_2 polymerisation that the expected degree of branching for a hyperbranched polymer, with a statistical distribution of the different units, is 0.5.

The degree of branching is determined in most cases by nuclear magnetic resonance (nmr) spectroscopy or where spectroscopic methods fail by chemical degradation. Typically degrees of branching of ~0.5 have been obtained for AB_2 based hyperbranched polymers,[11] agreeing well with the expected degree of branching calculated by Frey. Recently hyperbranched polymers with degrees of branching approaching 1 have been reported by Hobson and Feast,[12] with their hyperbranched poly(amidoamine)s, and by Fomine *et al*,[13] with their hyperbranched coumarin containing polymers. However a DB = 1 in a hyperbranched polymer does not necessarily indicate the formation of perfect dendrimer topology, since a perfectly branched hyperbranched polymer with irregular growth would also have DB = 1, this is illustrated in Figure 1.8. It is important to realise that the degree of branching is not an indicator of topology; for example, in Figure 1.8 there are examples of AB_2 polymers with essentially linear topologies but with DB values of 0 and 1. The degree of branching for hyperbranched polymers is discussed in more detail in Chapter 5.



Hyperbranched polymer
Statistical branching DB =0.5

Hyperbranched polymers
with linear topologies and
DB values of 0 or 1



DB = 1
Hyperbranched polymer
perfect branching
irregular growth

DB = 1
Dendron
perfect branching
regular growth

Figure 1.8: Variations in the extent of branching and topology in AB_2 hyperbranched polymers

Whereas dendrimers are truly unique molecules, hyperbranched polymers resemble conventional polymers in that they display dispersity in molecular weight and structure. During the polymerisation the addition of each monomer takes place randomly, therefore a large number of structural isomers can be formed even for a given molecular weight and degree of branching. Figure 1.9 shows two hyperbranched poly(phenylene)s that have the same molecular weight and degree of branching but differ in structure. This variation in geometry could influence properties such as the solubility or the solid-state packing structure of the polymer.

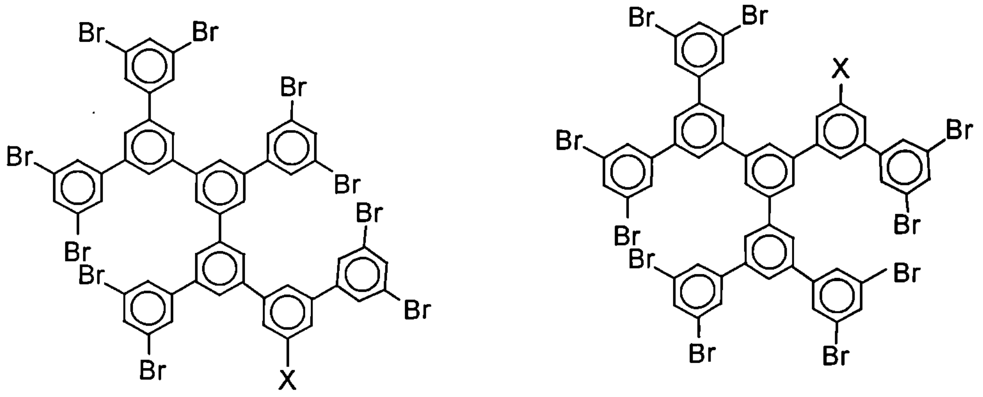


Figure 1.9: Two hyperbranched poly(phenylene)s

This dispersity of isomerism is difficult to quantify, however Flory in his theoretical treatment of the polymerisation of AB_{f-1} monomers, derived the expression below to calculate the number of possible configurations (structures) for a hyperbranched polymer at a particular degree of polymerisation x, and for a monomer with functionality f:[7]

$$\frac{(fx-x)!}{(fx-2x+1)!x!}$$

The table overleaf shows the number of possible configurations, calculated using this expression, for a hyperbranched polymer derived from an AB_2 (f=3) and AB_3 (f–4) monomer, with degrees of polymerisation of 4, 10, 22, 46. These degrees of polymerisation correspond to those found in an AB_2 dendrimer of generation 1, 2, 3 and 4, which by definition of a dendrimer, have only 1 configuration. It is clear from these calculations that the number of isomers increases very rapidly with the complexity of the monomer and the molecular weight of the polymer.

Number of configurations in an AB_2 and AB_3 hyperbranched polymer:

Degree of polymerisation x	Generation number for AB_2 dendrimers	Number of configurations	
		AB_2 $f = 3$	AB_3 $f = 4$
4	1	14	55
10	2	16 800	1 430 000
22	3	9.15×10^{10}	4.05×10^{15}
46	4	8.74×10^{24}	1.09×10^{35}

It should be noted that the same assumptions stated previously (1-3) apply to the expression given above. To simplify enumeration of configurations, Flory assumes also that all the B groups in the polymer are distinguishable, thus the dimeric structures shown below will be regarded as different from each another.

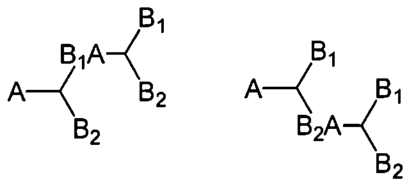


Figure 1.10: Two distinguishable dimeric structures

Although throughout Flory's statistical treatment of highly branched molecules he assumes that intramolecular cyclisation reactions can not occur between an A and B group within the same molecule, experimentally this has been found not to be the case.[14,15] Analysis of hyperbranched polymers by nmr spectroscopy or MALDI-TOF (matrix assisted laser desorption ionisation – time of flight) mass spectrometry have shown the presence of cyclic hyperbranched material. From reports in the literature of cyclised hyperbranched polymers it appears that this cyclisation is system specific; this matter is discussed in detail in Chapter 5.

1.2.1 Molecular weight distributions in hyperbranched polymers

The theoretical treatment of the polymerisation of AB_{f-1} monomers was first considered by Flory over forty years ago, using a statistical approach he derived equations to describe the molecular weight distribution in the resulting highly branched molecules.[7] Before examining these equations it is useful to consider the much simpler case of the step-growth polymerisation of AB monomers. The statistical arguments are based on the probabilities of A and B reacting to provide a distribution of species of varied size and structure. In order to simplify the statistical analysis the following assumptions were made:

1. The only reaction which can occur is between the A and B functionality in the polymerisation step.
2. No intramolecular cyclisation reactions can occur.
3. The reactivity of A and B are assumed to be independent of their location in the molecule.

If N_o is the original number of AB molecules present in a system, and N is the number of all the molecules remaining after time t, then the total number of functional groups of either A or B which have reacted is $(N_o - N)$. At the time t the extent of reaction, p, is given by:

$$p = (N_o - N)/N_o \quad \text{or} \quad N = N_o(1-p) \qquad \text{Equation 1.3}$$

The term p could equally be called the probability of reaction of A or B and in this case, since we have a stoichiometric balance of A and B, p_A and p_B are equal.

The number average degree of polymerisation, χ_n, is given by $\chi_n = N_o/N$. By combining this equation with equation 1.3 we obtain the Carother's equation:

$$\chi_n = 1/(1\text{-p}) \qquad \text{Equation 1.4}$$

The Carother's equation provides a measure of the number average size distribution in the product of an AB polymerisation.

In the polymerisation of x AB molecules;

$$\text{i.e. } x\ \text{A—B} \rightarrow \text{A—[BA]}_{x\text{-}1}\text{—B}$$

the probability that A, or B, has reacted is p^{x-1}, the probability that A, or B, has not reacted is 1-p and so the probability of finding a molecule with a degree of polymerisation x is the product of these two probabilities:

$$(1\text{-p})\, p^{x-1}$$

If we start with N_0 molecules of AB and have N molecules in the sample at a particular time, we can write an expression for the fraction of molecules, N_x, having a degree of polymerisation of x:

$$N_x = N(1\text{-p})\, p^{x-1} \qquad \text{Equation 1.5}$$

Substituting from equation 1.3 we obtain:

$$N_x = N_o(1\text{-p})^2 p^{x-1} \qquad \text{Equation 1.6}$$

This expression gives the mole fraction of molecules N_x having a degree of polymerisation x.

The weight fraction of molecules w_x, having a degree of polymerisation x is given by:

$$w_x = x(1\text{-p})^2 p^{x-1} \qquad \text{Equation 1.7}$$

The number and weight average molecular weights, M_n and M_w, for an AB system are defined as:

$$M_n = M_o/(1\text{-p}) \qquad \text{Equation 1.8}$$

$$M_w = M_o(1\text{+p})/(1\text{-p}) \qquad \text{Equation 1.9}$$

where M_0 represents the repeat unit mass.

By combining equations 1.8 and 1.9 the polydispersity (M_w/M_n) of the polymer is obtained:

$$M_w/M_n = 1+p \qquad \text{Equation 1.10}$$

Clearly for a linear polymer derived from the step growth polymerisation of AB monomers, the polydispersity tends to 2 as the reaction proceeds (i.e. as p approaches 1).

Using the same statistical approach, Flory has addressed the step growth polymerisation of AB_{f-1} monomers, where f represents the number of reactive functional groups in the monomer. In order to simplify the statistical analysis the following assumptions were made:

1. The only reaction which can occur is between the A and B functionality in the polymerisation step.
2. No intramolecular cyclisation reactions can occur.
3. The reactivity of A and B are assumed to be independent of their location in the molecule.
4. All the B groups are distinguishable, regardless of their location in the polymer.

If one considers x AB_{f-1} monomers reacting together, the resulting molecule will contain 1 A group and ($fx-2x+1$) unreacted B groups. The branching probability, α, (defined as the probability that a functional group on a branch unit is connected to another branch unit) is equal to the fraction of B groups which have reacted, p_B. Since the numbers of A and B groups which react must be equal then $p_B(f\text{-}1) = p_A$, where p_A represents the extent of reaction, or the fraction of A groups reacted.

$$\text{Replacing } p_A \text{ with p: } \alpha = p/(f\text{-}1) \qquad \text{Equation 1.11}$$

The maximum value which α may approach but never reach is $1/f\text{-}1$, therefore for the polymerisation of an AB_2 monomer, where $f = 3$, the maximum value of α theoretically possible is 0.5.

Flory derived expressions to describe the molecular weight distribution for polymers derived from $AB_{f\text{-}1}$ monomers. The mathematical argument is complex and lengthy and the expressions obtained are simply presented below:

$$N_x = \frac{(fx-x)!\quad \alpha^{x-1}.(1-\alpha)^{(fx-2x+1)}}{(fx-2x+1)!x!} \qquad \text{Equation 1.12}$$

$$w_x = [1-\alpha(f-1)]x.\ \frac{(fx-x)!\quad \alpha^{x-1}.(1-\alpha)^{(fx-2x+1)}}{(fx-2x+1)!x!} \qquad \text{Equation 1.13}$$

where N_x and w_x are the mole fraction and weight fraction of molecules with a degree of polymerisation x.

The number and weight average degrees of polymerisation, χ_n and χ_w, for an AB_2 system are defined as:

$$\chi_n = \frac{1}{[1-\alpha(f-1)]} \qquad \text{Equation 1.14}$$

$$\chi_w = \frac{[1-\alpha^2(f-1)]}{[1-\alpha(f-1)]^2} \qquad \text{Equation 1.15}$$

A general expression for the polydispersity of polymers derived from $AB_{f\text{-}1}$ monomers is obtained by combining equations 1.14 and 1.15:

$$M_w/M_n = \frac{[1-\alpha^2(f-1)]}{[1-\alpha(f-1)]} \qquad \text{Equation 1.16}$$

For polymerisations based on AB_2 monomers this equation simplifys to:

$$M_w/M_n = \frac{[1-2\alpha^2]}{[1-2\alpha]} \qquad \text{Equation 1.17}$$

Using these results the theoretical variation of polydispersity with the extent of reaction for an AB and an AB_2 system is shown in Figure 1.11. Clearly for an AB_2 system as the reaction proceeds and p approaches 1 (and α approaches 0.5), the polydispersity (M_w/M_n) will become infinitely large, tending to infinity. This is in marked contrast to the linear step-growth polymerisation of an AB monomer where the polydispersity tends to 2 as the extent of reaction p, approaches 1. From this theoretical analysis it can be seen that large differences in the molecular weight distribution are expected to be found for linear and hyperbranched polymers.

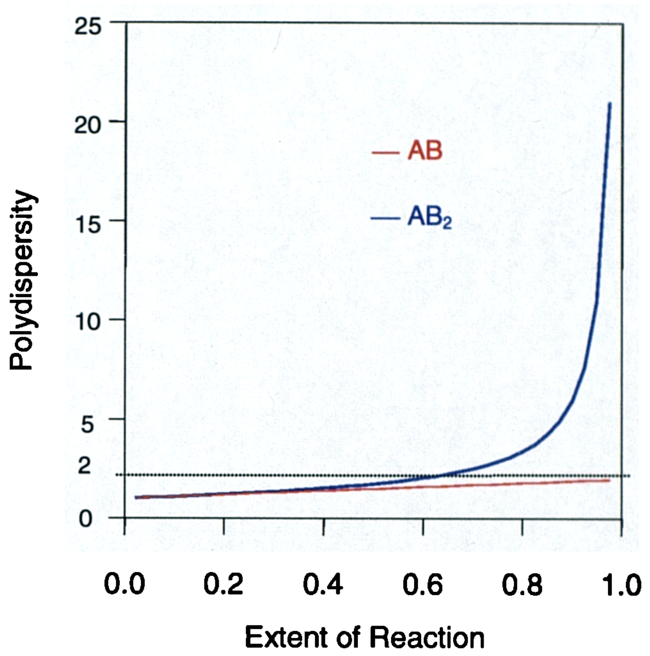
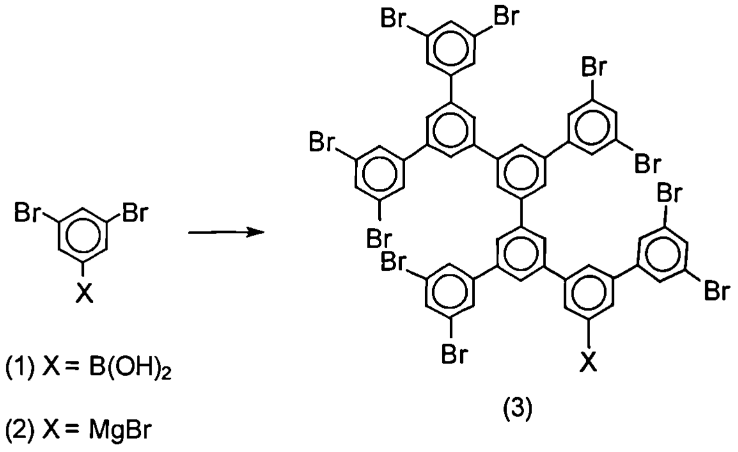


Figure 1.11: Theoretical variation of polydispersity with the extent of reaction for an AB and an AB_2 system

1.2.2 Synthesis of hyperbranched polymers

Hyperbranched polymers were first discussed by Flory[7] in 1952 in his theoretical treatment of the polymerisation of AB_{f-1} monomers, however synthetic attempts to prepare these materials were not made for approximately 40 years, when Kim and Webster reported the synthesis of their hyperbranched poly(phenylene)s via the polycondensation of the AB_2 monomers 3, 5 -dibromophenylboronic acid and 3, 5 – dibromophenylmagnesium bromide (see Figure 1.12).[8] The most surprising feature for the hyperbranched poly(phenylene)s was their excellent solubility properties in a range of organic solvents. This is in direct contrast to linear polyphenylene which is one of the most intractable polymers known.



(1) X= $B(OH)_2$

(2) X= MgBr

(3)

Figure1.12: Hyperbranched poly(phenylene) synthesis

The presence of a large number of bromine functional groups at the chain ends and the excellent solubility of these materials in THF allowed chemical modification of the end groups. This manipulation of the terminal bromo functionalities resulted in vastly different physical properties for the hyperbranched polymers. For example, the carboxylate derivative of (3) proved to be water soluble. Kim and Webster's initial report presenting novel topology polymers with new and intriguing properties generated much interest in this area of polymer science. Consequently in the past 10 years a large number of publications concerning the synthesis of hyperbranched polymers have appeared in the literature as their novel properties become desirable and potential uses are found.

1.2.3 Condensation polymerisation

Although a wide variety of hyperbranched polymers have been reported in the literature the majority of these materials have been prepared using condensation reactions. For example hyperbranched polyphenylenes,[8,16] polyesters,[17,18] polyethers,[19] polyether-ketones,[11] polycarbosilanes,[20] polysiloxysilanes,[21,22] polyamides,[23,24,] polyester-amides,[25,26] polyamines,[27,28] polyurethanes[29,30] and polyureas[31] have all been prepared by the condensation reaction of the appropriate AB_x monomers. Rather than listing the numerous hyperbranched polymers prepared via a polycondensation reaction, the author directs the reader to recent comprehensive reviews concerning hyperbranched polymers.[32,33]

Figure 1.13 below shows a small selection of AB_2 monomers used to prepare hyperbranched polymers, the variety and differences in structure and chemistry between these monomers demonstrates the versatility of the condensation reaction.

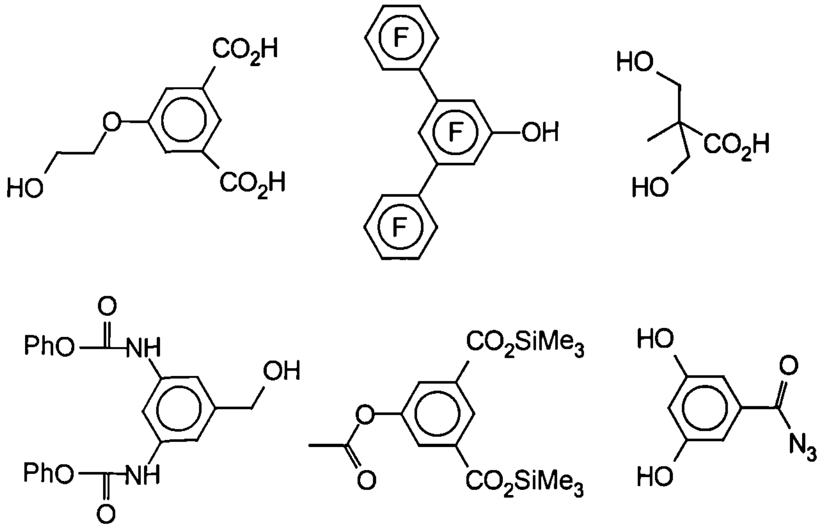


Figure1.13: AB_2 monomers used to prepare hyperbranched polymers

In order to prepare high molecular weight hyperbranched polymers via the condensation reaction of AB_x monomers (where x represents the number of B functional groups), several conditions must be met. Firstly the reactive groups A and B should only react with each other in the polymerisation step. Often the addition of a catalyst or the application of a suitable activation step (e.g. thermal activation) is used to initiate the condensation reaction. The reactivity of the A and B groups should be high and any condensation products formed should be removed easily to facilitate polymer formation. Deactivation of any of the functional groups in the polymer should be avoided since this could limit the growth of the polymer. Side reactions or intramolecular cyclisation reactions of the polymer should be kept to an absolute minimum, since these could disturb the growth of the polymer leading to low molecular weight materials. These conditions also apply for the condensation polymerisation of AB monomers. Interchanging the A and B functionalities in an AB$_x$ monomer (i.e. AB$_x$ to A$_x$B) will produce a polymer with significantly different properties. This difference arises from the fact the numerous B functionalities in a hyperbranched polymer based on an AB$_x$ monomer will have a large influence on the physical properties of the material.

Most hyperbranched polymers reported have been prepared from the polycondensation of AB$_2$ monomers with the elimination of a stable molecule such as water or methanol. For example an extensively studied class of hyperbranched polymer is based on 1,3,5 – substituted phenylene repeat units. This is illustrated in Figure 1.14 where a range of AB$_2$ monomers, based on the 1,3,5 – substituted benzenes used to prepare hyperbranched polyesters are presented.

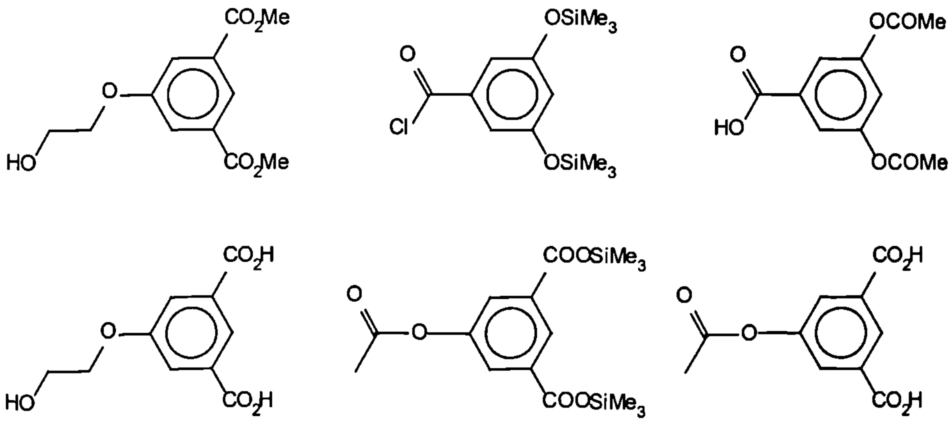


Figure 1.14: AB$_2$ monomers, based on the 1,3,5 – substituted benzenes, used to prepare hyperbranched polyesters

A small number of hyperbranched polymers have been prepared using more highly functionalised AB$_3$ or AB$_4$ monomers. Hawker[11] produced AB$_4$ and AB$_3$ monomers by the deliberate insertion of either a dendritic or linear fragment into an AB$_2$ monomer, see Figure 1.15. In this work he showed that AB$_3$ or AB$_4$ monomers can be used to control the degree of branching in hyperbranched poly(ether ketone)s. The hyperbranched poly(ether ketone) derived from the AB_2 monomer 3, 5-difluro-4'-hydroxybenzophenone, was shown by ^{19}F nmr to have a degree of branching of 0.5. However hyperbranched poly(ether ketone)s derived from the AB_3 and AB_4 monomers were found to have degrees of branching of 0.39 and 0.72 respectively, significantly different from the value obtained for the AB_2 based hyperbranched polymer.

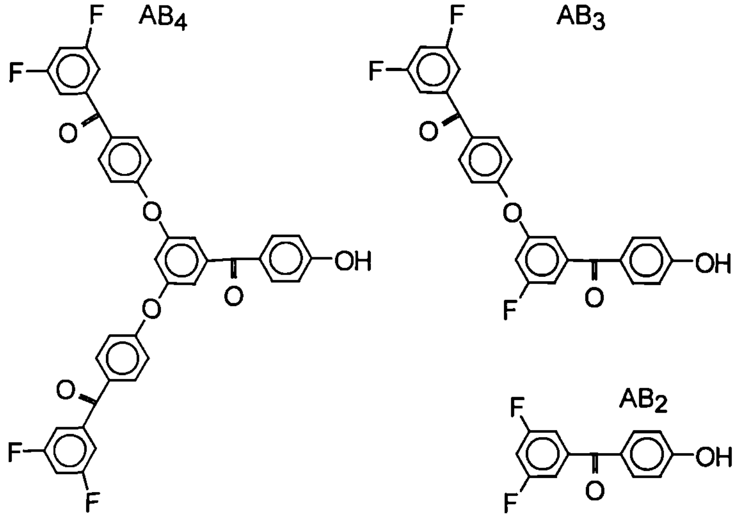
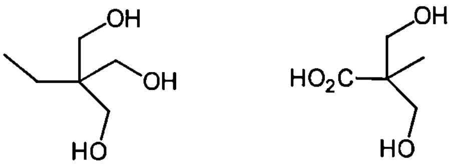


Figure 1.15: AB_2, AB_3 and AB_4 monomers used in the preparation of hyperbranched poly(ether-ketones)

The introduction of a core molecule in the synthesis of hyperbranched polymers has been reported by a number of research groups. The core molecule should in theory improve control of both the molecular weight and the molecular weight distribution of the resulting hyperbranched polymer. Malström and Hult[34] first proposed the addition of a core molecule with controlled addition of the monomer, in the synthesis of hyperbranched polyesters (see Figure 1.16). In this procedure, a polyfunctional core such as the tri-functional trihydroxymethylpropane (4) was reacted with 3 equivalents of the AB_2 monomer 2, 2 –dihydroxymethylpropanoic acid (5), until complete disappearance of the acid functionality was observed. Further repetition of the addition/polymerisation process, with incremental increases in the number of equivalents of monomer added to replicate the formation of a dendrimer, is continued until a hyperbranched macromolecule of the desired molecular weight is obtained. As expected the molecular weight of the polyester increases with each addition of monomer, and the final polymer was found to have a narrower polydispersity (< 2) than is commonly shown for AB_2 systems.



Core
(4)

AB_2 monomer
(5)

Figure 1.16: Polyfunctional core and AB_2 monomer used in the controlled synthesis of hyperbranched aliphatic polyesters

Further control over molecular weight and molecular weight distribution using a core molecule has recently been presented by Bharathi and Moore[35] who used a solid support to attach a B_2 molecule (3, 5 –diiodophenyl unit). Dropwise, addition of a suitable AB_2 monomer (3, 5 –diiodophenylacetylene) was used to prepare hyperbranched poly(phenylacetylene)s. Narrow polydispersities (1.3) were obtained after cleavage of the hyperbranched polymer from the support. Futhermore, for the same synthesis carried out in solution a broader bimodal molecular weight distribution was obtained confirming the control of molecular weight distribution using the solid support. Whereas most polycondensations have been carried out in solution or in the bulk, this is the first example of the preparation of a hyperbranched polymer using a solid support.

1.2.4 Addition polymerisation

While the synthesis of hyperbranched polymers has been performed via the condensation of AB_x monomers for several years, recently Fréchet *et al*[36] reported a new synthetic method for the preparation of hyperbranched macromolecules based on the "self-condensation" of activated functionalised vinyl monomers. Typically the AB monomer is activated by either a physical (application of heat or light) or chemical process to give an activated monomer, AB*, containing a vinyl group and initiating centre, B*, (see Figure 1.17). This is able to react with another AB* activated monomer to yield a dimer, containing a vinyl group, an initiating centre (B*) and a propagating centre (CH*), which can polymerise to produce a hyperbranched polymer.

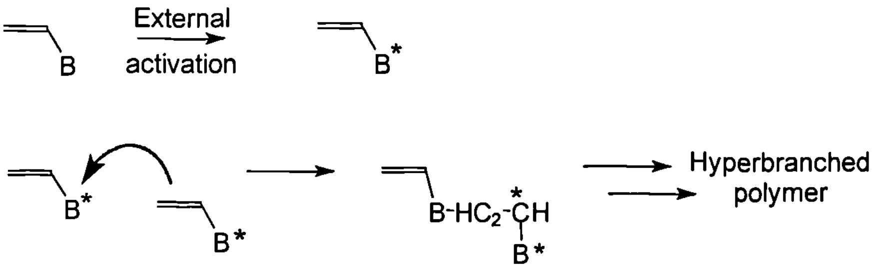


Figure 1.17: "Self-condensing" vinyl polymerisation (SCVP)

The "self-condensing" vinyl polymerisation process (SCVP) was first demonstrated using a living cationic polymerisation of the AB vinyl monomer 3-(1-chloroethyl)-ethenyl benzene, activated by $SnCl_4$ (see Figure 1.18).[36]

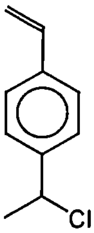


Figure 1.18: Vinyl monomer polymerised using SCVP to yield a hyperbranched polymer

SCVP was later extended to 'living' radical[37] polymerisations where Hawker *et al* demonstrated the preparation of hyperbranched polymers via a TEMPO (2, 2, 6, 6,-tetramethylpiperidinyl-1-oxy) mediated 'living' radical polymerisation (see Figure 1.19). The self-condensing AB* monomer (7), containing both a polymerisable double bond and an initiating alkoxyamine in the same molecule, was polymerised to afford a hyperbranched polymer.

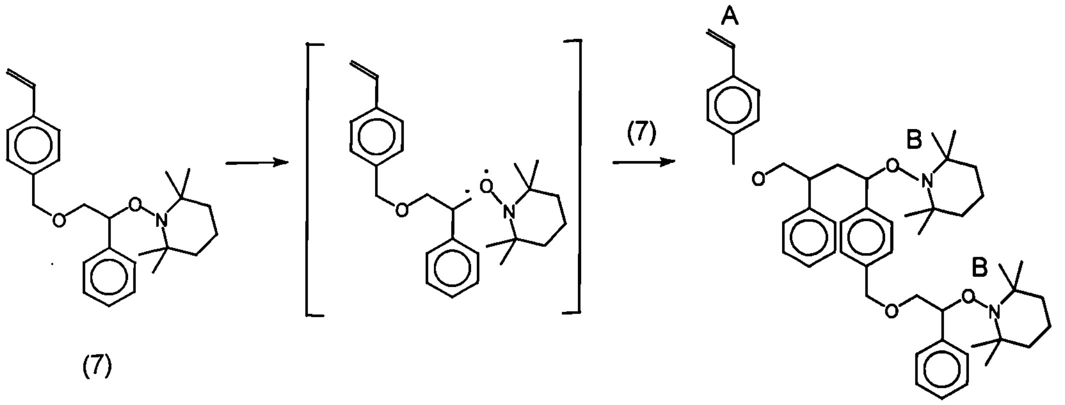


Figure 1.19: Schematic illustration of a TEMPO mediated 'living' radical polymerisation

Recent advances in transition metal catalysed 'living' free-radical polymersiation (MCLRP) have greatly expanded the scope of this method for the preparation of a hyperbranhced of materials.[38,39]

Although SCVP is still a relatively new concept in synthetic polymer science the increasing number of publications clearly indicate the general applicability of this technique in the synthesis of hyperbranched macromolecules. The increased synthetic availability of hyperbranched polymers via 'self-condensing vinyl polymerisation' will greatly facilitate the study of these materials and allow the preparation of a wider range of hyperbranched polymers including poly(styrene)s and poly(acrylate)s.

1.3 Properties of hyperbranched macromolecules

The properties of hyperbranched polymers have not yet been extensively examined, however, the number of studies is steadily increasing. Research has predominantly focussed on the comparison of linear polymers with structurally analogous dendrimers or hyperbranched polymers. Due to their regular structure, the physical properties of dendrimers can be empirically related to the number of end groups and branch points. However, hyperbranched polymers possess several imperfections, being polydisperse in molecular weight and in their number of branch points, thus defining the polymer structure precisely and relating the structure to the properties exhibited by that polymer becomes increasingly difficult.

In general the following characteristics have been found in many hyperbranched polymers:

- Low viscosity in solution.
- Enhanced solubility, when compared with their linear analogues.
- High chemical reactivity, depending on the nature of the terminal functional groups.
- Mechanical properties which reflect their compact highly branched structures.

All these features are elaborated below.

One of the most striking differences between dendrimers, hyperbranched polymers and linear polymers is in their respective intrinsic viscosity (η)/molecular weight (M) relationships (see Figure 1.20). Linear polymers obey the Mark Houwink equation $[\eta] = KM^a$, where a and K are constants and M is the average molecular weight. Therefore their intrinsic viscosity increases with increasing molecular weight. Dendrimers however do not obey this relationship across the full range of molecular weights. For a family of dendrimers (i.e. different generations), the intrinsic viscosity reaches a maximum and decreases thereafter with increasing molecular weight. This can be explained qualitatively on the basis of the conformational changes dendrimers undergo through increasing generations. At low generations the dendrimer adopts a relatively mobile conformation and, in terms of hydrodynamic volume, will show behaviour similar to that of a linear polymer. Therefore at low generations dendrimers will have a molecular weight/viscosity relationship which is qualitatively similar to that defined by the Mark-Houwink equation. However, as the dendrimer increases in size the structure becomes gradually more rigid and eventually approximates to a hard sphere. During this change the density increases since the molecular mass of the dendrimer increases faster than its hydrodynamic volume. The relationship between the molecular mass and intrinsic viscosity of hard spheres obeys Einstein's hard spheres relationship:

$$[\eta] \propto V_h / M$$

where V_h is the hydrodynamic volume, M is the mass and $[\eta]$ is the intrinsic viscosity. Since dendrimers of higher generations approximate to hard spheres, this expression is more appropriate for accounting for trends in their intrinsic viscosity. Since their hydrodynamic volumes increase more slowly than their masses, their intrinsic viscosity will decrease with increasing mass.

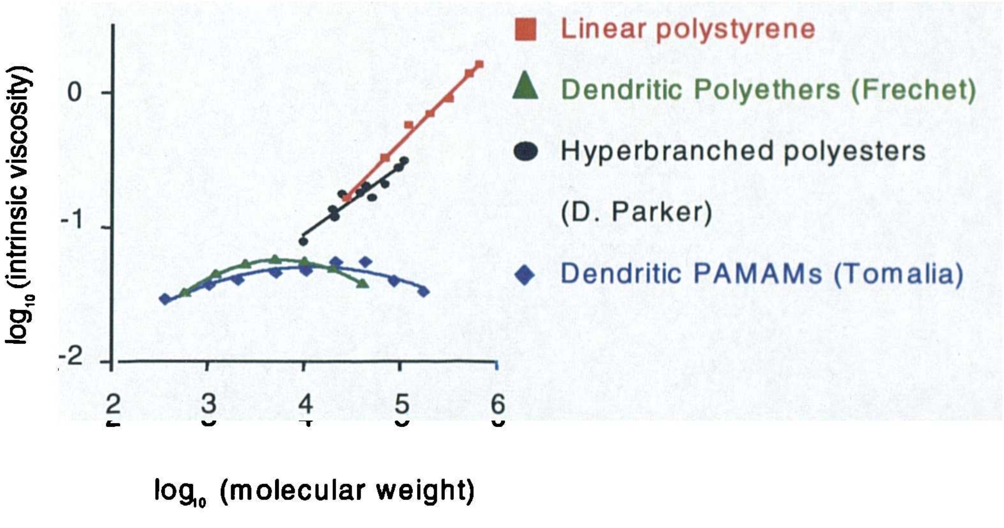


Figure 1.20: Graph to show the intrinsic viscosity / molecular weight relationship for linear polymers, dendrimers and hyperbranched polymers

Generally it has been found that hyperbranched polymers obey the Mark Houwink equation so that their intrinsic viscosity increases with increasing molecular weight. Thus although hyperbranched polymers possess some structural features similar to dendrimers, their solution viscosity properties are significantly different.

Recently however, Hobson *et al*[40] reported that core terminated hyperbranched poly(amidoamine)s, with a degree of branching ≥ 0.9, exhibited a molecular weight/intrinsic viscosity relationship similar to that shown by dendrimers i.e. the intrinsic viscosity passes through a characteristic maximum and then decreases with increasing molecular weight. This result suggests that the topology of these systems resembles that of dendrimers and that the intrinsic viscosity/molecular weight relationship for hyperbranched structures is dependent on the specific system under consideration.

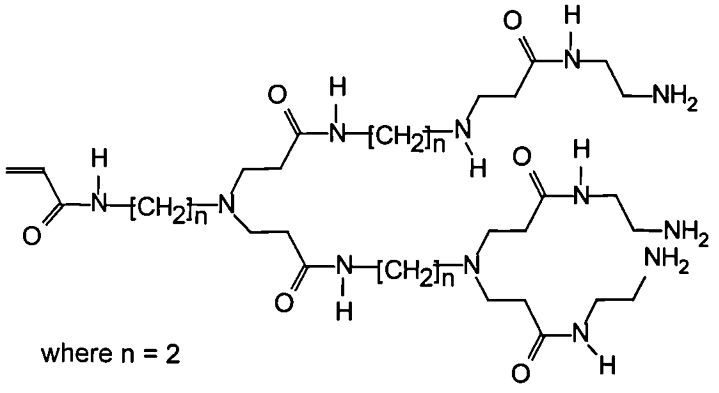


Figure 1.21: Hyperbranched poly(amidoamine)s

Another interesting solution property of dendritic macromolecules is their enhanced solubility compared to analogous linear polymers. Their increased solubility is attributed to both their branched architecture and large number of chain end groups.

Depending on the nature of the chain ends, the presence of a large number of terminal functional groups allows further chemical reactions to be performed on hyperbranched polymers. This feature of dendritic macromolecules has been demonstrated by a number of groups. For example, Brenner and Voit[41] reported the modification of both acid and alcohol terminated hyperbranched polyesters to introduce azo functionalities at the surface, capable of initiating free radical polymerisation. Using this approach grafts of controlled size and number were introduced from the hyperbranched core (see figure 1.21).

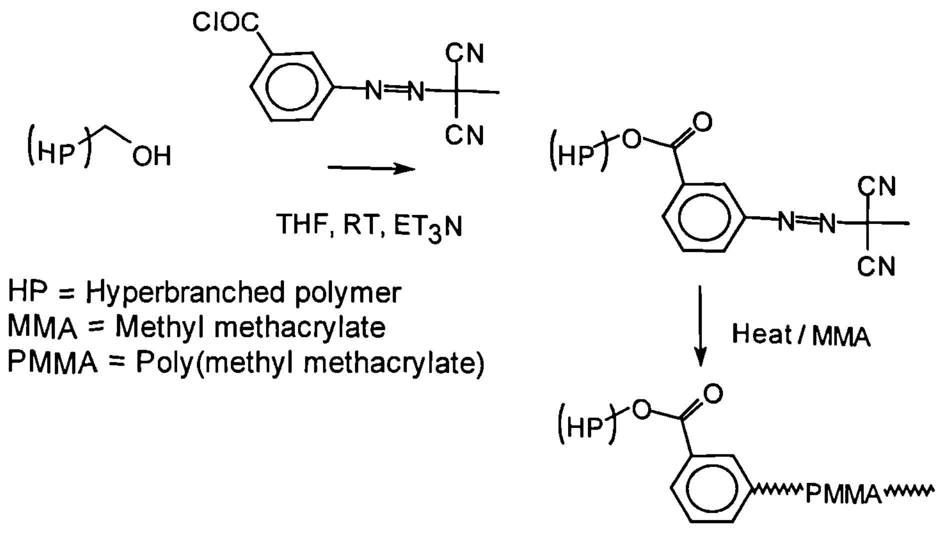


Figure 1.21: Modification of terminal functional groups in hyperbranched polymers

Interesting mechanical properties are now emerging for some hyperbranched systems which are a reflection of their compact highly branched structures. Boogh and Petterrson[42] showed that modified hyperbranched polyesters can act as tougheners for epoxy-based composites at a fairly low loading (~5%), with no effect on the thermal properties or processing characteristics.

When considering the thermal properties of dendritic macromolecules, it appears from the literature that the factors governing the glass transition temperature in dendrimers or hyperbranched polymers is not well understood. Generally it has been found in dendrimers and hyperbranched polymers that the glass transition temperature is affected by both the nature of the backbone as well as the terminal groups,[16,43] An example is given in the table overaleaf for the hyperbranched poly(phenylenes) prepared by Kim and Webster.[16] For this system the authors reported that there was no effect of the molecular weight on the glass transition in the M_n range of 2000 to 35000.

The effect of the functional groups on the T_g of hyperbranched poly(phenylene)s:

Terminal functional groups	Br	CH_2Cl	CH_3	H	$(CH_3)_3Si$
T_g (°C)	221	182	177	121	141

Frechet [44]showed that for polyether and polyester dendrimers, their glass transition temperature increased with molar mass up to a certain limit above which it remained virtually constant. Interestingly this observation is similar to that found in linear polymers. For hyperbranched polymers the situation is more complex with some research groups reporting little variance of the glass transition temperature with changes in the average molecular weight,[16] while other groups have reported an increase in the glass transition temperature with increasing average molecular weight.[45] Such conflicting results indicate that the glass transition/molecular weight relationship for hyperbranched polymers is dependent on the specific system under consideration.

1.4 Conclusions

Over the last 10 years the field of highly branched macromolecules has expanded rapidly, in particular with the synthesis of these novel topology polymers. However, before these materials can be exploited further a better understanding of their structural and physical properties is essential. Their relative ease of synthesis and lower cost makes them particularly favourable for commercial applications with possible uses already emerging for these new and exciting materials. The low viscosity of the hyperbranched polymers, even at high concentration, is an attractive property for coating applications, for example in reducing the volatile organic content in paints. Akzo Nobel are presently claiming to use dendrimer technology in their surface coatings materials although the nature of the technology has not been disclosed. Since the hyperbranched polymers are nonentangled amorphous systems they do not show properties which make common linear polymers useful, such as strength or toughness. However, recently a number of research groups have shown that hyperbranched polymers display property modifying attributes when blended with conventional systems. This suggests that hyperbranched materials may be useful in the area of blends, composites or as rheology modifiers.

It is evident that further fundamental and applied research is required before we can extend control of the backbone structure, degree of branching and end group modification in these systems. This will then enable us to establish the structure/property relationships in hyperbranched polymers so that we can then begin to 'tailor-make' polymers for specific applications.

1.5 Background and aim of work

Work in this area of hyperbranched polymer science began with the preparation of aryl ester dendrimers by Feast and Stainton,[18] who demonstrated that these dendrimers blended with poly(ethylene terephthalate) (PET) acted as plasticisers or antiplasticisers, depending on the dendrimer generation (see Figure 1.22). Establishing that these dendrimers had property modifying attributes was an extremely encouraging result, however, the laborious and time consuming iterative synthesis used to prepare these unique macromolecules remained a major disadvantage, particularly if this process was ever to be of any commercial use.

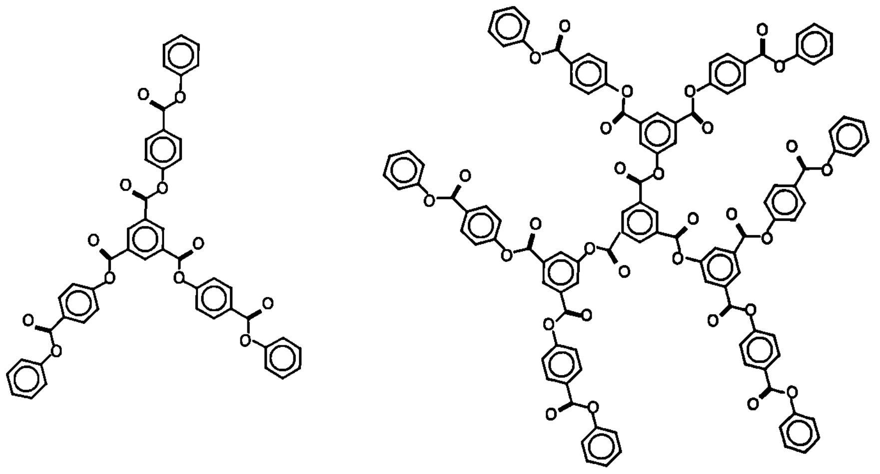
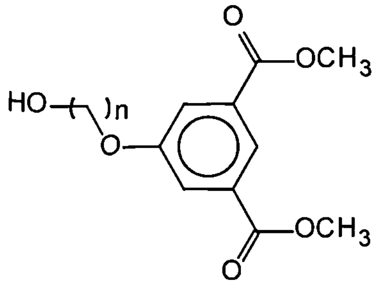


Figure 1.22: Aryl ester dendrimers used in blending studies with PET

As a natural extension to this work the synthesis of hyperbranched polyesters via a single step polycondensation reaction was investigated, these materials were expected to replicate some of the unusual properties of dendrimers, whilst avoiding the difficulties associated with their step-wise synthesis. The hyperbranched polyester, based on the AB_2 monomer (**I**) shown in Figure 1.23 overleaf, was prepared and found to replicate the effects brought about by blending dendrimers with PET.[45] In contrast to dendrimers, the effect appeared to be independent of the molecular weight of the hyperbranched polymer incorporated in the blend. Further work is still required in order to understand this phenomenon fully, however these results do indicate that hyperbranched polyesters provide a more accessible route to materials with novel properties.



Stainton *et al*
n = 2 (**I**)

Target AB$_2$ monomers
n = 3 (**II**)
n = 4 (**III**)
n = 5 (**IV**)
n = 6 (**V**)

Figure 1.23: AB$_2$ monomers used to prepare hyperbranched polyesters

The aim of the work reported in this thesis was to develop a range of analogous hyperbranched polyesters which could be used to investigate the structure/property relationships in this hyperbranched system. This required developing a synthetic strategy to prepare the AB$_2$ monomers (**II-V**) and the corresponding hyperbranched polyesters containing between 3 and 6 methylene units in the alkylene chain, see Figure 1.23. Subsequent structural and physical characterisation of these materials using a variety of analytical techniques would allow investigation of the influence of the alkylene chain length on the physical properties of the hyperbranched polymers. It was anticipated that results arising from these investigations could provide a valuable insight into the structure/property relationships exhibited by these hyperbranched polyesters.

1.6 References

[1] Buhleier, E., Wehner, W., Vögtle, F., *Synthesis*, 1978, 155-158.

[2] Tomalia, D. A., Baker, H., Dewald, J., Hall, M., Kallos, G., Martin, J. R., Ryder, J., Smith., P., *Polym. J.*, 1985, **17**, 117.

[3] Newkome , G. R., Yao, Z., Baker, G. R., Gupta, V. K., *J. Org. Chem.* 1985, **50**, 2003-2004.

[4] Hawker. C. J., Fréchet, J. M. J., *J. Am. Chem. Soc.*, 1990, **112**, 7638-7647.

[5] de Brabander-van den Berg, E. M. M., Meijer, E. W., *Angew. Chem. Int. Ed. Engl.* 1993, **32**, 1308-1311.

[6] Davis, N. and Rannard, S., *Abstracts of Papers of the American Chemical Society*, 1997, **214**, 145-PMSE.

[7] Flory, P. J., *J. Am. Chem. Soc.*, 1990, **75**, 2718-2723.

[8] Kim, Y. H., Webster, O. W., *J. Am. Chem. Soc.*, 1990, **112**, 4592-4593.

[9] Hawker. C. J., Lee, R., Fréchet, J. M. J., *J. Am. Chem. Soc.*, 1991, **113**, 4583-4588.

[10] Holter, D., Burgath, A. and Frey, H., *Acta Polym.*, 1997, **48**, 30-35.

[11] Hawker, C. J. and Chu, F. K., *Macromolecules*, 1996, **29**, 4370-4380.

[12] Hobson, L. J., Kenwright, A. M. and Feast, W. J., *J. Chem. Soc., Chemical Commun.*, 1997, 1877-1878.

[13] Fomine, S., Rivera, E., Fomina, L., Ortiz, A. and Ogawa, T., *Polymer*, 1998, **39**, 3551-3558.

[14] Feast, W. J., Keeney, A. J., Kenwright, A. M. and Parker, D., *J. Chem. Soc., Chemical Commun.*, 1997, 1749-1750.

[15] Percec, V., Chu, P., Kawasumi, M., *Macromolecules*, 1994, **27**, 4441-4453.

[16] Kim, Y. H., Webster, O. W., *Macromolecules*, 1992, **25**, 5561-5572.

[17] Wooley, K. L., Fréchet, J. M. J., Hawker. C. J., *Polymer,* 1994, **35**, 4489-4495; Kambouris, P., Hawker. C. J., *J. Chem. Soc., Perkin. Trans. 1.,* 1993, 2717-2721; Wooley, K. L., Hawker. C. J., Lee, R., Fréchet, J. M. J., *Polymer Journal,* 1994, **2**, 187-197: Turner, S. R., Voit. B. I., Mourey, T. M., *Macromolecules,* 1993, **26**, 4617-4623; Kricheldorf, H. R., Stober, O., *Macromol. Rapid Commun.,* 1994, **15**, 87-93; Malmström, E., Johansson, M., Hult, A., *Macromolecules*, 1995, **28**, 1698-1703.

[18] Feast. W. J., Stainton, N. M., *J. Mat. Chem.,* 1995, **5**, 405-411.

[19] Ulrich, K. E., Hawker. C. J., Fréchet, J. M. J., Turner, S. R., *Macromolecules,* 1992, **25**, 4583-4587; Ulrich, K. E., Hawker. C. J., Fréchet, J. M. J., *Polym. Mat. Sci. Eng.,* 1991, **64**, 237-238; Chu, F., Hawker, C. J., *Polym. Bull.* 1993, **30**, 265-272; Miller, T. M., Neenan, T. X., Kwock, E. W., Stein, S. M., *J. Am. Chem. Soc.,* 1993, **115**, 356-357; Percec, V., Kawasumi, M., *Macromolecules,* 1992, **25**, 3843-3850.

[20] Lach, C., Muller, P., Frey, H. and Mulhaupt, R., *Macromol. Rapid Commun.*, 1997, **18**, 253-260.

[21] Mathias, L. J., Carothers, T. W., *J. Am. Chem. Soc.,* 1991, **113**, 4043-4044.

[22] Miravet, J. F. and Fréchet, J. M. J., *Macromolecules*, 1998, **31**, 3461-3468.

[23] Ulrich, K. E., Boegeman, S., Fréchet, J. M. J., Turner, S. R., *Polym. Bull.* 1991, **25**, 551-558.

[24] Kim, Y. H., *Adv. Mater.,* 1992, **4**, 764-766.

[25] Kricheldorf, H. R., Loheden, G., *Macromol. Chem. Phys,.* 1995, **196**, 1839-1854.

[26] Kricheldorf, H. R., Loheden, G., *J. M. S. -Pure Appl. Chem.,* 1995, A32(11), 1915-1930.

[27] Suzuki, M., Ii, A., Saegusa, T., *Macromolecules,* 1992, **25**, 7071-7072.

[28] Suzuki, M., Yoshida, S., Shiraga, K. and Saegusa, T., *Macromolecules*, 1998, **31**, 1716-1719.

[29] Spindler, R., Fréchet, J. M. J., *Macromolecules,* 1993, **26**, 4809-4813.

Kumar. A., Ramakrishnan, S., *J. Chem. Soc. Chem. Commun.,* 1993, 1453-1454.

[30] Kumar, A. and Ramakrishnan, S., *J. Polym. Sci., Part A-Polym. Chem.*, 1996, **34**, 839-848.

[31] Kumar, A. and Meijer, E. W., *J. Chem. Soc., Chem. Commun.,* 1998, 1629-1630.

Hawker, C. J. and Chu, F. K., *Macromolecules*, 1996, **29**, 4370-4380.

chet, J. M. J., Hawker, C. J., Gitsov, I. and Leon, J. W., *J. Macromol. Sci., Pure Appl. Chem.,* 1996, **A33**, 1399-1425.

[33] Fréchet, J. M. J. and Hawker, C. J., *Reactive & Functional Polymers*, 1995, **26**, 127-136.

[34] Malmström, E. and Hult, A., *Abstracts of Papers of the American Chemical Society*, 1995, **210**, 186-PMSE.

[35] Bharathi, P. and Moore, J. S., *J. Am. Chem. Soc.,* 1997, **119**, 3391-3392.

[36] Fréchet, J. M. J., Hemmi, M., Gitsov., I., Ashima, S., Leduc, M. R., Grubbs, R. B., *Science*, 1995, **269**, 1080-1083.

[37] Hawker, C. J., Fréchet, J. M. J., Grubbs, R. B. and Dao, J., *J. Am. Chem. Soc.,* 1995, **117**, 10763-10764.

[38] Weimer, M. W., Fréchet, J. M. J. and Gitsov, I., *J. Polym. Sci., Part A-Polym. Chem.*, 1998, **36**, 955-970.

[39] Gaynor, S. G., Edelman, S. and Matyjaszewski, K., *Macromolecules*, 1996, **29**, 1079-1081.

[40] Hobson, L. J. and Feast, W. J., *J. Chem. Soc., Chemical Commun.*, 1997, 2067-2068.

[41] Brenner, A. R., Voit, B. I., Massa, D. J. and Turner, S. R., *Macromol. Symp.*, 1996, **102**, 47-54.

[42] Boogh, L., Pettersson, B., Kaiser, P. and Manson, J. A., *Sampe Journal*, 1997, **33**, 45-49.

[43] Chu, F. K. and Hawker, C. J., *Polymer Bull.*, 1993, **30**, 265-272.

[44] Wooley, K. L., Hawker, C. J., Pochan, J. M. and Fréchet, J. M. J., *Macromolecules*, 1993, **26**, 1514-1519.

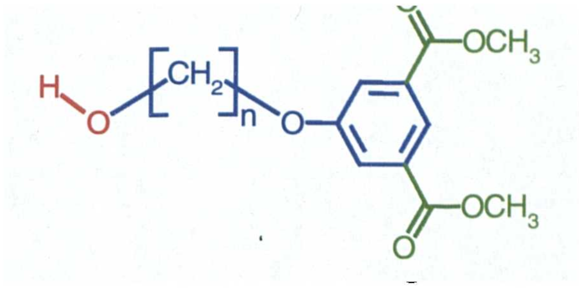
[45] Stainton, N.M., *Ph.D. Thesis*, University of Durham, 1994.

CHAPTER TWO

THE SYNTHESES OF AB_2 DIMETHYL 5-(ω-HYDROXYALKOXY)ISOPHTHALATE MONOMERS

2.1 Introduction

In this chapter the syntheses of the monomers required for this study are described. The monomer dimethyl 5-(2-hydroxyethoxy)isophthalate,[1] had been made previously and the synthetic route established for this monomer was extended in order to prepare a series of analogous dimethyl 5-(ω-hydroxyalkoxy)isophthalate monomers. The generalised structure of this set of monomers is shown in Figure 1.1.



n = 3, 4, 5 and 6

Figure 1.1: Dimethyl 5-(ω-hydroxyalkoxy)isophthalate monomers

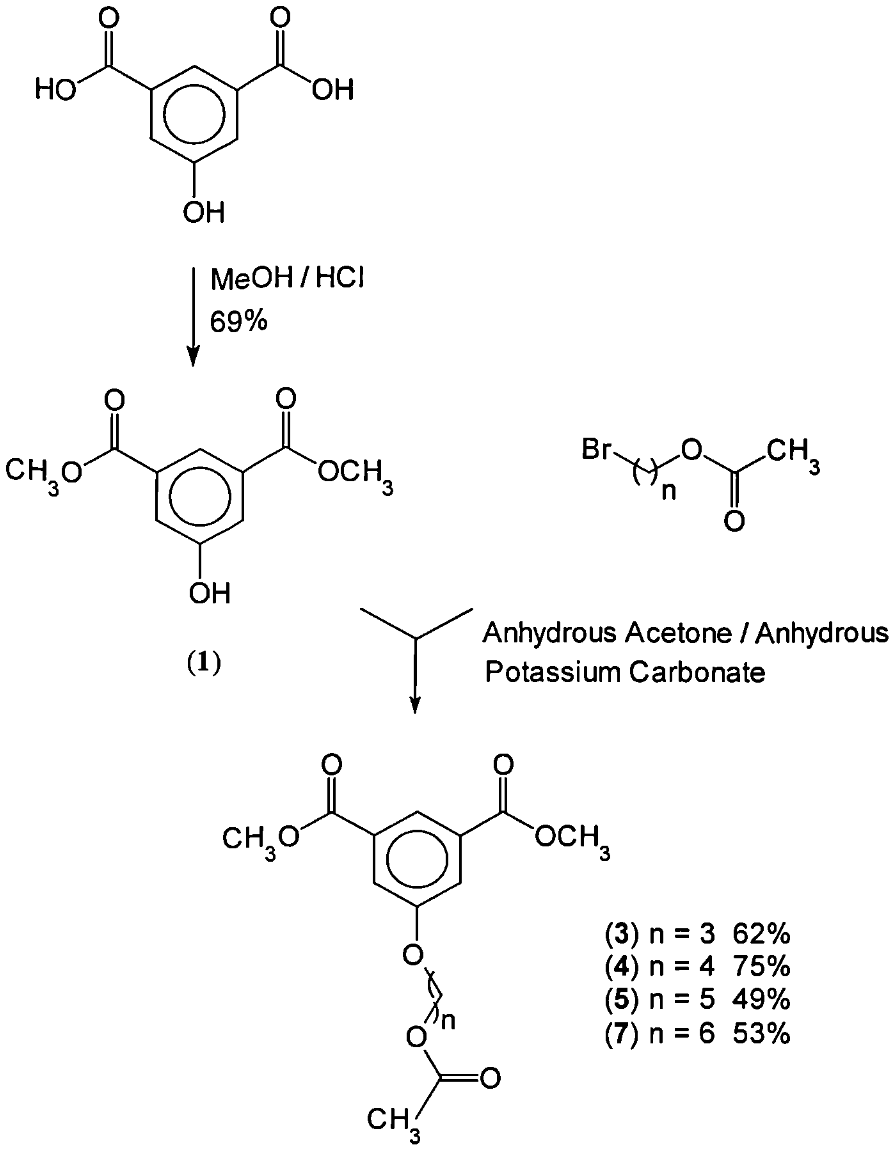
2.2 Monomer Syntheses: Discussion

2.2.1 The syntheses of AB$_2$ dimethyl 5-(ω-acetoxyalkoxy)isophthalate monomers

Dimethyl 5-(2-hydroxyethoxy)isophthalate[1] was prepared from 5-hydroxyisophthalic acid in a three stage process. First the 5-hydroxyisophthalic acid was esterified in acidic methanol solution to give dimethyl 5-hydroxyisophthalate (**1**), as shown in Scheme 2.1. In the second stage an excess of dimethyl 5-hydroxyisophthalate was reacted with 2-bromoethyl acetate, in a suspension of potassium carbonate in anhydrous acetone,[1] to produce dimethyl 5-(2-acetoxyethoxy)isophthalate, which was selectively hydrolysed in basic methanol solution to yield dimethyl 5-(2-hydroxyethoxy)isophthalate. An excess of dimethyl 5-hydroxyisophthalate was used because the 2-bromoethyl acetate was expensive, however, this turned out to be a false economy since it resulted in a complex recovery procedure with a relatively low yield of

37%. The excess dimethyl 5-hydroxyisophthalate was removed from the product mixture by washing with sodium hydroxide solution, which probably resulted in partial hydrolysis of both the acetate and the methyl ester groups, accounting for the poor yield since the resulting sodium salts would remain in the aqueous layer.

This earlier procedure was modified to prepare the analogous monomers, dimethyl 5-(3-acetoxypropoxy)isophthalate (**3**), dimethyl 5-(4-acetoxybutoxy) isophthalate (**4**), dimethyl 5-(5-acetoxypentoxy)isophthalate (**5**) and dimethyl 5-(6-acetoxyhexoxy)isophthalate (**7**). In this work dimethyl 5-hydroxyisophthalate was reacted with a 10% excess of the appropriate bromoalkyl acetate to yield the corresponding dimethyl 5-(ω-acetoxyalkoxy)isophthalate monomers, which were recovered in yields of 48-75%. The product recovery in this procedure involved filtration to remove the potassium carbonate, evaporation of the acetone and recovery of the product either by washing with hexane to remove the residual bromoalkyl acetate, or recrystallisation from hexane. The syntheses of the acetate protected AB_2 monomers are shown in Scheme 2.1. As the alkyl chain length increased, it became increasingly difficult to purify the product, however it was possible to produce all the acetoxy derivative AB_2 monomers in approximately 100g batches. This method has distinct advantages over the earlier dimethyl 5-(2-hydroxyethoxy)isophthalate synthesis,[1] requiring less time, giving increased yields and easier purification, and being at least as cost effective.

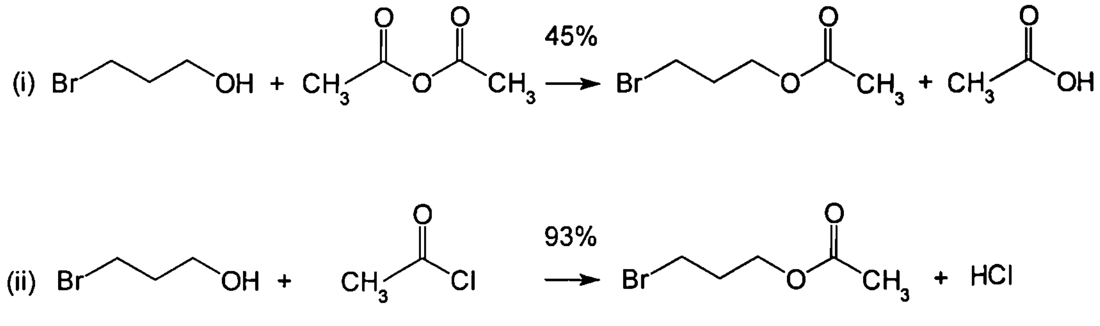


Scheme 2.1: The syntheses of dimethyl 5-(ω-acetoxyalkoxy)isophthalate monomers

2.2.2 Preparation of 3-bromopropyl acetate and 6-bromohexyl acetate

Although 4-bromobutyl acetate and 5-bromopentyl acetate were commercially available, the 3- and 6- analogues had to be prepared from the bromoalcohols. Attempts to prepare 3-bromopropyl acetate via the reaction of acetic anhydride with 3-bromo-1-propanol,[2,3] gave a mixture of 3-bromo-1-propanol and 3-bromopropyl acetate, in a 1:9 ratio, which could not be separated by simple distillation. Fractional distillation of this mixture was not attempted since a more direct synthetic route was found.

3-Bromopropyl acetate (**2**) was prepared cleanly by the addition of acetyl chloride to 3-bromo-1- propanol.[3] These synthetic routes are shown in Scheme 2.2.



(**2**)

Scheme 2.2: Preparation of 3-bromopropyl acetate via: (i) acetic anhydride route

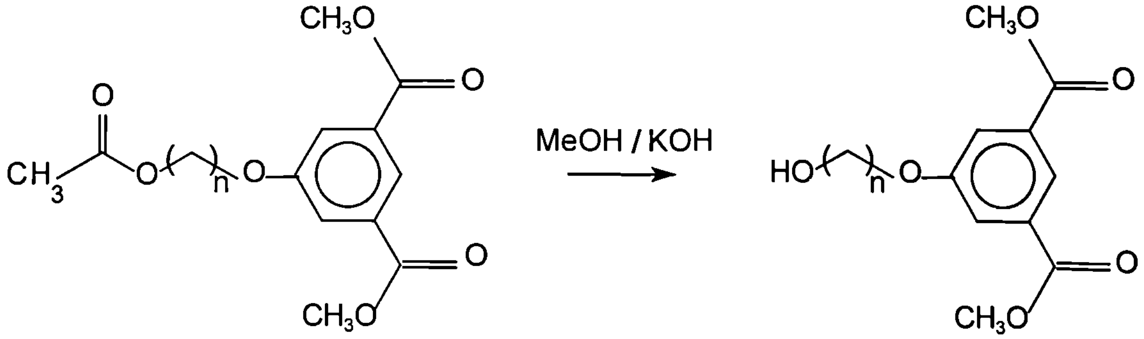
(ii) acetyl chloride route

6-Bromohexyl acetate (**6**) was prepared from 6-bromohexan-1-ol by the reaction with acetyl chloride.

2.2.3 Syntheses of AB$_2$ dimethyl 5-(ω-hydroxyalkoxy)isophthalate monomers

The hydrolysis of the acetate protected monomers to the corresponding hydroxy monomers was carried out cleanly with a catalytic amount of potassium hydroxide in methanol solution.[1,4] The judicious choice of solvent and a low reaction temperature of 30°C assured the selective cleavage of the alkyl acetate ester. The synthesis of AB$_2$ monomers **8**, **9**, **10** and **11** is shown in Scheme 2.3 overleaf.

It should be noted that the synthesis of dimethyl 5-(3-hydroxypropoxy) isophthalate (**8**) was attempted by directly coupling 3-bromopropan-1-ol with dimethyl 5-hydroxyisophthalate, however, the purification of the product from the starting material, 3-bromopropan-1-ol, proved extremely difficult. Consequently the monomers **8**, **9**, **10** and **11** were prepared via the acetate protected monomer which can be purified more easily. Their subsequent hydrolysis in methanolic potassium hydroxide yielded the required AB_2 monomers cleanly without the need for further purification.



(3) n = 3
(4) n = 4
(5) n = 5
(7) n = 6

(8) n = 3 71%
(9) n = 4 84%
(10) n = 5 81%
(11) n = 6 67%

Scheme 2.3: The syntheses of dimethyl 5-(ω-hydroxyalkoxy)isophthalate monomers

2.3 Experimental

All organic reagents were obtained from Aldrich Chemical Co. and used without further purification. Melting points were obtained using an Electrothermal digital melting point apparatus. Infrared (IR) spectra were recorded using a Perkin-Elmer 1600 series FTIR spectrometer. The spectra were recorded as KBr discs or between sodium chloride plates. ^{1}H Nmr and ^{13}C nmr spectra were recorded using a Varian Gemini 200 NMR spectrometer operating at 199.532 MHz (^{1}H) and 50.289 MHz (^{13}C), or a Varian VXR 400 NMR spectrometer operating at 399.953 MHz (^{1}H) and 100.577 MHz (^{13}C). Deuterated acetone or deuterated chloroform were used as solvents with tetramethylsilane as an internal reference. Mass spectra were recorded on a VG Analytical Model 7070E Mass Spectrometer. Elemental analyses were performed using a Carlo-Elba-466 elemental analyser. The IR, MS, ^{1}H and ^{13}C nmr spectra for all compounds discussed in Chapter 2 are recorded in Appendix 1.

2.3.1 Synthesis of dimethyl 5-hydroxyisophthalate (1)

5-Hydroxyisophthalic acid (250g, 1.4mol) and anhydrous methanol (1750cm^3) were charged into a 3000cm^3 3-necked round bottomed flask equipped with stirrer, gas inlet and outlet, and reflux condenser. Anhydrous HCl (32.0g, 0.88mol) was bubbled through the stirred solution. The reaction mixture was heated under reflux with stirring for 6 hours.

On allowing the reaction mixture to cool to room temperature, crude dimethyl 5-hydroxyisophthalate crystallised from the yellow acidic methanol solution as white needles. The crystals were collected by filtration, washed with cold methanol and distilled water, then recrystallised from the minimum amount of hot methanol. The recrystallised product was collected by filtration, washed with cold methanol and dried under reduced pressure to yield dimethyl 5-hydroxyisophthalate, (199.5g, 0.95mol, 69%), as fine white needles. m.p.164-165°C (lit[5] 159-160°C). Calculated for $C_{10}H_{10}O_5$: C, 57.08; H, 4.79%. Found: C, 57.14; H, 4.80%. ^{1}H Nmr (acetone-d^6, 400 MHz), δ3.5 (s, residual methanol), δ3.90 (s, 6H, $OC\underline{H}_3$), δ7.68 (d, $^4J = 1.60$ Hz, 2H, Ar$\underline{H}$), δ8.10 (t, $^4J = 1.60$ Hz, 1H, Ar$\underline{H}$), δ9.23 (s, 1H, O$\underline{H}$). ^{13}C Nmr (acetone-d^6, 100 MHz), δ51.6 ($\underline{C}H_3$), δ120.1, 121.1 (aromatic $\underline{C}$-H), δ131.9 (aromatic $\underline{C}$-$COOCH_3$), δ157.6 (aromatic $\underline{C}$-O), δ165.4 ($\underline{C}$=O).

IR (KBr disc), 3362cm^{-1} (broad, H-bonded O-H stretch), 3011cm^{-1} (w, aryl-H C-H stretch), 2967cm^{-1} (w, saturated C-H stretch), 1703cm^{-1} (s, aromatic ester C=O vibration), 754cm^{-1} (s, aryl-H C-H out of plane vibration).

MS (EI+): 210 (M), 179 (M-OCH_3).

See Appendices 2.1-2.3 for full details of IR, ^{1}H nmr and ^{13}C nmr spectra of dimethyl 5-hydroxyisophthalate.

2.3.2 Synthesis of 3-bromopropyl acetate: acetic anhydride route

Concentrated sulphuric acid (4.3cm^3) was added to a mixture of acetic anhydride (435.0g, 4.3mol) and 3-bromopropan-1-ol (162.0g, 1.16mol) contained in a 1000cm^3 2-necked round bottom flask fitted with a thermometer, stirrer and reflux condenser, with a drying tube ($CaCl_2$) attached to the top of the condenser. The reaction mixture was heated under reflux with stirring for 18 hours.

On allowing the reaction mixture to cool to room temperature, the mixture was poured into distilled water (2000cm^3) and extracted with dichloromethane (4 x 500cm^3). Excess solvent was removed under reduced pressure. The remaining mixture was distilled at atmospheric pressure (182-186°C) to yield a mixture of 3-bromopropyl acetate (10.6g, 0.08mol) and 3-bromopropan-1-ol (94.5g, 0.52mol) as a pale yellow oil in a 1:9 ratio, as determined by ^{1}H nmr. ^{1}H Nmr ($CDCl_3$, 200MHz) showed signals for 3-bromopropyl acetate @ δ1.97 (s, 3H, $C\underline{H}_3$), δ2.08 (m, 2H, $C\underline{H}_2$), δ3.38 (t, $^3J = 6.5$Hz, 2H, C$\underline{H}_2$Br) δ4.10 (t, ^{3}J = 6.1Hz, 2H, C$\underline{H}_2$OAc); with signals for 3-bromopropan-1-ol @ δ2.48 (s, O$\underline{H}$), δ3.45 (t, 2H, C$\underline{H}_2$Br), δ3.67 (t, 2H, C$\underline{H}_2$OH), the middle methylene signals overlap with the equivalent methylene signals in the 3-bromopropyl acetate. The relative intensities of the O$\underline{H}$ and the acetate C$\underline{H}_3$ signals were used to establish the composition of the mixture.

See Appendix 2.4 for the ^{1}H nmr spectrum.

2.3.3 Synthesis of 3-bromopropyl acetate: acetyl chloride route (2)

Acetyl chloride (171.2g, 2.18mol) was added via a dropping funnel to 3-bromopropan-1-ol (166.19g, 1.20mol) contained in a 1000cm^3 3-necked round bottomed flask equipped with a stirrer, gas inlet and gas outlet. The reaction mixture was stirred under nitrogen for 18 hours. The mixture was distilled under nitrogen at atmospheric pressure to yield 3-bromopropyl acetate, (194.99g, 1.08mol, 93%), as a clear liquid. b.p. 182-186°C. Calculated for $C_5H_9O_2Br$: C, 33.19; H, 5.05%. Found: C, 33.18; H, 5.01%. ^{1}H Nmr (CDCl$_3$, 400 MHz), δ1.94 (s, 3H, C$\underline{H}_3$), δ2.06 (m, 2H, C$\underline{H}_2$), δ3.36 (t, ^{3}J = 6.4 Hz, 2H, C$\underline{H}_2$Br), δ4.08 (t, ^{3}J = 6.0 Hz, 2H, C$\underline{H}_2$O). ^{13}C Nmr (CDCl$_3$, 100 MHz), δ20.6 ($\underline{C}$H$_3$), δ29.20 ($\underline{C}$H$_2$), δ31.3 ($\underline{C}$H$_2$Br), δ61.8 (C$\underline{H}_2$O), δ170.4 (O-$\underline{C}$=O). IR (thin film), 2917cm^{-1} (w, saturated C-H stretch), 1747cm^{-1} (s, aliphatic ester stretch). See Appendices 2.5-2.7 for IR, ^{1}H nmr and ^{13}C nmr spectra of 3-bromopropyl acetate.

2.3.4 Synthesis of dimethyl 5-(3-acetoxypropoxy)isophthalate (3)

Anhydrous potassium carbonate (65.0g, 0.47mol), dimethyl 5-hydroxyisophthalate (100g, 0.47mol), 3-bromopropyl acetate (80.2g, 0.44mol) and anhydrous acetone (1600cm^3) were charged into a 2000cm^3, 3-necked round bottomed flask fitted with a mechanical stirrer, thermometer and reflux condenser with a drying tube ($CaCl_2$) attached to the top of the condenser. The reaction mixture was stirred and heated under reflux for 72 hours.

On allowing the reaction mixture to cool to room temperature, the mixture was filtered and the residue washed with acetone. The acetone was removed from the combined filtrates under reduced pressure to yield a pale pink solid. This was recrystallised from hot hexane to yield *dimethyl 5-(3-acetoxypropoxy)isophthalate*, (90.24g, 0.29mols, 62%), as a fine white powder. m.p. 86.4-88.6°C. Found: C, 58.05; H, 5.85%, $C_{15}H_{18}O_7$ requires: C, 58.04; H, 5.95%. ^{1}H Nmr ($CDCl_3$, 400 MHz), δ2.04 (s, 3H, $\underline{H}$: C$\underline{H}_3$-C=O), 2.12 (m, 2H, C$\underline{H}_2$), δ3.91 (s, 6H, OC$\underline{H}_3$), δ4.11 (t, $^3J = 6.0$ Hz, 2H, ArOC$\underline{H}_2$), δ4.25 (t, $^3J = 6.2$ Hz, 2H, C$\underline{H}_2$O-C=O), δ7.71 (d, $^4J = 1.2$ Hz, 2H, Ar-$\underline{H}$), δ8.24 (t, $^4J = 1.6$ Hz, 1H, Ar-$\underline{H}$). ^{13}C Nmr ($CDCl_3$, 100 MHz), δ20.9 ($\underline{C}$H$_3$-C=O), δ28.4 ($\underline{C}$H$_2$), δ52.4 (ester O$\underline{C}$H$_3$), δ61.0 ($\underline{C}$H$_2$O-C=O), δ64.7 (ArO$\underline{C}$H$_2$), δ119.7, δ123.0 (aromatic $\underline{C}$-H), δ131.7 (aromatic $\underline{C}$-COOCH$_3$), δ158.8 (aromatic $\underline{C}$-O), δ166.0 (ester $\underline{C}$=O), δ171.0 (acetate $\underline{C}$=O).

IR (KBr disc), 3077cm^{-1} (w, aryl-H C-H stretch), 2951cm^{-1} (w, saturated C-H stretch), 1732cm^{-1} (s, aliphatic C=O stretch), 1717cm^{-1} (s, aromatic C=O stretch), 1594cm^{-1} (m, aryl-H C-H vibration), 1447cm^{-1} (saturated C-H bend), 1244cm^{-1} (s, aryl C-O stretch), 759cm^{-1} (s, aryl-H out of plane vibration).

MS (CI+): 328 (M+NH_4), 311 (M+1), 296 (M-CH_3), 279 (M-OCH_3), 101 (M-(CH_3OC=O)$_2C_6H_3O$).

See Appendices 2.8-2.11 for full details of IR, MS, ^{1}H nmr and ^{13}C nmr spectra of dimethyl 5-(3-acetoxypropoxy)isophthalate.

2.3.5 Synthesis of dimethyl 5-(4-acetoxybutoxy)isophthalate (4)

Anhydrous potassium carbonate (41.9g, 0.31mol), dimethyl 5-hydroxyisophthalate (64.9g, 0.31mol), 4-bromobutyl acetate (72.4g, 0.37mol) and anhydrous acetone ($1200cm^3$) were charged into a $2000cm^3$, 3-necked round bottomed flask fitted with a mechanical stirrer, thermometer and reflux condenser with a drying tube ($CaCl_2$) attached to the top of the condenser. The reaction mixture was stirred and heated under reflux for 120 hours.

On allowing the reaction mixture to cool to room temperature, the mixture was filtered and the residue washed with acetone. The acetone was removed from the combined filtrates under reduced pressure to yield a pale brown solid. This solid was ground and stirred in hexane ($750cm^3$) for 18 hours. The solid was collected by filtration, washed in hexane and dried under reduced pressure to yield *dimethyl 5-(4-acetoxybutoxy)isophthalate*, (75.23g, 0.30mol, 75%), as a fine white powder. m.p. 49.1-50.5°C. Found: C, 59.82; H, 6.13%, $C_{16}H_{20}O_7$ requires: C, 59.25; H, 6.22%. ^{1}H Nmr ($CDCl_3$, 400 MHz), δ1.88 (m, 2H, $CH_2\underline{CH_2}\underline{CH_2}CH_2$), δ2.06 (s, 3H, $\underline{CH_3}$-C=O), δ3.94 (s, 6H, $O\underline{CH_3}$), δ4.08 (t, $^3J = 6.0$ Hz, 2H, $ArO\underline{CH_2}$), δ4.15 (t, $^3J = 6.2$ Hz, 2H, $\underline{CH_2}$O-C=O), δ7.74 (d, $^4J = 1.6$ Hz, 2H, Ar-$\underline{H}$), δ8.27 (s, 1H, Ar-$\underline{H}$). ^{13}C Nmr ($CDCl_3$, 100 MHz), δ20.9 ($\underline{C}H_3$-C=O), δ25.7, 25.2 ($\underline{C}H_2$), δ52.3 (ester $O\underline{C}H_3$), δ63.9 ($\underline{C}H_2$O-C=O), δ67.8 ($ArO\underline{C}H_2$), δ119.7, δ122.9 (aromatic $\underline{C}$-H), δ131.7 (aromatic $\underline{C}$-$COOCH_3$), δ158.9 (aromatic $\underline{C}$-O), δ166.0 (ester $\underline{C}$=O), δ171.0 (acetate $\underline{C}$=O).

IR (KBr disc), $3109cm^{-1}$ (w, aryl-H C-H stretch), $2953cm^{-1}$ (w, saturated C-H stretch), $1741cm^{-1}$ (s, aliphatic C=O stretch), $1724cm^{-1}$ (s, aromatic C=O stretch), $1594cm^{-1}$ (m, aryl-H C-H vibration), $1440cm^{-1}$ (m, saturated C-H bend), $1245cm^{-1}$ (s, aryl C-O stretch), $757cm^{-1}$ (s, aryl-H out of plane vibration).

MS (EI+): 324 (M), 210 (M-$(CH_2)_4OC(O)CH_3$+H), 179 (M-$(CH_2)_4OC(O)CH_3$ -OCH_3,+H), 115 (M-$(CH_3OC{=}O)_2C_6H_3O$).

See Appendices 2.12-2.15 for full details of IR, MS, ^{1}H nmr and ^{13}C nmr spectra of dimethyl 5-(4-acetoxybutoxy)isophthalate.

2.3.6 Synthesis of dimethyl 5-(5-acetoxypentoxy)isophthalate (5)

Anhydrous potassium carbonate (84.8g, 0.61mol), dimethyl 5-hydroxyisophthalate (125.6g, 0.60mol), 5-bromopentyl acetate (167.6g, 0.80mol) and anhydrous acetone (2200cm^3) were charged into a 5000cm^3 flange flask fitted with a mechanical stirrer, thermometer and reflux condenser with a drying tube ($CaCl_2$) attached to the top of the condenser. The reaction mixture was stirred and heated under reflux for 144 hours.

On allowing the reaction mixture to cool to room temperature, the mixture was filtered and the residue washed with acetone. The acetone was removed from the combined filtrates under reduced pressure to yield a pale yellow oil. The oil was washed in hexane (4 x 500cm^3), and dried under reduced pressure to yield a white solid. This solid was ground and stirred in hexane (750cm^3) for 18 hours. The solid was collected by filtration, washed in hexane and dried under reduced pressure to yield *dimethyl 5-(5-acetoxypentoxy)isophthalate*, (98.3g, 0.29mol, 48.6%), as a white powder. m.p. 44.8-46.5 °C. Found: C, 60.23; H, 6.60%, $C_{17}H_{22}O_7$ requires: C, 60.35; H, 6.56%. ^{1}H Nmr ($CDCl_3$, 400 MHz), δ1.57 (q, 2H, $CH_2\underline{CH_2}CH_2$), δ1.72 (m, 2H, $O{=}COCH_2\underline{CH_2}CH_2$), δ1.86 (m, 2H, $CH_2\underline{CH_2}CH_2OAr$), δ2.07 (s, 3H, $\underline{CH_3}\text{-}C{=}O$), δ3.94 (s, 6H, $O\underline{CH_3}$), δ4.04 (t, $^3J = 6.4$ Hz, 2H, $ArO\underline{CH_2}$), δ4.11 (t, $^3J = 6.6$ Hz, 2H, $\underline{CH_2}OC{=}O$), δ7.74 (d, $^4J = 1.2$ Hz, 2H, Ar-$\underline{H}$), δ8.26 (s, 1H, Ar-$\underline{H}$). ^{13}C Nmr ($CDCl_3$, 100 MHz), δ20.9 ($\underline{C}H_3\text{-}C{=}O$), δ28.3, 22.5 and 28.7 ($\underline{C}H_2$), δ52.3 (ester $O\underline{C}H_3$), δ64.2 ($\underline{C}H_2O\text{-}C{=}O$), δ68.2 ($ArO\underline{C}H_2$), δ119.7, δ122.8 (aromatic $\underline{C}$-H), δ131.6 (aromatic $\underline{C}$-$COOCH_3$), δ159.0 (aromatic $\underline{C}$-O), δ166.1 (ester $\underline{C}{=}O$), δ171.1 (acetate $\underline{C}{=}O$).

IR (KBr disc), 3090cm^{-1} (w, aryl-H C-H stretch), 2953cm^{-1} (w, saturated C-H stretch), 1735cm^{-1} (s, aliphatic C=O stretch), 1719cm^{-1} (s, aromatic C=O stretch), 1595cm^{-1} (m, aryl-H C-H vibration), 1437cm^{-1} (m, saturated C-H bend), 1248cm^{-1} (s, aryl C-O stretch), 759cm^{-1} (s, aryl-H out of plane vibration).

MS (EI+): 338 (M), 307 (M -OCH_3), 210 (M -$(CH_2)_5OC(O)CH_3$ +H), 179 (M -$(CH_2)_5OC(O)CH_3$, -OCH_3,+ H).

See Appendices 2.16-2.19 for full details of IR, MS, ^{1}H nmr and ^{13}C nmr spectra of dimethyl 5-(5-acetoxypentoxy)isophthalate.

2.3.7 Synthesis of 6-bromohexyl acetate (6)

Acetyl chloride (92.5, 1.19mol) was added via a dropping funnel to 6-bromohexan-1-ol (98.0g, 0.54mol) contained in a 500cm^3 3-necked round bottomed flask equipped with a stirrer, gas inlet and gas outlet. The reaction mixture was stirred under nitrogen for 18 hours. The mixture was distilled under nitrogen at atmospheric pressure to yield 6-bromohexyl acetate, (110.0g, 0.493mol, 91.3 %), as a clear liquid. b.p. 80-82°C. Calculated for $C_8H_{15}O_2Br$: C, 43.07%; H, 6.77%. Found: C, 43.02%; H, 6.57%. ^{1}H Nmr ($CDCl_3$, 400 MHz), δ1.39 (m, 2H, $\underline{CH_2}CH_2CH_2Br$), δ1.48 (m, 2H, $\underline{CH_2}CH_2CH_2OAc$), δ1.65 (m, 2H, $CH_2\underline{CH_2}CH_2Br$), δ1.87 (m, 2H, $CH_2\underline{CH_2}CH_2OAc$), δ2.05 (s, 3H, $COO\underline{CH_3}$), δ3.41 (t, $^3J = 6.8$ Hz, 2H, $\underline{CH_2}Br$), δ4.06 (t, $^3J = 6.6$ Hz, 2H, $\underline{CH_2}OAc$). ^{13}C Nmr ($CDCl_3$, 100 MHz), δ21.0 ($\underline{C}H_3$), δ25.1, δ27.7, δ28.4 and δ32.6 ($\underline{C}H_2$), δ33.7 ($\underline{C}H_2Br$), δ64.3 ($C\underline{H_2}O$), δ171.1 (O-$\underline{C}$=O).

IR (thin film), 2937cm^{-1} (w, saturated C-H stretch), 1738cm^{-1} (s, aliphatic ester stretch).

MS (CI+): 243 (M+NH_4), 240, 242 (M+NH_4-1).

See Appendices 2.20-2.23 for full details of MS, IR, ^{1}H nmr and ^{13}C nmr spectra of 6-bromohexyl acetate.

2.3.8 Synthesis of dimethyl 5-(6-acetoxyhexoxy)isophthalate (7)

Anhydrous potassium carbonate (139.0g, 1.0mol), dimethyl 5-hydroxyisophthalate (57.0g, 0.27mol), 6-bromohexyl acetate (70.0g, 0.31mol) and anhydrous acetone (1500cm^3) were charged into a 2000cm^3, 3-necked round bottomed flask fitted with a mechanical stirrer, thermometer and reflux condenser, with a drying tube ($CaCl_2$) attached to the top of the condenser. The reaction mixture was stirred and heated under reflux for 144 hours.

On allowing the reaction mixture to cool to room temperature, the mixture was filtered and the residue washed with acetone. The acetone was removed from the combined filtrates under reduced pressure to yield a pale yellow oil. The oil was washed in hexane (4 x 500cm^3), dried under reduced pressure to yield a white solid which was recrystallised from hot hexane. The solid was collected by filtration, washed in hexane and dried under reduced pressure to yield *dimethyl 5-(6-acetoxyhexoxy) isophthalate*, (50.37g, 0.14mol, 53.0%), as a fine white powder. m.p. 48.2-50.0°C. Found: C, 61.37; H, 6.98%, $C_{18}H_{24}O_7$ requires: C, 61.35; H, 6.86%. ^{1}H Nmr ($CDCl_3$, 400 MHz), δ1.46 (m, 2H, $CH_2CH_2C\underline{H}_2C\underline{H}_2CH_2CH_2$), δ1.65 (m, $CH_2C\underline{H}_2CH_2OAr$), δ1.81 (m, 2H, $O{=}C\text{-}OCH_2C\underline{H}_2CH_2$), δ2.03 (s, 3H, $C\underline{H}_3\text{-}C{=}O$), δ3.92 (s, 6H, $OC\underline{H}_3$), δ4.02 (t, $^3J = 6.4$ Hz, 2H, $ArOC\underline{H}_2$), δ4.06 (t, $^3J = 6.4$ Hz, 2H, $C\underline{H}_2O\text{-}C{=}O$), δ7.71 (d, $^4J = 1.6$ Hz, 2H, Ar-$\underline{H}$), δ8.24 (s, 1H, Ar-$\underline{H}$). ^{13}C Nmr ($CDCl_3$, 100 MHz), δ21.0 ($\underline{C}H_3\text{-}C{=}O$), δ25.7, δ28.5 and δ28.9 ($\underline{C}H_2$), δ52.4 (ester $O\underline{C}H_3$), δ64.4 ($ArO\underline{C}H_2$), δ68.2 ($\underline{C}H_2O\text{-}C{=}O$), δ119.7, δ122.7 (aromatic $\underline{C}$-H), δ131.6 (aromatic $\underline{C}\text{-}COOCH_3$), δ159.1 (aromatic $\underline{C}$-O), δ166.1 (ester $\underline{C}{=}O$), δ171.2 (acetate $\underline{C}{=}O$).

IR (KBr disc), 3089cm^{-1} (w, aryl-H C-H stretch), 2947cm^{-1} (w, saturated C-H stretch), 1734cm^{-1} (s, aliphatic C=O stretch), 1723cm^{-1} (s, aromatic C=O stretch), 1596cm^{-1} (m, aryl-H C-H vibration), 1440cm^{-1} (m, saturated C-H bend), 1241cm^{-1} (s, aryl C-O stretch), 749cm^{-1} (s, aryl-H out of plane vibration).

MS (CI+): 371 ($M+1+NH_4$), 353 (M+1), 338 ($M+1-CH_3$), 321 ($M-OCH_3$), 210 ($M-(CH_2)_6OC(O)CH_3,+H$), 179 ($M-(CH_2)_6OC(O)CH_3,-OCH_3,+H$).

See Appendices 2.24-2.27 for full details of IR, MS, ^{1}H nmr and ^{13}C nmr spectra of dimethyl 5-(6-acetoxyhexoxy)isophthalate.

2.3.9 Synthesis of dimethyl 5-(3-hydroxypropoxy)isophthalate (8)

Dimethyl 5-(3-acetoxypropoxy)isophthalate (20.0g, 0.07mol), potassium hydroxide (0.15g, 0.003mol) and anhydrous methanol (400cm^3) were charged into a 1000cm^3, 2-necked round bottomed flask equipped with a thermometer, stirrer and reflux condenser with a drying tube ($CaCl_2$) attached to the top of the condenser. The reaction mixture was stirred and heated at 30°C for 18 hours.

The reaction mixture was poured into distilled water (600cm^3) and the solution acidified to pH 1 with aqueous hydrochloric acid solution (1M). The methanol was removed from the reaction mixture under reduced pressure and the resulting mixture was extracted with dichloromethane (3 x 100cm^3). The combined organic extracts were dried ($MgSO_4$) and the solvent removed under reduced pressure to yield a yellow oil which solidified on standing to produce *dimethyl 5-(3-hydroxypropoxy)isophthalate* (12.4g, 0.046mol, 70.9%), as a white solid. m.p. 49.6-52.8°C. Found: C, 57.93; H, 6.01%, $C_{13}H_{16}O_6$ requires: C, 58.20; H, 6.01%. ^{1}H Nmr ($CDCl_3$, 400 MHz), δ2.00 (q, 2H, $^3J = 6.0$ Hz, $CH_2C\underline{H}_2CH_2$), δ2.05 (s, $CH_2O\underline{H}$), δ3.81 (t, 2H, $^3J = 6.0$ Hz, $C\underline{H}_2OH$), δ3.86 (s, 6H, $OC\underline{H}_3$), δ4.13 (t, 2H, $^3J = 6.0$ Hz, $ArOC\underline{H}_2$), δ5.23 (s, residual $C\underline{H}_2Cl_2$), δ7.67 (d, 2H, $^4J = 1.2$ Hz, Ar-$\underline{H}$), δ8.18 (t, 1H, $^4J = 1.4$ Hz, Ar-$\underline{H}$). ^{13}C Nmr ($CDCl_3$, 100 MHz), δ31.8 ($\underline{C}H_2$), δ52.4 (ester $O\underline{C}H_3$), δ59.6 ($\underline{C}H_2OH$), δ65.9 ($ArO\underline{C}H_2$), δ119.7, δ123.0 (aromatic $\underline{C}$-H), δ131.6 (aromatic $\underline{C}$-$COOCH_3$), δ158.8 (aromatic $\underline{C}$-O), δ166.1 (ester $\underline{C}$=O).

IR (KBr disc), 3333cm^{-1} (broad O-H stretch), 3079cm^{-1} (w, aryl-H C-H stretch), 2948cm^{-1} (w, saturated C-H stretch), 1724cm^{-1} (s, C=O absorption), 1596cm^{-1} (s, aryl-H C-H vibration), 1458cm^{-1} (m, saturated C-H bend), 1243cm^{-1} (s, aryl C-O stretch), 754cm^{-1} (s, aryl-H out of plane vibration).

MS (CI+): 286 ($M+NH_4$), 268 (M), 253 ($M-CH_3$), 237 ($M-OCH_3$) 209 ($M-(CH_2)_3OH$), 179 ($M-(CH_2)_3OH,-OCH_3,+H$), 151 ($M-(CH_2)_3OH,-CO_2CH_3,+H$).

See Appendices 2.28-2.31 for full details of IR, MS, ^{1}H nmr and ^{13}C nmr spectra of dimethyl 5-(3-hydroxypropoxy)isophthalate.

2.3.10 Synthesis of dimethyl 5-(4-hydroxybutoxy)isophthalate (9)

Dimethyl 5-(4-acetoxybutoxy)isophthalate (46.1g, 0.14mol), potassium hydroxide (0.36g, 0.006mol) and anhydrous methanol (1000cm^3) were charged into a 2000cm^3, 2-necked round bottomed flask equipped with a thermometer, stirrer and reflux condenser with a drying tube ($CaCl_2$) attached to the top of the condenser. The reaction mixture was stirred and heated at 30°C for 18 hours.

The reaction mixture was acidified to pH 1 with aqueous hydrochloric acid solution (1M). The methanol was removed from the reaction mixture under reduced pressure. The resulting oil was dissolved in dichloromethane and the mixture washed with distilled water (4 x 500cm^3). The combined organic extracts were dried ($MgSO_4$) and the solvent removed under reduced pressure to yield a yellow oil which solidified on standing to produce *dimethyl 5-(4-hydroxybutoxy)isophthalate*, (33.68g, 0.12mol, 84.1%), as a white solid. m.p. 59.8-63.2 °C. Found: C, 59.39; H, 6.41%, $C_{14}H_{18}O_6$ requires: C, 59.63; H, 6.43%. ^{1}H Nmr ($CDCl_3$, 400 MHz), δ1.71 (m, 2H, $HOCH_2C\underline{H}_2$), δ1.87 (m, 2H, $ArOCH_2C\underline{H}_2$), δ2.53 (s, $CH_2O\underline{H}$), δ3.68 (t, 2H, ^3J = 6.4 Hz, $C\underline{H}_2OH$), δ3.87 (s, 6H, $OC\underline{H}_3$), δ4.02 (t, 2H, ^3J = 6.4 Hz, $ArOC\underline{H}_2$), δ5.25 (s, residual $C\underline{H}_2Cl_2$), δ7.65 (d, 2H, ^4J = 1.2 Hz, Ar-$\underline{H}$), δ8.17 (t, 1H, ^4J = 1.2 Hz, Ar-$\underline{H}$). ^{13}C Nmr ($CDCl_3$, 100 MHz), δ25.5 ($HOCH_2C\underline{H}_2$), δ29.0 ($ArOCH_2C\underline{H}_2$), δ52.3 (ester $O\underline{C}H_3$), δ62.1 ($\underline{C}H_2OH$), δ68.2 ($ArO\underline{C}H_2$), δ119.6, δ122.7 (aromatic $\underline{C}$-H), δ131.5 (aromatic $\underline{C}$-$COOCH_3$), δ158.8 (aromatic $\underline{C}$-O), δ166.0 (ester $\underline{C}$=O).

IR (KBr disc), 3279cm^{-1} (broad O-H stretch), 3089cm^{-1} (w, aryl-H C-H stretch), 2953cm^{-1} (w, saturated C-H stretch), 1718cm^{-1} (s, C=O absorption), 1594cm^{-1} (s, aryl-H

C-H vibration), 1434cm^{-1} (m, saturated C-H bend), 1234cm^{-1} (s, aryl C-O stretch), 755cm^{-1} (s, aryl-H out of plane vibration).

MS (EI+): 282 (M), 251 (M-OCH_3), 210 (M-$(CH_2)_4OH$ +H), 179 (M-$(CH_2)_4OH$,-OCH_3,+H), 151 (M-$(CH_2)_4OH$,-CO_2CH_3,+H).

See Appendices 2.32-2.35 for full details of IR, MS, ^{1}H nmr and ^{13}C nmr spectra of dimethyl 5-(4-hydroxybutoxy)isophthalate.

2.3.11 Synthesis of dimethyl 5-(5-hydroxypentoxy)isophthalate (10)

Dimethyl 5-(5-acetoxypentoxy)isophthalate (92.5g, 0.27mol), potassium hydroxide (0.62g, 0.01mol) and anhydrous methanol (1500cm^3) were charged into a 2000cm^3, 2-necked round bottomed flask equipped with a thermometer, stirrer and reflux condenser with a drying tube ($CaCl_2$) attached to the top of the condenser. The reaction mixture was stirred and heated at 30°C for 18 hours.

The reaction mixture was acidified to pH 1 with aqueous hydrochloric acid solution (1M). The methanol was removed from the reaction mixture under reduced pressure. The resulting oil was dissolved in dichloromethane and the mixture washed with distilled water (4 x 500cm^3). The combined organic extracts were dried ($MgSO_4$) and the solvent removed under reduced pressure to yield a yellow oil which solidified on standing to produce *dimethyl 5-(5-hydroxypentoxy)isophthalate*, (65.7g, 0.22mol, 81.3%), as a white solid. m.p. 48.1-50.3°C. Found: C, 58.68; H, 6.63%, $C_{15}H_{20}O_6$ requires: C, 60.8; H, 6.8%. ^{1}H Nmr ($CDCl_3$, 400 MHz), δ1.56 (m, 2H, $CH_2\underline{CH_2}CH_2$), δ1.65 (m, 2H, $HOCH_2\underline{CH_2}CH_2$), δ1.84 (m, 2H, $CH_2\underline{CH_2}CH_2OAr$), δ3.68 (t, ^3J = 6.4 Hz, 2H, $\underline{CH_2}OH$), δ3.94 (s, 6H, $O\underline{CH_3}$), δ4.05 (t, ^3J = 6.4 Hz, 2H, $ArO\underline{CH_2}$), δ7.72 (d, ^4J = 1.2 Hz, 2H, Ar-$\underline{H}$), δ8.24 (s, 1H, Ar-$\underline{H}$). ^{13}C Nmr ($CDCl_3$, 100 MHz), δ20.9 ($\underline{C}H_3$-C=O), δ22.1, 28.7 and 32.2 ($\underline{C}H_2$), δ52.3 (ester $O\underline{C}H_3$), δ62.4 ($\underline{C}H_2OH$), δ68.3

(ArO$\underline{C}H_2$), δ119.6, δ122.6 (aromatic $\underline{C}$-H), δ131.5 (aromatic $\underline{C}$-$COOCH_3$), δ158.9 (aromatic $\underline{C}$-O), δ166.1 (ester $\underline{C}$=O).

IR (KBr disc), 3281cm^{-1} (broad O-H stretch), 3089cm^{-1} (w, aryl-H C-H stretch), 2933cm^{-1} (w, saturated C-H stretch), 1719cm^{-1} (s, C=O absorption), 1594cm^{-1} (s, aryl-H C-H vibration), 1434cm^{-1} (m, saturated C-H bend), 1246cm^{-1} (s, aryl C-O stretch), 753cm^{-1} (s, aryl-H out of plane vibration).

MS (CI+): 314 ($M+NH_4$), 296 (M), 281 ($M-CH_3$), 151 ($M-(CH_2)_5OH,-CO_2CH_3,+H$).

See Appendices 2.36-2.39 for full details of IR, MS, ^{1}H nmr and ^{13}C nmr spectra of dimethyl 5-(5-hydroxypentoxy)isophthalate.

2.3.12 Synthesis of dimethyl 5-(6-hydroxyhexoxy)isophthalate (11)

Dimethyl 5-(6-acetoxyhexoxy)isophthalate (40.0g, 0.11mol), potassium hydroxide (0.36g, 0.006mol) and anhydrous methanol (700cm^3) were charged into a 1000cm^3, 2-necked round bottomed flask equipped with a thermometer, stirrer and reflux condenser with a drying tube ($CaCl_2$) attached to the top of the condenser. The reaction mixture was stirred and heated at 30°C for 18 hours.

The reaction mixture was acidified to pH 1 with aqueous hydrochloric acid solution (1M). The methanol was removed from the reaction mixture under reduced pressure. The resulting oil was dissolved in dichloromethane and the mixture washed with distilled water (4 x 500cm^3). The combined organic extracts were dried ($MgSO_4$) and the solvent removed under reduced pressure to yield a yellow oil which solidified on standing to produce *dimethyl 5-(6-hydroxyhexoxy)isophthalate*, (22.8g, 0.07mol, 67.1%), as a white solid. m.p. 47.6-48.8°C. Found: C, 61.67; H, 6.98%, $C_{16}H_{22}O_6$ requires: C, 61.37; H, 7.14%. ^{1}H Nmr ($CDCl_3$, 400 MHz), δ1.49 (m, 4H, $CH_2CH_2C\underline{H_2}C\underline{H_2}CH_2CH_2$), δ1.61 (m, 2H, $CH_2C\underline{H_2}CH_2OH$), δ1.82 (m, 2H, $ArOCH_2C\underline{H_2}CH_2$), δ2.17 (s, 3H, $C\underline{H_3}C(=O)$, residual acetone), δ3.66 (t, ^3J = 6.4 Hz, 2H, C$\underline{H}_2$OH), δ3.93 (s, 6H, OC$\underline{H}_3$), δ4.04 (t, $^3J = 6.4$ Hz, 2H, ArOC$\underline{H}_2$), δ5.29 (s, residual C$\underline{H}_2$Cl$_2$), δ7.73 (d, $^4J = 1.2$ Hz, 2H, Ar-$\underline{H}$), δ8.25 (t, $^4J = 1.6$ Hz, 1H, Ar-$\underline{H}$). ^{13}C Nmr (CDCl$_3$, 100 MHz), δ25.8, δ25.5, δ29.0 and δ32.6 ($\underline{C}$H$_2$), δ30.9 (residual C$\underline{H}_2$Cl$_2$), δ52.4 (ester O$\underline{C}$H$_3$), δ62.8 ($\underline{C}$H$_2$OH), δ68.4 (ArO$\underline{C}$H$_2$), δ119.8, δ122.6 (aromatic $\underline{C}$-H), δ131.7 (aromatic $\underline{C}$-COOCH$_3$), δ159.1 (aromatic $\underline{C}$-O), δ166.2 (ester $\underline{C}$=O).

IR (KBr disc), 3543 cm^{-1} (m, O-H stretch), 3093cm^{-1} (w, aryl-H C-H stretch), 2943cm^{-1} (m, saturated C-H stretch), 1725cm^{-1} (s, C=O absorption), 1596cm^{-1} (s, aryl-H C-H vibration), 1440cm^{-1} (m, saturated C-H bend), 1240cm^{-1} (s, aryl C-O stretch), 757cm^{-1} (s, aryl-H out of plane vibration).

MS (CI+): 328 (M+NH$_4$), 311 (M+1), 279 (M-CH$_3$), 279 (M-OCH$_3$) 210 (M-(CH$_2$)$_6$OH, +H), 179 (M-(CH$_2$)$_6$OH, -OCH$_3$,+H), 151 (M-(CH$_2$)$_6$OH,-CO$_2$CH$_3$,+H).

See Appendices 2.40-2.43 for full details of IR, MS, ^{1}H nmr and ^{13}C nmr spectra of dimethyl 5-(6-hydroxyhexoxy)isophthalate.

2.4 References

[1] Stainton, N. M., *Ph. D. Thesis,* University of Durham, 1994.

[2] Furniss, B. S., Hannaford, A. J., Smith, P. W. and Tatchall, A. R., "*Vögel's Textbook of Practical Organic Chemistry*" 5th Edn., Longman, 1989.

[3] March, J., "*Advanced Organic Chemistry*", 4th Edn., John Wiley and Sons, New York, 1992, 392.

[4] March, J., "*Advanced Organic Chemistry*", 4th Edn., John Wiley and Sons, New York, 1992, 378.

[5] Buckingham, J., and Donaghy, S. M, "*Dictionary of Organic Compounds*" (5th edn.), Chapman and Hall (1982).

CHAPTER THREE

THE SYNTHESIS OF HYPERBRANCHED POLY(DIMETHYL 5-(ω-HYDROXYALKOXY)ISOPHTHALATE)S

3.1 Introduction

In this chapter the syntheses of the hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s are described. Earlier work had established the polymerisation of dimethyl 5-(2-hydroxyethoxy)isophthalate,[1] given the structural similarity of this monomer to the monomers used in this study, it was anticipated that a similar polymerisation procedure would be effective in the melt polycondensation of these closely related dimethyl 5-(ω-hydroxyalkoxy)isophthalate monomers.

3.2 General polymerisation procedure

In the bulk polymerisation of neat monomer, large changes in viscosity are encountered during the reaction. To obtain effective mixing throughout the reaction efficient stirring is crucial in such polymerisations. Consequently, the polycondensation reaction is carried out using the specially designed apparatus shown schematically in Figure 3.1. In this reaction vessel the clearance between the stirrer blades and the vessel walls is small (~2mm), which facilitates intimate mixing. An IKA Eurostar power-b overhead mechanical stirrer, with a 6mm diameter stirrer rod held in place by a rubber seal inserted into a glass gland, drives the stainless steel stirrer which forces the molten mass against the bottom of the flask and rotates at 125 r.p.m. throughout the reaction. The stirrer and reaction vessel are securely clamped onto a stable heavy duty stand with an H footprint. This arrangement ensures that there is no twisting or misalignment during the reaction despite the large change in viscosity. The reaction time and temperature are controlled using a Eurotherm temperature controller with thermocouples and a 1kW heating band surrounding an oil bath. Polymerisations were carried out using approximately 4-5g of the AB_2 monomer, this ensured that sufficient polymer was made for characterisation of the sample and for further investigations of the physical properties and structure of the materials. Triphenylphosphate was added to the reaction mixture to restrict thermal degradation of the polymer.

The AB_2 monomer sample (~5.0g), catalyst and triphenylphosphate (3mg, 0.008mmol), were added to the reaction vessel which was then purged with nitrogen. Whilst stirring the reaction mixture under a flow of nitrogen gas, the oil bath was heated at a rate of 10°C min^{-1} from room temperature to 210°C, where the reaction temperature was held for varying lengths of time. On completion of the polymerisation the reaction mixture was cooled to room temperature under a flow of nitrogen. The viscous mass solidified to give a brittle brown glass, which in most cases was readily soluble in tetrahydrofuran or chloroform. The solid was obtained without further purification by chipping it out of the reaction vessel, or dissolving it in tetrahydrofuran or chloroform and evaporating the solvent. Alternatively, the polymer was obtained as a white powder by adding a tetrahydrofuran solution of the polymer to a large excess of hexane. The polymer precipitated and was collected by filtration and dried under reduced pressure. Analogously the polymer could be dissolved in chloroform and precipitated into an excess of methanol. Precipitation from THF into hexane was preferred, as it was easier to dry the product.

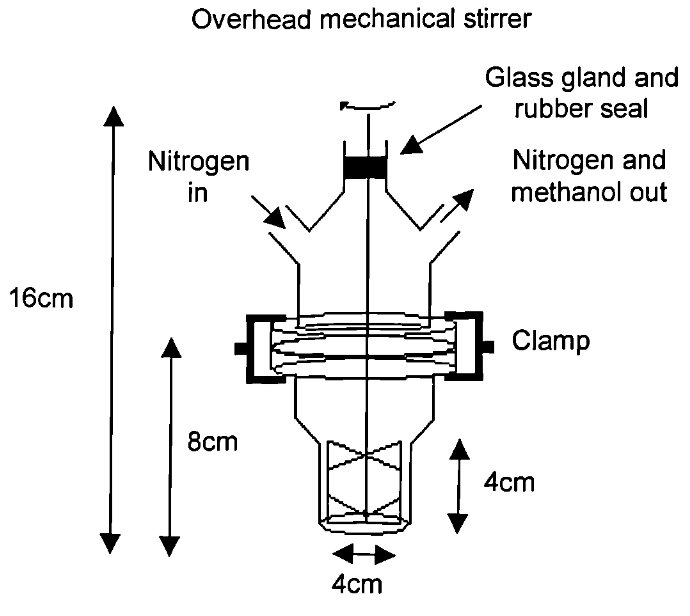


Figure 3.1: Schematic of the polymerisation reaction vessel

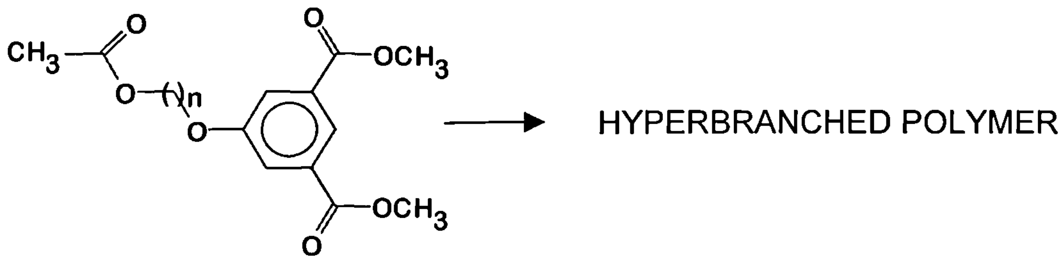
Various parameters including catalyst, temperature, duration of reaction, and atmosphere (nitrogen or vacuum) could be varied. Specific reaction conditions for individual polymerisations are given throughout the discussion

3.2.1 Preliminary polymerisations

The synthesis of polyesters via the condensation reaction between an alcohol and an ester group is well established.[2, 3, 4] Stainton used this reaction to prepare hyperbranched polyesters derived from dimethyl 5-(2-hydroxyethoxy)isophthalate.[1] It was found in the preparation of the analogous dimethyl 5-(ω-hydroxyalkoxy) isophthalate monomers, described in Chapter 2, that they were most readily obtainable via the dimethyl 5-(ω-acetoxyalkoxy)isophthalate intermediates. Since, if polymerisation via the condensation reaction between the ω-acetoxy and aromatic methyl ester group was efficient, it would have been possible to omit one step in the route to hyperbranched polyesters, initial experiments sought to investigate the relative reactivity of the dimethyl 5-(ω-acetoxyalkoxy)isophthalates and dimethyl 5-(ω-hydroxyalkoxy)isophthalates.

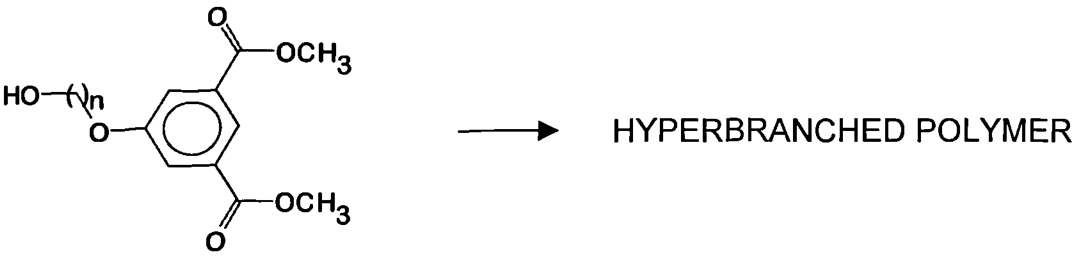
Preliminary polymerisation studies of monomers **3**, **4**, **5** and **8**, shown schematically overleaf in Figure 3.2, were carried out using the general polymerisation procedure described above, with a reaction temperature of 240°C maintained for 4 hours. The catalyst and pressure were varied in the polymerisations and a summary of the different polymerisation conditions (a – e) is shown overleaf.

For the acetoxy AB_2 monomers (**3**, **4** and **5**) three catalyst systems were investigated in the preliminary polymerisations. Firstly a combination of antimony trioxide and manganese acetate was used as catalyst since this system had been successfully used in the preparation of a similar hyperbranched polyester.[1] Titanium (IV) butoxide,[3, 5, 6] a well known catalyst for polyesterification reactions, and sodium



"Acetoxy AB_2 monomers"

n = 3, AB_2 monomer **3**	n = 3, Hyperbranched polymers **3a-e**
n = 4, AB_2 monomer **4**	n = 4, Hyperbranched polymer **4a**
n = 5, AB_2 monomer **5**	n = 5, Hyperbranched polymer **5c**



"Hydroxy AB_2 monomer"

n = 3, AB_2 monomer **8**	n = 3, Hyperbranched polymers **8a-c**

Figure 3.2: Dimethyl 5-(ω-acetoxyalkoxy)isophthalate and dimethyl 5-(ω-hydroxyalkoxy)isophthalate monomers used in the preliminary polymerisation experiments

Summary of reaction conditions a-e

a	No catalyst
b	Catalyst: Sb_2O_3 (4.0mg, 0.014mmol), $Mn(OAc)_2$ (3.5mg, 0.02mmol).
c	Catalyst: Sb_2O_3 (4.0mg, 0.014mmol), $Mn(OAc)_2$ (3.5mg, 0.02mmol). Vacuum applied (~10mmHg) for final 30 minutes of the reaction.
d	Catalyst: $Ti(O(CH_2)_3CH_3)_4$, (40mg, 0.12 mmol).
e	Catalyst: NaOMe, (4.0mg, 0.074 mmol).

methoxide,[7] used as a general base catalyst for the esterification reaction, were also examined as potential catalysts. For the polymerisation of the dimethyl 5-(3-hydroxypropoxy)isophthalate monomer, only the antimony trioxide and manganese acetate catalyst system was used since this had been established as a successful catalyst in the preparation of a similar hyperbranched polyester,[1] and this system is also well documented as an efficient catalyst for synthesis of linear polycondensation polymers such as poly(ethylene terephthalate).[8]

In three experiments a vacuum was applied for the final 30 minutes of the reaction (**3c**, **5c** and **8c**), it was anticipated that this would facilitate the removal of the eliminated units, methyl acetate or methanol, from the reaction vessel and move the equilibrium of the reaction towards the formation of polymer.

The polymers prepared in these experiments were analysed by size exclusion chromatography (SEC), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and ^{1}H nmr spectroscopy. SEC was performed using chloroform or tetrahydrofuran as solvent, in both cases linear polystyrene standards were used as calibrants. The reaction conditions, yields and SEC results are summarised in table 3.1. Thermal analysis results are shown in table 3.2. Instrument and experimental details for SEC, TGA, DSC and ^{1}H nmr spectroscopy are given in Appendix 2.

In experiments where conversion of monomer to polymer was low, yields were determined by ^{1}H nmr spectroscopy from the relative intensities of the methylene protons in the monomer, $C\underline{H}_2OH$ or $C\underline{H}_2OAc$, with that of the corresponding methylene protons in the polymer, $C\underline{H}_2OC(=O)Ar$. Where conversion of monomer to polymer was higher, approximate yields were determined gravimetrically.

Table 3.1: Preliminary polymerisation studies: conditions, yields and SEC results

Experiment No see below for reaction conditions a -e	**Yield** %	**SEC: solvent THF**			**SEC: solvent $CHCl_3$**		
		Mw	**Mn**	**Mw/Mn**	**Mw**	**Mn**	**Mw/Mn**
3a	2[a]	251	237	1.05	1 165	1 161	1.00
3b	20[a]	279	237	1.18	758	647	1.17
3c	11[a]	247	210	1.18	777	670	1.16
3d	0	250	248	1.01	596	555	1.07
3e	Insoluble product						
4a	0	214	211	1.01	533	531	1.00
5c	0	281	267	1.05	612	578	1.06
8a	66[b]	54 450	12 940	4.20	41 062	7 583	5.42
8b	47[b]	65 110	15 520	4.28	48 034	9 023	5.32
8c	67[b]	60 240	16 000	3.68	44 428	8 323	5.34

Reaction conditions a –e:

All polymerisations were carried out with stirring under nitrogen. The temperature of the reaction vessel was increased at a rate of 10°C min^{-1} from room temperature to 240°C, then held at 240°C for 4 hours. Triphenylphosphate was added to surpress thermal degradation.

a No catalyst.
b Catalyst: Sb_2O_3 (4.0mg, 0.014mmol), $Mn(OAc)_2$ (3.5mg, 0.02mmol).
c Catalyst: Sb_2O_3 (4.0mg, 0.014mmol), $Mn(OAc)_2$ (3.5mg, 0.02mmol).
Vacuum applied (~10mmHg) for final 30 minutes of the reaction.
d Catalyst: $Ti(O(CH_2)_3CH_3)_4$, (40mg, 0.12 mmol).
e Catalyst: NaOMe, (4.0mg, 0.074 mmol).

[a] Yields determined by ^{1}H nmr spectroscopy.

[b] Approximate yields determined gravimetrically.

Table 3.2: Thermal analysis of preliminary polymerisations.

Experiment number	Onset of decomposition temperature(/°C) (2% mass loss)	Tg(/°C)
3a	176	
3b	164	
3c	169	
3d	186	
3e	313	65.8
4a	169	
5c	157	
8a	324	65.2
8b	424	65.6
8c	338	64.4

All the attempted polymerisations of the acetoxy AB_2 monomers, **3-5**, failed. At best they produced low average molecular weight oligomers in low yields. ^{1}H Nmr spectroscopy indicated a low monomer conversion. Thermogravimetric analysis revealed low thermal stability with temperatures between 164°C and 176°C for the onset of decomposition. No glass transitions were detected.

In contrast, those polymers prepared from the dimethyl 5-(3-hydroxypropoxy) isophthalate monomer, **8a**, **8b** and **8c,** had higher average molecular weights and were obtained in higher yields. The polymer obtained from the uncatalysed polymerisation (**8a**) had a slightly lower average molecular weight than that obtained from the equivalent catalysed polymerisation (**8b**) although this is negligible considering the errors on the SEC measurement. Thermogravimetric analysis revealed that these polymers had higher thermal stabilities with temperatures between 324°C and 424°C for the onset of decomposition. A well-defined glass transition temperature was observed by DSC for these polymers at a temperature of 65±1°C. There was no evidence for a melting point which is consistent with the formation of amorphous polymer.

One exception to the observed failure of the acetoxy derivatives to polymerise was experiment **3e**. In this case titanium (IV) butoxide was used as catalyst in the polymerisation of dimethyl 5-(3-acetoxypropoxy)isophthalate, to produce an insoluble brown solid. Thermal analysis of the material indicated formation of a polymer with a high decomposition temperature (onset at 313°C) and a glass transition temperature of 65°C. This product, in contrast to most hyperbranched polymers produced in this work, was insoluble and no further physical characterisation was attempted.

^{1}H Nmr spectroscopy confirmed that there was no residual methanol in the polymers prepared under atmospheric pressure. Therefore it was decided that no vacuum was required during future reactions. Unexpectedly it was found that in polymerisations where a vacuum had been applied, a product with a marginally lower average molecular weight was obtained. The effect is small but reproducible and the author has no explanation for this observation.

Since the dimethyl 5-(3-hydroxypropoxy)isophthalate monomer (**8**) produced high average molecular weight polymers in reasonable yields (**8a-c**), it was thought advantageous to carry out all polymerisations using the hydroxy monomers. For polymerisations of the AB_2 monomers it was also decided to employ the same antimony trioxide and manganese acetate catalyst system which had been successfully used in the preparation of hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalate)s, and had also produced high average molecular weight polymers in the preliminary polymerisations of dimethyl 5-(3-hydroxypropoxy) isophthalate (**8b and 8c**). This would make further polymerisations comparable with those already carried out for the dimethyl 5-(2-hydroxyethoxy)isophthalate monomer.

Although initially a polymerisation temperature of 240°C was used, emulating the reaction temperature for the polymerisation of dimethyl 5-(2-hydroxyethoxy) isophthalate, this was later lowered to 210°C. This was required for safety reasons since the stability of the oil in the oil bath was found to be unreliable during polymerisations at 240°C for long reaction times. To examine the effect of decreasing the temperature of the reaction, polymerisations of dimethyl 5-(2-hydroxyethoxy)isophthalate and dimethyl 5-(3-hydroxypropoxy) isophthalate were carried out at 210°C and 240°C, for different lengths of time. SEC results from these experiments, shown in Figures 3.3 and 3.4, showed that lowering of the reaction temperature decreases the rate of the polymerisation as expected. For polymerisations of dimethyl 5-(3-hydroxypropoxy) isophthalate, the lower temperature does not affect the maximum average molecular weight obtained for the polymer, see Figure 3.3 below.

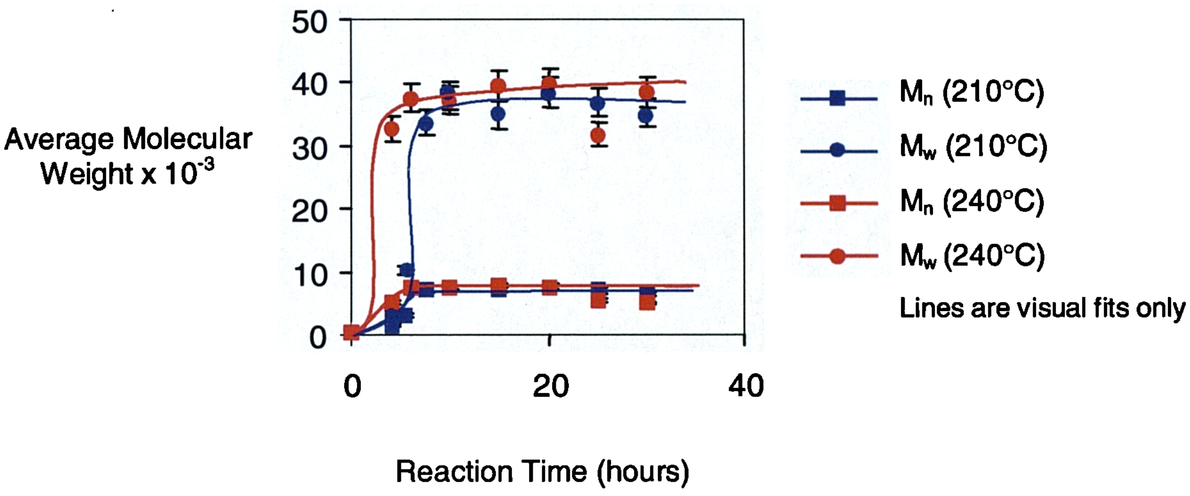


Figure 3.3: Graph to show the change in M_n and M_w with reaction time, in the polymerisation of dimethyl 5-(3-hydroxypropoxy)isophthalate at 210°C and 240°C

However, for polymerisations of dimethyl 5-(2-hydroxyethoxy)isophthalate the decrease in rate of polymerisation at lower reaction temperatures is much more marked, see Figure 3.4. In this case although M_n values are the same, there appear to be higher M_w for samples prepared at higher temperatures. All average molecular weights shown in Figures 3.3 and 3.4 were obtained using size exclusion chromatography with chloroform as the solvent and linear polystyrene standards as calibrants.

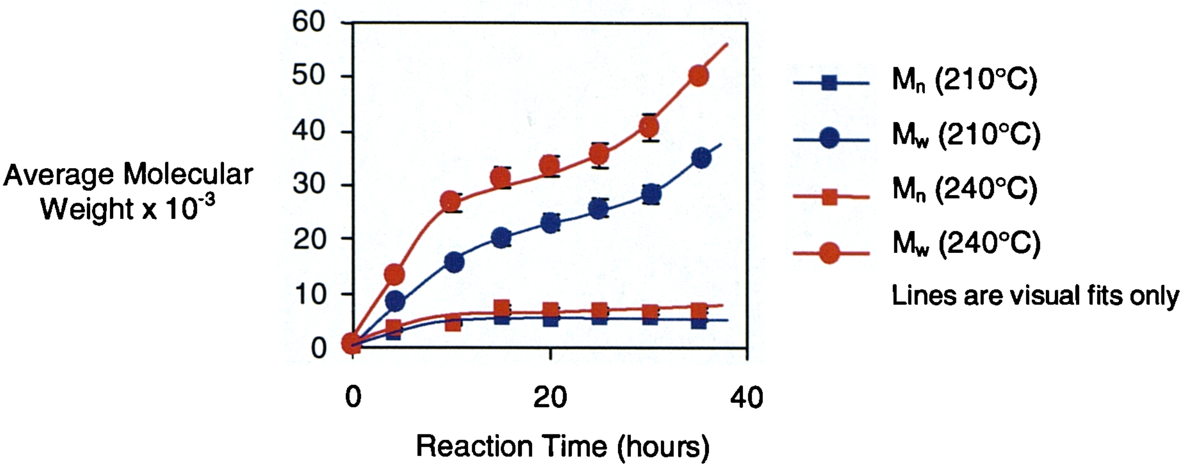


Figure 3.4: Graph to show the change in M_n and M_w with reaction time, in the polymerisation of dimethyl 5-(2-hydroxyethoxy)isophthalate at 210°C and 240°C

To summarise, from the results of these preliminary polymerisations it was decided that the reagents and conditions listed below would be employed as standard in further studies, using the polymerisation procedure described in Section 3.2:

REAGENTS AND POLYMERISATION CONDITIONS

- ~4-5g of AB_2 monomer sample.
- Catalyst: Antimony trioxide (4mg, 0.014mmol), and manganese acetate (3.5mg, 0.020mmol).
- Triphenylphosphate (3mg, 0.009mmol).
- Temperature gradient: 10°C min^{-1} from room temprature.
- Stir at 125r.p.m. under a flow of nitrogen gas.
- Polymerisation temperature: 210°C.

3.2.2 Synthesis of hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy) isophthalate)s

After establishing the reaction conditions, a series of polymerisations were carried out for each AB_2 monomer, **8**, **9**, **10** and **11**, to produce the corresponding hyperbranched polymer **12**, **13**, **14** and **15**. The general polymerisation procedure described in Section 3.2 was used and the duration of the reaction was varied between 1 and 40 hours. Structural and physical characterisation of the hyperbranched polyesters was conducted using a variety of analytical techniques. The results arising from these investigations are discussed in Chapter 5. A schematic representation of the hyperbranched polymers discussed in this thesis is presented in Figure 3.5 overleaf.

3.2.3 Variation of catalyst in the polymerisation of the AB_2 monomer dimethyl 5-(4-hydroxybutoxy)isophthalate

As previously discussed, Section 3.2, a range of catalysts were used in the preliminary polymerisations of the dimethyl 5-(3-acetoxypropoxy)isophthalate monomer (**3**). However, for the corresponding hydroxy monomer, dimethyl 5-(3-hydroxypropoxy)isophthalate (**8**), only the antimony trioxide and manganese acetate catalyst system was used. This was due to the fact that this catalyst system had been established as a suitable catalyst, both in the polymerisation of the analogous AB_2 monomer dimethyl 5-(2-hydroxyethoxy)isophthalate,[1] and in the commercial production of a structurally similar linear polymer, poly(ethylene terephthalate).[8] However, in further discussions regarding the use of catalysts in the synthesis of hyperbranched polyesters, it was discovered that the unsuccessful polymerisation of the acetoxy monomer **3** with titanium (IV) butoxide, was probably due to the use of an excess of catalyst. It became apparent that titanium (IV) butoxide ought to be as effective, if not more effective than the antimony trioxide and manganese acetate catalyst system. In addition, should the material ever be of any practical use titanium residues would be more acceptable than antimony and manganese residues in any polymer product.

Consequently it was decided to investigate the use of other catalysts in the polymerisation of dimethyl 5- (4-hydroxybutoxy)isophthalate (**9**), using both titanium (IV) butoxide and a range of catalysts used in the preparation of hyperbranched

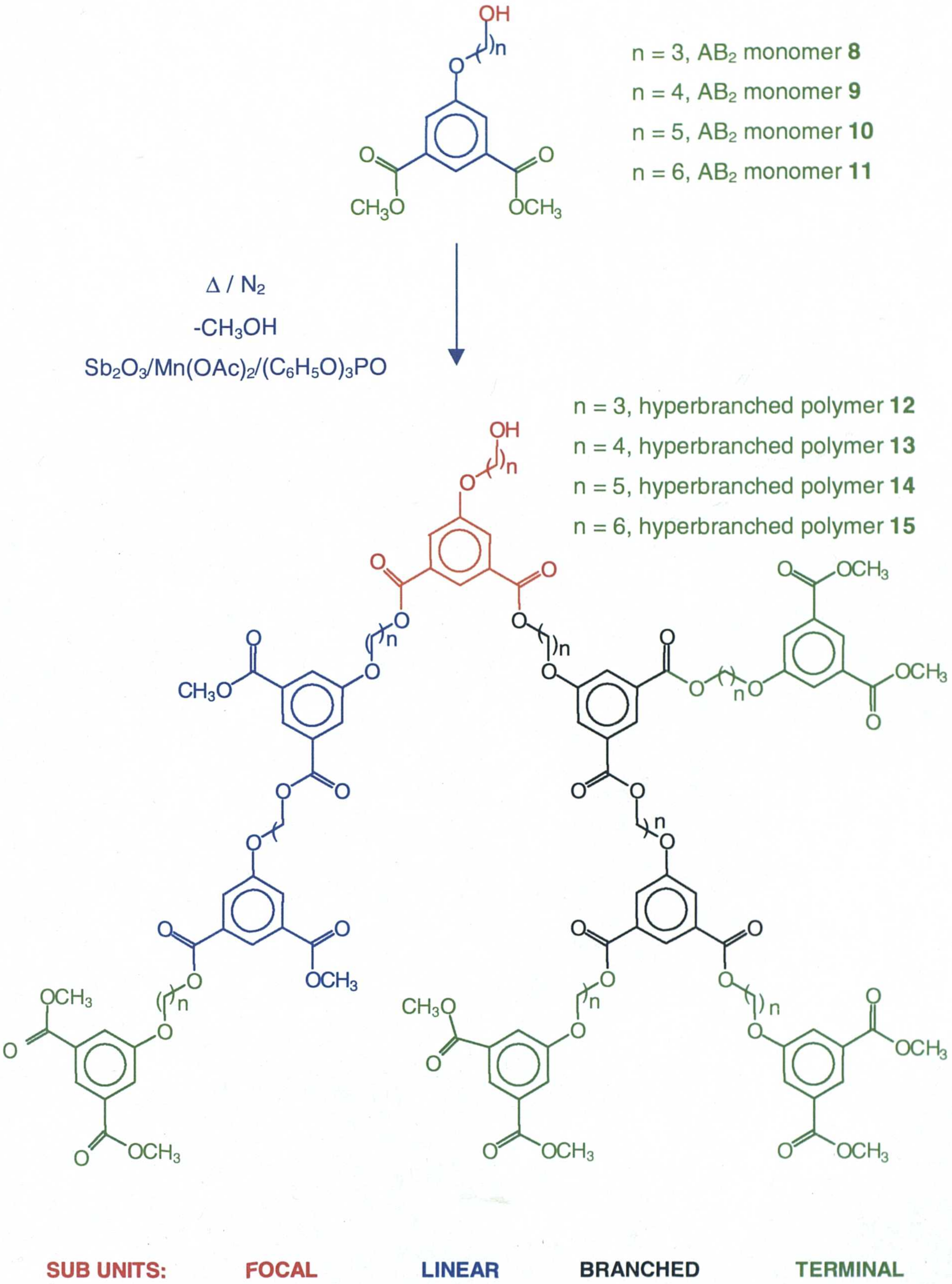


Figure 3.5: Schematic representation of the synthesis of the hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s

polyesters reported by Hawker.[9] These included antimony trioxide, manganese acetate, cobalt acetate and dibutyltin acetate. The polymerisations were using carried out using the general procedure described in Section 3.2, in the presence of 0.1 weight percent of the catalyst. The hyperbranched polyesters obtained from these polymerisations were analysed by SEC, and these results are discussed in Chapter 5.

3.3 References

[1] Stainton, N. M., *PhD Thesis*, University of Durham, 1994.

[2] Pilati, F., "*Comprehensive Polymer Science*," Pergamon Press, Oxford, 1989, **5**, 289.

[3] Dean, B. D., Matzner, M. and Tibbitt J. M., "*Comprehensive Polymer Science*," Pergamon Press, Oxford, 1989, **5**, 321.

[4] Bier, G., *Polymer*, 1974, **15**, 527.

[5] Pilati, F., "*Comprehensive Polymer Science*," Pergamon Press, Oxford, 1989, **5**, 290.

[6] Hamilton, L. M., *PhD Thesis*, University of Durham, 1994.

[7] March, J., "*Advanced Organic Chemistry,*" 4th Edn., John Wiley and Sons, New York, 1992, 378.

[8] Gumther, B. and Zacchmann, H. G., *Polymer*, 1983, **24**, 1008.

[9] Chu, F. K., Hawker, C. J., Pomery, P. J. and Hill, D. J. T., *J. Polym. Sci., Part A-Polym. Chem.*, 1997, **35**, 1627-1633.

CHAPTER FOUR

PHYSICAL TECHNIQUES USED IN THE CHARACTERISATION OF HYPERBRANCHED POLYMERS

4.1 Introduction

The increasing use of synthetic polymers by industry has stimulated the search for more versatile polymeric materials, covering a range of properties. In this quest for materials with novel properties, full characterisation is essential to enable us to understand structure/property relationships exhibited by polymers. It is only when we have established the structure/property correlation for a given system that we can begin to 'tailor-make' polymers for specific applications. Although the characterisation of linear polymers is generally well established, this is not the case for hyperbranched polymers. Only in recent years has the characterisation of such highly branched species been addressed with extensive work still required in this area.

Average molecular weights of the hyperbranched polyesters have been obtained using size exclusion chromatography (SEC). Structural information can be obtained from a variety of techniques including, ^{1}H and ^{13}C nuclear magnetic resonance (nmr) spectroscopy and matrix assisted laser desorption ionisation time of flight mass spectrometry (MALDI-TOF MS). The physical characterisation of the materials has been investigated using solution viscometry and differential scanning calorimetry. The following sections discuss the use of SEC and MALDI-TOF MS in characterising hyperbranched polyesters, identifying the valuable information that can be gained, as well as the limitations of the individual techniques.

4.2 Size exclusion chromatography (SEC) analysis

SEC has been used to determine the relative average molecular weights and molecular distributions of the hyperbranched polyesters. However, in order to discuss the limitations of this technique with respect to such highly branched species, one should consider the physical processes occurring during the acquisition of average molecular weight data.

In SEC, a dilute polymer solution is injected into the solvent stream which then flows through a column or series of columns. The columns are composed of a cross-linked gel containing a distribution of pore sizes. The solvent molecules pass through and around the gel particles carrying with them where possible the polymer molecules. The larger molecules, with their larger hydrodynamic volume, are excluded from the smaller pores and thus have a shorter flow path, eluting from the column first. The smaller molecules however can penetrate into the smaller pore sizes and channels of the gel, and therefore have a relatively longer flow path through the column. Hence SEC effects separation of a polymer sample into fractions on the basis of their hydrodynamic volume. The different fractions of polymer solution elute from the column and are detected by a suitable concentration detector, e.g. differential refractometer (RI), ultraviolet absorption (UV) or infrared (IR) detector, to produce a plot of elution volume *vs* concentration.

A distribution can be produced after calibration with low polydispersity polymer standards, usually linear polystyrene. Consequently, molecular weights reported using this method are linear polystyrene equivalent masses. Alternatively a universal calibration curve is constructed, this consists of a plot of $\log[\eta]M$ *vs* elution volume for linear polymer standards of known narrow molecular weight distribution (where $[\eta]$ is the intrinsic viscosity and M is the molecular weight). Since the elution volume is related to hydrodynamic volume, which is a measure of the size of the polymer molecule in solution, for a polymer of an unknown molecular weight it is possible to extract a value of [η]M using the universal calibration curve for a known elution volume. The intrinsic viscosity can be readily determined by use of an on-line viscometer detector, and thus a molecular weight for the sample can be obtained.

Both these calibrations are based on the use of low polydispersity polymer standards, but one would expect that there might be significant differences in the relationship between the elution volume and hydrodynamic volume for hyperbranched polymers, compared with that for their linear analogues. Thus, interpretation of results obtained for highly branched polymers is difficult. Although absolute values are uncertain, it seems reasonable to assume that comparison of results obtained for hyperbranched polymers of similar structures are likely to be reliable indicators of trends in molecular size.

Such uncertainties concerning relative average molecular weights determined using calibrations based on linear polymers have been confirmed from absolute molecular weight measurements using low-angle laser light scattering (LALLS). Frechet[1] showed that for hyperbranched aromatic polyethers, the determination of the weight average molecular weight using LALLS, consistently yields values that are 3-5 times higher than those determined by SEC calibrated using linear polystyrene standards. This is consistent with the intuitive prediction that the hydrodynamic volumes of highly branched systems are likely to be smaller than those of their linear analogues.

Recent advances in SEC include on-line light scattering detection. By combining the outputs from the concentration and light scattering detector, it is claimed that absolute measurements of molecular weight and molecular weight distributions, independent of column calibration or assumptions concerning the hydrodynamic size to molecular weight relationships, can be obtained. The combination of an on-line viscometer (VIS) and right-angle laser light scattering (RALLS) detector coupled with SEC has recently been used to determine average molecular weights in our hyperbranched polyesters. Results from this method for determination of average molecular weight will be discussed in Chapter 5. However, uncertainties arise from these measurements since the theory behind this technique corresponds to narrow disperse linear or branched coils, rather than the highly branched polydisperse structures represented by hyperbranched polymers. Nevertheless, this triple detection system, RI-VIS-RALLS, offers the best available capability for characterising molecular weight of these kinds of polymer at present.

Another factor that may effect the SEC results is the presence of a large number of end groups in a hyperbranched polymer. It is possible for the polar end groups to interact with the SEC columns, thus producing longer retention times and consequently lower average molecular weights. This phenomenon has been observed in linear polymers with polar functional groups, e.g. poly(acrylic acid).[2]

It is reasonable to suggest that calibrations using dendrimers would provide a more realistic view of the molecular weight distribution of hyperbranched polymers. Although this has been reported in the literature for use in aqueous SEC,[3] the materials of interest in this thesis are not water soluble and appropriate dendritic standards are not available. No further work in this area has been reported.

To conclude, although the molecular weights obtained by SEC are not absolute, we believe that comparisons can be made between results obtained for similar hyperbranched polyesters. Furthermore, with the emergence of a new RALLS on line detector we may be able to gain a more realistic view of the average molecular weight distribution. However, at present SEC is the only analytical technique that can be used to examine the molecular weight distribution of the whole sample thus making it a useful tool in the quest of characterisation of hyperbranched polymers.

4.3 Matrix assisted laser desorption- ionisation time of flight mass spectroscopy (MALDI-TOF MS)

The basic principle underlying the MALDI technique is the same as that for any other mass spectroscopic technique. The sample to be analysed, the analyte, is placed in a vacuum or low pressure environment where it is ionised by means of a pulse of laser light into positive and negative ions. A voltage is instantaneously applied to transport the ions down the flight tube where the mass of the individual ions arriving at a detector is calculated.

In MALDI-TOF MS the sample to be analysed, is uniformly mixed in a matrix which is selected to absorb the laser light strongly. In this way, the energy is transferred indirectly to the sample in a controlled manner which avoids sample fragmentation. The matrix is chosen to have solubility properties similar to those of the sample, this then allows dispersion of the sample molecules in the matrix, thus avoiding desorption of the sample as high molecular weight aggregates. A pulse of laser light (3ns from a nitrogen laser of wavelength 337nm) is directed onto a very small target area (typically 100μm in diameter) of the sample on a sample slide. This causes the sample molecules to be vaporised and the charged species in the gas phase are detected as either proton, cation or matrix adducts.

After the ions are produced, they are accelerated by means of an electric field into a field–free drift region (flight tube) with a kinetic energy of zV_0, where z is the ion charge and V_0 is the applied voltage. Since the ion kinetic energy is $0.5mv^2$ (where m is the mass of the ion and v is the velocity of the ion), lighter ions have a higher velocity than heavier ions and reach the detector at the end of the drift region sooner.

The time the ions take to reach the detector can be determined by Equation 4.1:

$$t = L/v = L(m/2zV_o)^{1/2} \qquad \text{Equation 4.1}$$

Where L is the length of the drift tube, z is the ion charge, V_o is the applied voltage, m is the mass of the ion and v is the velocity of the ion.

By rearranging Equation 4.1; $m/z = 2V_0t^2/L^2$ Equation 4.2

Therefore the time taken to travel from the start to detection is directly proportional to the mass/charge ratio (m/z) of the ion. Since arrival times between successive ions can be less than 10^{-7} s, a very high resolution time measurement circuit is required. For example, in a device where $V_o = 20$kV, and L = 0.7m, a mass difference of 1 amu would require a time resolution of ≤ 5.7 ns.

MALDI-TOF mass spectra were obtained using a Kratos Kompact MALDI IV time of flight mass spectrometer, a schematic diagram of the instrument set-up is shown in Figure 4.1.

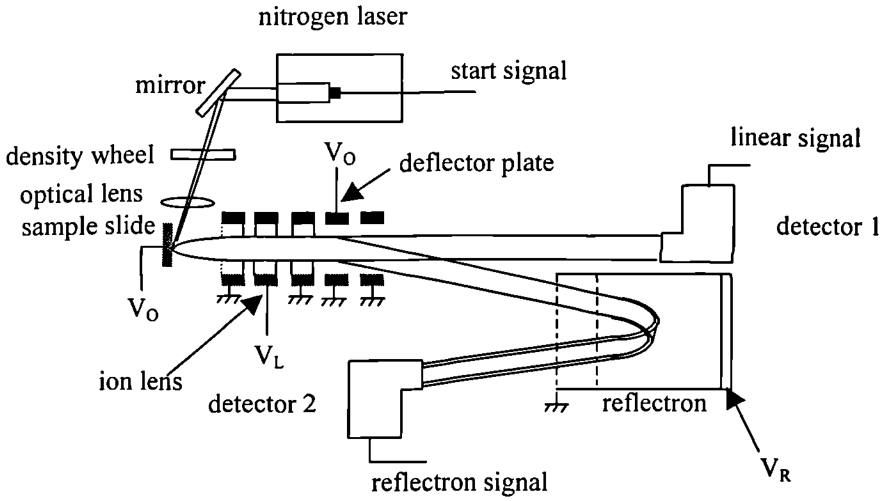


Figure 4.1: Schematic diagram of the instrument set-up in a Kratos Kompact MALDI IV time of flight mass spectrometer

Two different acquisition methods can be selected for time of flight measurements of the ions, namely the linear and reflectron methods.

With the linear time of flight method the ions drift towards the detector after they have been created. Although this method has high sensitivity, the resolution is not as high since the distribution of initial energies when the ion is generated is maintained in the time of flight.

The reflectron time of flight method is used when high mass resolution is required. The ions extracted from the ion source are repelled by a deflector, a voltage is then applied to the reflectron and this causes the ions to turn back towards the ion source. By applying an ion reflecting field, the distribution in the time of flight for the ions having the same mass is eliminated and they are 'time focussed'. Ions having a higher energy penetrate deeper into the reflectron which increases their time of flight in the reflectron. Similarly, ions having a lower energy have a longer time of flight through the drift space. Using this technique ions having equivalent mass/charge ratios are detected at essentially the same time irrespective of their initial energies, this results in high mass resolution.

Ions pass down the mass spectrometers flight tube and enter the detector which converts the energy of the arriving particles into electrical signals. At the detector the incoming particles strike a surface called the first dynode. This is a special surface that is capable of releasing one or more electrons when struck by a particle having an energy above a certain level. By means of a positive difference in potential between the first dynode and the second dynode, the electrons released at the first dynode are accelerated towards the second dynode, striking it in a similar manner causing further electrons to be released. This process is repeated 10 times, increasing the number of electrons in a geometrical progression (10^6 to 10^8 times). Thus a large number of electrons flow to create a current as the result of the incidence of a single incoming ion in the detector.

4.3.1 The use of matrix assisted laser desorption- ionisation time of flight mass spectroscopy (MALDI-TOF MS) in the characterisation of hyperbranched polymers

The introduction of MALDI-TOF MS[4] has greatly extended the mass range amenable to direct analysis by means of mass spectroscopy. This soft ionisation method was initially developed for the determination of high molecular weight biomolecules in a mass range above 100 000 Daltons[5]. Its use has since been extended to synthetic polymers where it has been found to be a powerful tool in the investigation of polymer structure and average molecular weight distribution.[6,7] The majority of the studies have focussed on narrowly dispersed linear polymers[8,9] or well defined monodisperse systems such as dendrimers.[10]

The MALDI TOF MS technique is particularly attractive for dendrimers that are prepared in stepwise processes involving intermediate purifications because the precise analysis of these high molecular weight materials by classical techniques is difficult. For example, nmr or elemental analysis fail to detect minute amounts of structurally related impurities, while SEC is of limited value since the dendrimers themselves are much less polydisperse than the polymer standards used to calibrate the columns. Consequently many examples now exist in the literature where MALDI-TOF MS has been successfully applied in the analysis of dendrimers.

Xu[11] reported in 1994 the first determination of mass for a dendrimer using MALDI-TOF MS, confirming the coupling of core molecules to a wedge. This work was extended by Kawaguchi *et al,*[12] who used MALDI-TOF MS to analyse phenylacetylene dendrimers which had been synthesised via a double exponential growth scheme shown in Figure 4.2 overleaf.

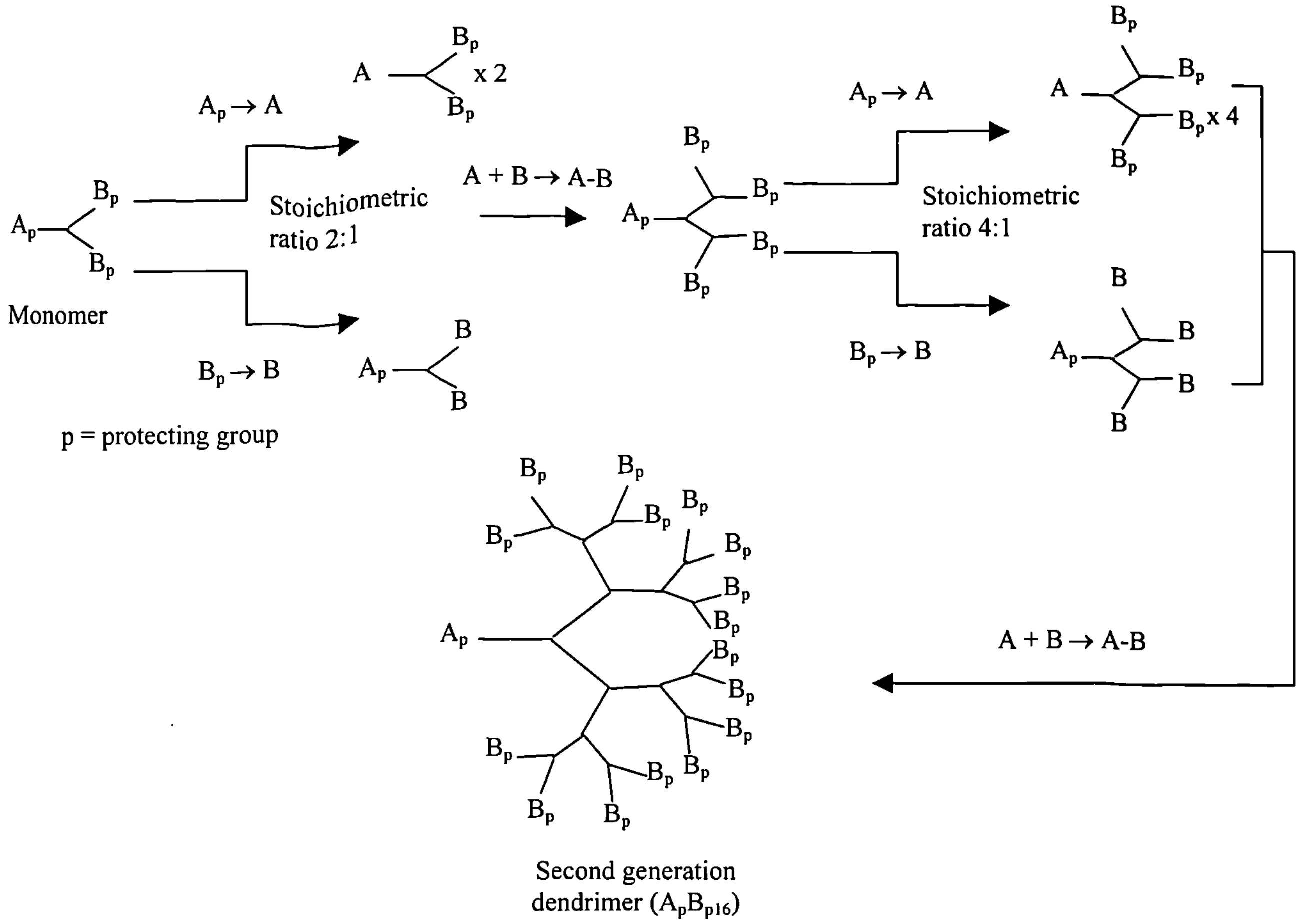


Figure 4.2: The first two generations of double exponential dendrimer growth

MALDI-TOF mass spectroscopy proved that the coupling of the A_pB_{16} molecule with 16 equivalents of the $A_{16}B_p$ molecule, to generate the third generation dendrimer, had not gone to completion. Such defects in the structure can only be resolved using MALDI-TOF MS. A further study of the applicability of MALDI-TOF MS in the characterisation of dendrimers was carried out by Haddleton *et al.*[10] Two aromatic polyester dendrimers were synthesised, one of which had benzyloxy terminal groups and the other hydroxy terminal groups. The mass spectrum of each dendrimer showed the presence of only one peak, proving that the dendrimers were monodisperse. Although this can in theory be proved by SEC, in practice hydroxy surface functionalities can interact with the SEC column packing thus giving broadening and larger retention leading to erroneous results. Since these early reports demonstrating the application of MALDI-TOF MS to dendrimers, its use as an analytical tool has greatly increased in this field of polymer science.

More recently MALDI-TOF MS has been applied in the analysis of a number of hyperbranched polymer systems.[13, 14, 15] Examples include the characterisation of hyperbranched aryl ether sulfone macromolecules with aryl fluoride and phenol terminal functionalities (see Figure 4.3), prepared by Martinez and Hay.[13] MALDI-TOF MS enabled them to identify the different oligomeric species present, as well as indicating that an internal cyclisation reaction was competing with the polymerisation.

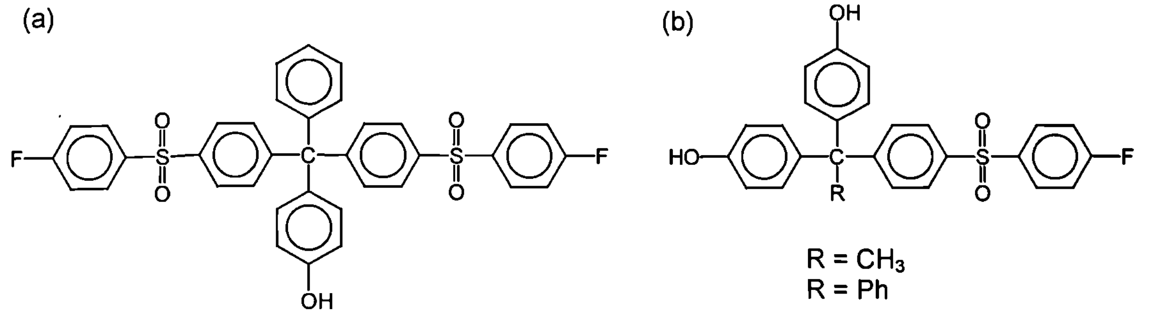


Figure 4.3: AB_2 monomers used to prepare hyperbranched aryl ether sulfone polymers with (a) aryl fluoride and (b) phenol terminal functionalities

Ueda and co-workers[14] prepared a hyperbranched aromatic polyamide from 5-aminoisophthalic acid. The resulting polymer (I), shown in Figure 4.4 below, was then reacted with *p*-anisidine to produce the methoxy-end-capped polymer (II). In this case MALDI-TOF MS confirmed that no side reactions were occurring, and that all the terminal groups had been capped in this reaction.

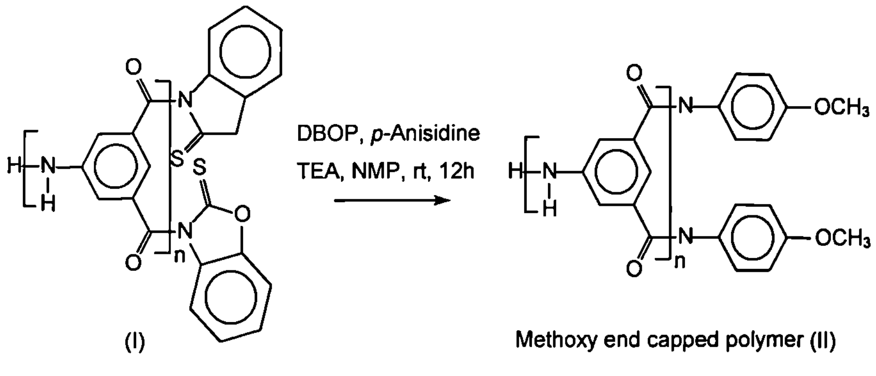


Figure 4.4: Hyperbranched aromatic polyamide: reacting terminal groups

MALDI-TOF MS is strictly a soft ionisation technique which should not cause fragmentation of the sample, however, in a study carried out by Hobson *et al*[18] on hyperbranched poly(amidoamine)s derived from N-acryloyl-1,2- diaminoalkane hydrochloride, fragmentation of the hyperbranched polymer was observed which was consistent with the loss of the focal unit CH_2=CHCO, this is shown schematically in Figure 4.5 below.

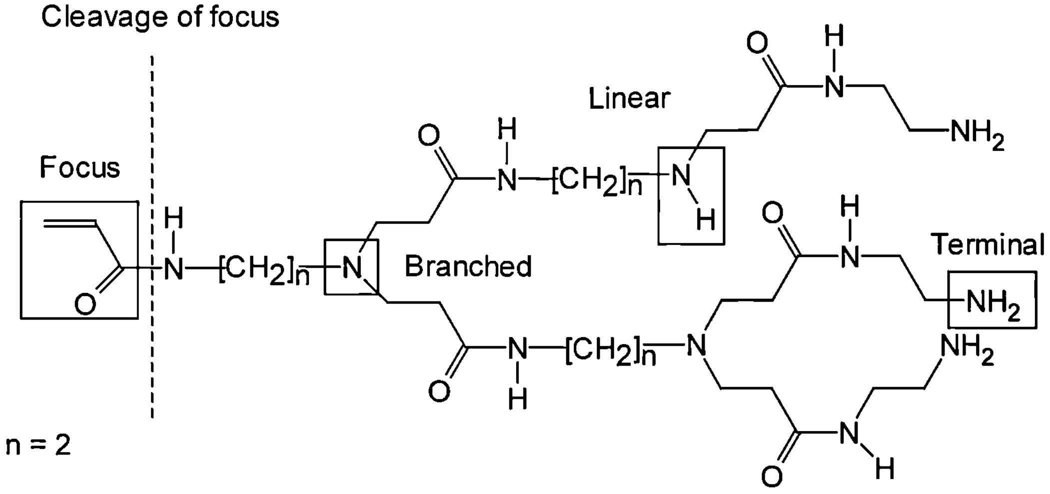


Figure 4.5: Amide cleavage at the focus in a poly(amidoamine) hyperbranched system, as observed in the MALDI-TOF spectra.

MALDI-TOF MS has also been used in the characterisation of hyperbranched aliphatic polyesters derived from the AB_2 monomer diethyl 3-hydroxyglutarate, shown in Figure 4.6 overleaf.[15] MALDI-TOF MS was used to quantify the extent of possible side reactions, particularly those resulting from alkoxide exchange with the titanium (IV) butoxide catalyst. The influence of the laser power on the observed MALDI-TOF mass spectra was also investigated for these hyperbranched aliphatic polyesters.[24] This study established that the incident laser power has a marked effect on the distribution of peak intensities in the spectra observed for these systems.

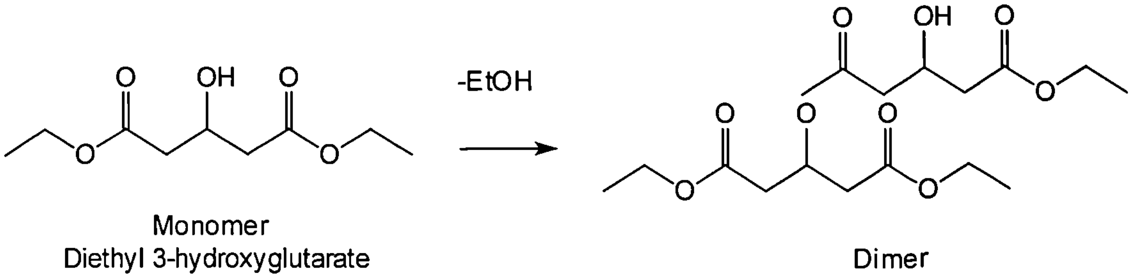


Figure 4.6: First step in the step-growth polymerisation of diethyl 3-hydroxyglutarate

When considering determination of average molecular weights of polydisperse, non-linear polymers, it is widely accepted there is no universally applicable technique that can be used. Although it has been shown that MALDI- TOF MS can be an invaluable tool in the determination of polymer structure, providing useful insights into mechanistic details of a polymerisation, or the occurrence of side reactions, many groups have reported that this technique fails to provide a realistic interpretation of either molecular weight or molecular weight distribution for polydisperse systems,[9, 16, 17] a classification which includes that of hyperbranched polymers.[18]

It is also well documented that the sample preparation technique,[19, 20] selection of matrix,[20, 21] polymer solvent,[21] doping ion[21, 22] and laser power[21, 23, 24] all have a significant effect on both the quality of the data obtained and the form of the distribution observed in the spectra. Such observations clearly make it difficult to define what constitutes a "representative spectrum" using this technique and therefore more systematic experiments are required before secure interpretation of recorded data can be made. At present this ionisation technique does not sample the polymer under examination in a uniform way, with preferential detection dependent on both mass, structure and experimental technique. If improvements in sampling can be made so that the whole polymer sample is analysed then this soft ionisation technique will give a very detailed picture of molecular weight and structure distribution.

Nevertheless, we have analysed the hyperbranched polyesters (**12**, **13**, **14** and **15**) using MALDI-TOF MS, this work is discussed in detail in Chapter 5. It is clear both from the work reported in the literature, as well as the work presented in Chapter 5 on the hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s, that despite the limitations of this technique, MALDI-TOF MS is invaluable in the investigation of structure in hyperbranched systems. Thus although at present MALDI-TOF MS will not replace conventional polymer analytical methods, it has become an indispensable and complementary method in polymer characterisation.

4.4 References

[1] K. E. Uhrich, C. J., Hawker, J. M. J. Frechet and S. R. Turner, *Macromolecules*, 1992, **25**, 4583.

[2] Dawkins. J. V., "Comprehensive Polymer Science", Pergamon Press, Oxford, 1989, **1**, 245.

[3] P. L. Dubin, S. L. Edwards, J. I. Kaplan, M. S. Mehta, D. Tomalia and J. Xia, *Anal. Chem.*, 1992, **64**, 2344.

[4] M. Karas and F. Hillenkamp., *Anal. Chem.*, 1988, **60**, 2299.

[5] F. Hillenkamp, M. Karas, R. C. Beavis and B.T. Chait. *Anal. Chem.*, 1991, **63**, 1193.

[6] C. Jackson and W. J. Simonsick Jr., *Current Opinion in Solid State and Materials Chemistry,* 1997, 2(6), 661.

[7] Dey. M., Castoro, J. A. and Wilkins, C. L., *Anal. Chem.*, 1995, **67**, 1575.

[8] Schweer, J., Mayer-Posner, F., Mullen, K., Rader, H. J., and Spickermann, J., *Macromolecules*, 1996, **29**, 4536.

[9] Montaudo, G., Garozzo, D., Montaudo, S., Puglisi, C., and Samperi, F., *Macromolecules*, 1995, **28**, 7983.

[10] Sahota, H. S., Lloyd, P. M., Yeates, S. G., Derrick, P. J., Taylor, P. C. and Haddleton, D. M., *J. Chem. Soc., Chem. Commun.*, 1994, 2445.

[11] Xu. Z., Kahr. M., Walker, K. L., Wilkins, C. L. and Moore, J. S., *J. Am. Chem. Soc.*, 1994, **116**, 4537.

[12] Kawaguchi, K. L., Walker, K. L., Wilkins, C. L. and Moore, J. S., *J. Am. Chem. Soc.*, 1995, **117**, 2159.

[13] Martinez, C. A. and Hay, A. S., *J. Poly. Sci Part A – Chem.*, 1997, **35(10)**, 2015.

[14] Haba, O., Tajima, H., Ueda, M., Nagahata, R., *Chem. Lett*, 1998, **4**, 333.

[15] Feast. W. J., Hamilton, L. M., Hobson, L. J., Rannard, S., *J. Mat. Chem.* 1998, **8(5)**, 1121.

[16] Martin, K., Spickermann, J., Rader, H. J., and Mullen, K., *Rapid Commun. Mass Spectrom.*, 1996, **10**, 1471.

[17] McEwen, C., Jackson, C. and Larson, B., *Anal. Chem.* 1996, **68**, 1303.

[18] Hobson, L. J., Kenwright, A. M. and Feast, W. J., *J. Chem. Soc., Chem. Commun.*, 1997, 1877.

[19] Axelsson, J., Hoberg, A., Waterson, C., Myatt, P., Shield, G. L., Varney, J., Haddleton, D. M. and Derrick, P. J., *Rapid Commun. Mass Spectrom.*, 1997, **11**, 209.

[20] Leon, J. W. and Frechet, J. M. J., *Polymer Bull.,* 1995, **35**, 449.

[21] Blais, J. C., Tessier, M., Bolbach, G., Remaud, B., Rozes, L., Guittard, J., Brunot, A., Marechal, E., Tabet, J. C., *Int. J. Mass. Spectrom. and Ion Proc.*, 1995, **144**, 131.

[22] Jackson, A. J., Yates, H. T., MacDonald, W. A., Scrivens, J. H., Critchley, G., Brown, J., Deery, M. J., Jennings, K. R., Brookes, C., *J. Am. Soc. Mass Spectrom.*, 1996, **8**, 132.

[23] Belu, A. M., deSimone, J. M., Linton, R. W., Lange, G. W. and Friedman, R. M., *J. Am. Soc. Mass Spectrom.*, 1996, **7**, 11.

[24] Feast. W. J., Hamilton, L. M., Rannard, S., *Polymer Bull.*, 1997, **39(3)**, 347.

CHAPTER FIVE

THE DETERMINATION OF AVERAGE MOLECULAR WEIGHT, STRUCTURE AND PHYSICAL PROPERTIES OF THE HYPERBRANCHED POLY(DIMETHYL 5-(ω-HYDROXYALKOXY)ISOPHTHALATE)S

5.0 Introduction

In this chapter the characterisation of the hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s, whose preparation was described in Chapter 3, is reported. All the hyperbranched polymers were readily soluble in a range of organic solvents, including chloroform and tetrahydrofuran, allowing a range of analytical techniques to be used. Information pertaining to average molecular weights and molecular weight distributions of these hyperbranched polyesters was obtained using size exclusion chromatography (SEC). Structural information was obtained using ^1H and ^{13}C nuclear magnetic resonance (nmr) spectroscopy, and matrix assisted laser desorption ionisation time of flight mass spectrometry (MALDI-TOF MS). The physical characterisation of these materials has been investigated using solution viscometry and differential scanning calorimetry (DSC).

5.1 Size exclusion chromatography analysis of the hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s

5.1.1 Experimental

SEC was carried out on the hyperbranched polyesters in order to obtain information concerning average molecular weights and molecular weight distributions. Chloroform or tetrahydrofuran were used as solvents and a variety of detection and calibration procedures were investigated, these are summarised in Table 5.1 overleaf. All molecular weights quoted in this work are in units of g/mol

Chloroform SEC was carried out at room temperature using a HPLC pump (PL: LC 110) with a solvent flow rate of $1cm^3min^{-1}$. Polymer solutions (4-10mg/ml) were filtered through a Whatman 0.2μm filter to remove particles before injection into the solvent flow using a 100μl Rheodyne loop. A guard column (5 x 0.75cm, mixed bed PL gel) was used to remove any remaining particles or aggregates. Three SEC columns (3 x 0.75cm) composed of PL gel (mixed styrene-divinyl benzene beads with diameters ranging between 3 and 100μm, pore sizes 100Å, 10^3Å and 10^5Å) were used in a series to separate the mixture on the basis of hydrodynamic volume. The columns were calibrated using Polymer Laboratories polystyrene standards (162-1040000 amu). A differential refractometer (ERC-7515A) and a data capture unit (PL-DCU) were used in conjunction with PL GPC software (version 5.2) to obtain SEC measurements.

Table 5.1: Summary of the different solvents, columns, detectors and calibration procedures used in SEC for the hyperbranched polyesters.

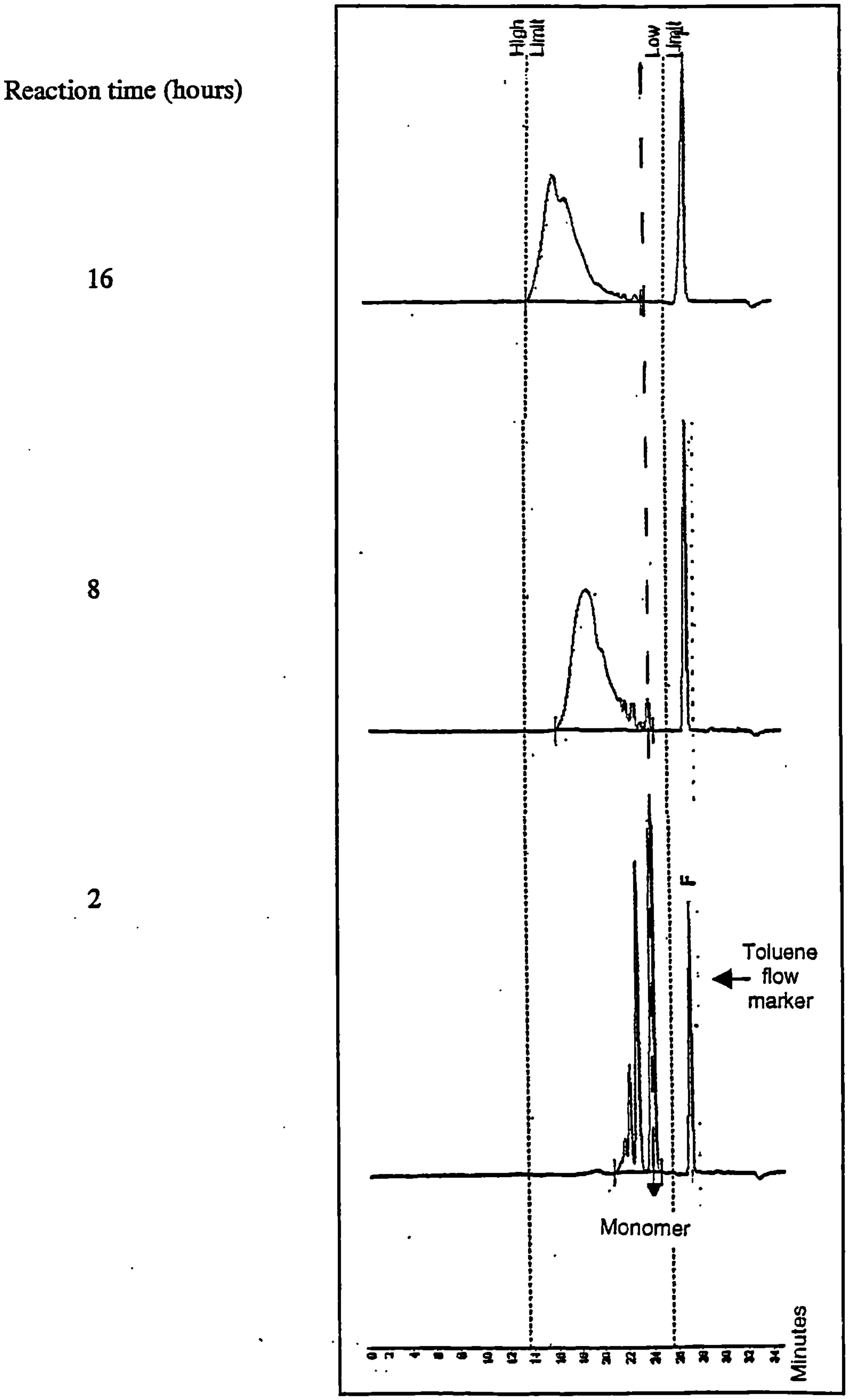
Solvent	Columns	Concentration detector	Additional detectors	Calibration
$CHCl_3$	3 columns of PL gel (pore size 100Å, 10^3Å and 10^5Å)	Differential refractometer (ERC-7515A)		polystyrene standards (PS
THF	3 columns of PL gel (mixed pore sizes)	Viscotek differential refractometer		polystyrene standards (PS
THF	3 columns of PL gel (mixed pore sizes)	Viscotek differential refractometer	Viscotek viscometer	Universal calibration (P
THF	3 columns of PL gel (mixed pore sizes)	Viscotek differential refractometer	Viscotek viscometer and RALLS detector	PS (90 000 and 218 000)

Tetrahydrofuran SEC was carried out using a HPLC pump (PL: LC 1120) with a solvent flow rate of $1cm^3min^{-1}$, maintained at 30°C using a Knauer oven and control unit. Polymer solutions (1mg/ml) were filtered through a Whatman 0.2μm filter to remove particles before injection. A guard column (5 x 0.75cm, mixed bed PL gel) was used to remove any remaining particles or aggregates. Three SEC columns (3 x 0.75cm) composed of PL gel (mixed styrene-divinyl benzene beads, mixed pore sizes) were used to separate the mixture. The columns were calibrated using Polymer Laboratories polystyrene standards (162-1 040 000 amu). A Viscotek differential refractometer, viscometer detector, right-angle laser light scattering (RALLS) detector and data capture unit (DM 400) were used in conjunction with TriSEC GPC software (version 3.0) to obtain SEC measurements. Refractive index increments (*dn/dc*) were measured using a Brice-Phoenix differential refractometer, these were necessary in order to evaluate molecular weights using the RALLS detector.

5.1.2 Results and discussion

Polymerisations of the monomers, **8** (n = 3), **9** (n = 4), **10** (n = 5) and **11** (n = 6), were carried out, to yield the corresponding hyperbranched polyesters, **12** (n = 3), **13** (n = 4), **14** (n = 5) and **15** (n = 6), where the duration of the reaction was varied between 1 and 40 hours. The evolution of the SEC trace as a function of reaction time was consistent with a step-growth polymerisation process. This is illustrated in Figure 5.1.1, which shows the SEC traces for samples obtained throughout the polymerisation of dimethyl 5-(4-hydroxybutoxy)isophthalate (**9**). The sample taken at 2 hours shows only monomer and oligomers and as the reaction progresses the relative abundance of monomer and low molecular weight oligomers decreases as higher molecular weight materials increase (8hours). The final sample (16 hours) shows what appears to be a bimodal trace with a broad molecular weight distribution, characteristic of hyperbranched polymer.[1,2] Representative SEC traces for high molecular weight samples of each of the hyperbranched polyesters, **12** (n = 3), **13** (n = 4), **14** (n = 5) and **15** (n = 6), have been recorded in Appendix 3. SEC traces shown in Figure 5.1.1 were obtained using chloroform as the solvent and calibrated using linear polystyrene standards.

Figure 5.1.1: Change in SEC trace with reaction time for hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophthalate)s



The changes in average molecular weights with reaction time for the polymerisations of the AB_2 monomers, **8** (n = 3), **9** (n = 4), **10** (n = 5) and **11** (n = 6), to the corresponding hyperbranched polyesters, **12** (n = 3), **13** (n = 4), **14** (n = 5) and **15** (n = 6), are shown in graphs 2 to 5 in Figure 5.1.2. For comparison the SEC results obtained for the equivalent polymerisations of the dimethyl 5-(2-hydroxyethoxy) isophthalate monomer are also included in Figure 5.1.2.[3] All the SEC measurements shown in the graphs were obtained using linear polystyrene standards and chloroform as the solvent. Therefore, although the average molecular weights reported are not absolute, it seems reasonable to assume that trends within one type (**12**, n = 3), and within the whole set (n = 2, 3, 4, 5 and 6) will be indicative of real changes in molecular weight.

On inspection of graphs 1 to 5, we can see clearly that for all the polymers the M_w increases at a faster rate than the M_n, this leads to the broad molecular distributions characteristic of hyperbranched polymers.[1,2]

For the hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalate)s, graph 1, we can see that the M_n increases at the beginning of the reaction after which it reaches a maximum M_n and remains at this value for the remainder of the polymerisation, this is in contrast to the M_w which is increasing steadily with reaction time. Consequently the polydispersity of the polymer increases with reaction time showing a similar growth in molecular weight and molecular weight distribution to that predicted by Flory, who showed in his theoretical treatment of the polymerisation of an AB_2 monomer that the polydispersity of the resulting highly branched molecule should tend towards infinity as the reaction tends to completion.

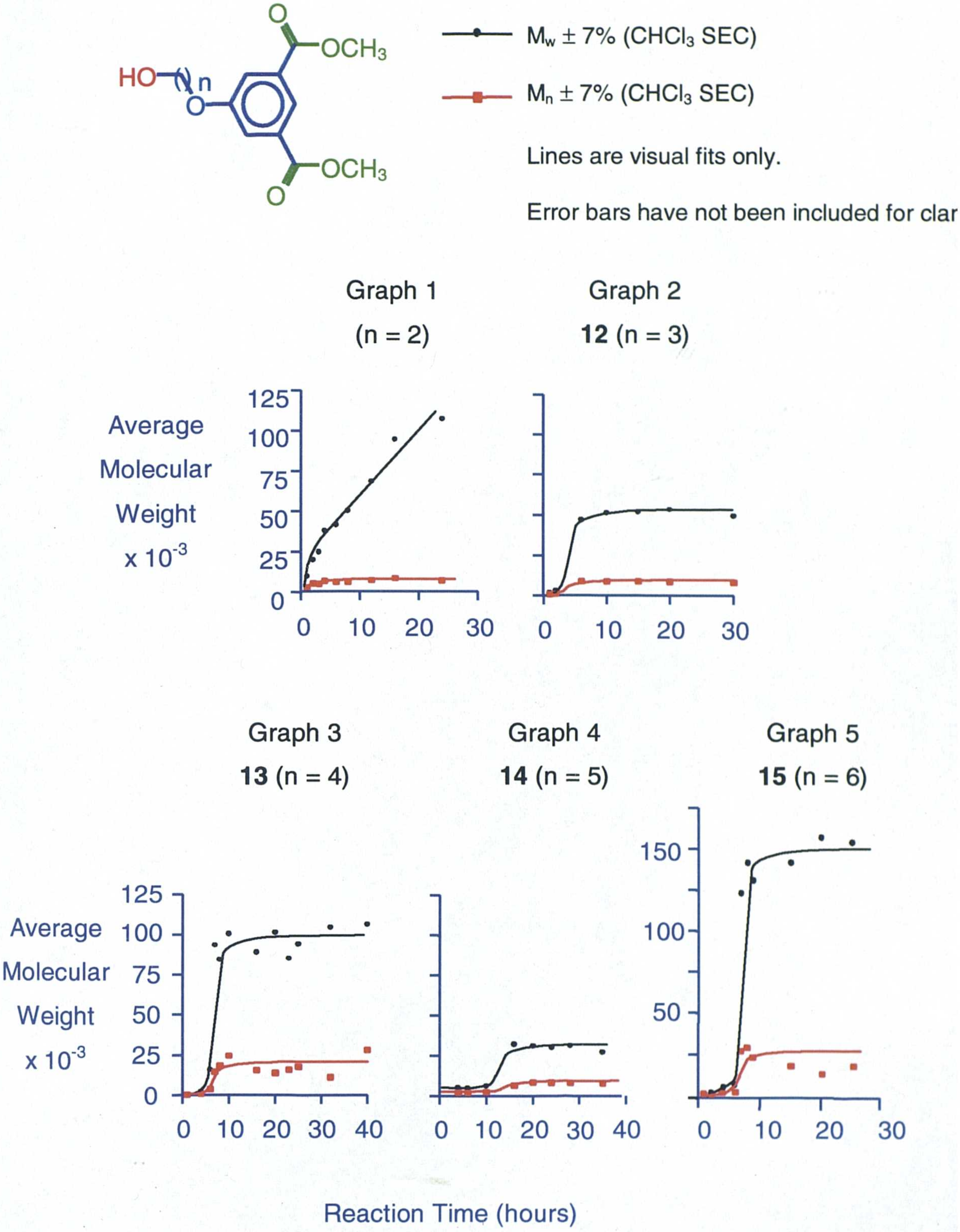
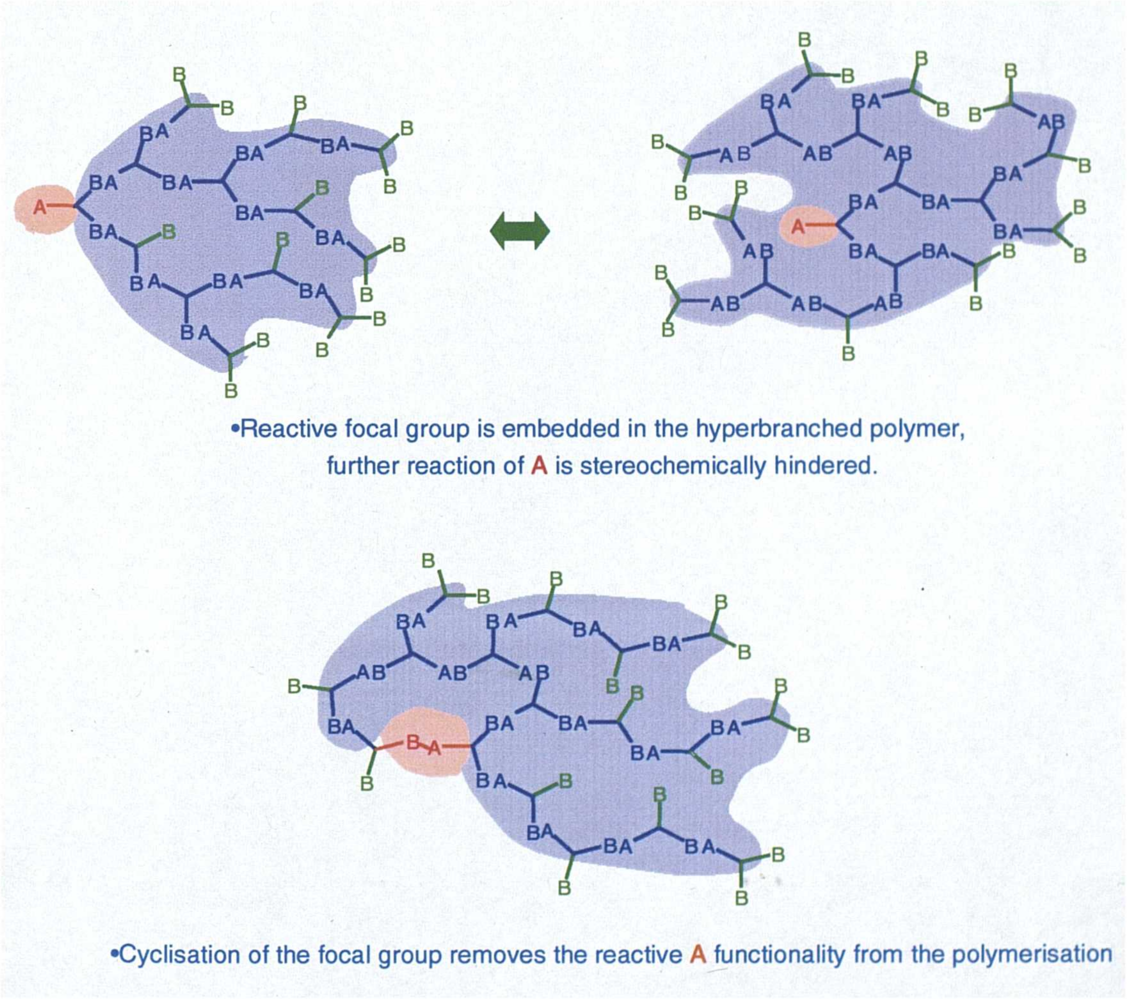


Figure 5.1.2: Graphs to show the change in average molecular weight with reaction time for the hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s

Upon examining the results of the polymerisations of monomers **8**, **9**, **10** and **11** (graphs 2 to 5), we observe a relationship between the change in M_n and M_w with reaction time, but one which is different from that of the dimethyl 5-(2-hydroxyethoxy)isophthalate monomer (graph 1). For these polymers both the M_n and M_w increase at the beginning of the reaction until a maximum M_n and M_w value is reached, after which the polymer remains at around this value for the remainder of the polymerisation. Thus, we observe both the polystyrene equivalent M_n and M_w values in these polymerisations tend to a plateau.

Two reasons which could account for this plateau effect could either be that the reactive focal hydroxyl group is embedded in the polymer and is stereochemically hindered from further reaction, or that cyclisation of the hyperbranched polymer has occurred (see Figure 5.3 below).



•Reactive focal group is embedded in the hyperbranched polymer, further reaction of A is stereochemically hindered.

•Cyclisation of the focal group removes the reactive A functionality from the polymerisation

Figure 5.3: Schematic illustration of the 'plateau effect'

The latter case refers to an intramolecular reaction between the hydroxyl group and an ester group within the same polymer molecule, this might be expected to terminate the polymerisation; further growth of the polymer would be possible only through a trans-esterification mechanism, that is an intermolecular reaction between two ester groups. These possibilities cannot be distinguished by analysis of SEC data, however, the relationship between average molecular weight and reaction time will be discussed further in section 5.2 where the determination of polymer structure using MALDI-TOF MS is discussed.

Where polymers reach a plateau M_n and M_w a corresponding plateau value for the polydispersity is obtained. These results are in contrast to predictions made by Flory for the growth in molecular weight for an AB_2 based polymer, who proposed that the polydispersity of a hyperbranched polymer should tend towards infinity as the reaction tens to completion. Deviations from this theory could be attributed to the assumptions Flory made in his theoretical approach to hyperbranched polymers since these may not necessarily hold experimentally, for example he assumed that no intramolecular cyclisation reactions occurred and, as will be shown later, this is not the case for these systems.

By comparing graphs 2 to 5 an odd even effect is observed with respect to the number of methylene units in the alkylene chain of the monomer. Substantially higher average molecular weights are obtained from the monomers **9** ($n = 4$) and **11** ($n = 6$), than those obtained from the monomers **8** ($n = 3$) and **10** ($n = 5$), this suggests that the length and geometry of the alkylene chain in the monomer might affect the efficiency of the condensation reaction and/or the hydrodynamic volume of the product.

To conclude, although SEC using linear polystyrene standards has been unable to provide absolute molecular weights, it has been possible to confirm that the hyperbranched materials are polydisperse. In addition, for the hyperbranched polymers

12, **13**, **14** and **15**, it appears from SEC that a constant value for M_n and M_w is reached after a certain polymerisation time. However, we cannot prove through SEC why this phenomenon is occurring in these hyperbranched polymers, and not in the analogous hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalate). Therefore, further structural analysis of the hyperbranched polyesters is required using different analytical techniques.

5.1.3 Determination of average molecular weights in hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophthalate)s using SEC with different detectors

In order to investigate if the observed average molecular weights for the polymers were affected by the SEC technique used to obtain them, weight average molecular weights were determined by SEC for the hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophthalate)s, using the following techniques:

- SEC using chloroform or THF as the solvent and calibrated using conventional linear polystyrene standards.
- SEC using THF as the solvent and an online viscometer detector with a universal calibration.
- SEC using THF as the solvent and an online viscometer detector and right-angle laser light scattering detector (RALLS).

The results, presented in Figure 5.1.4 overleaf, show that although the SEC measurements obtained when referenced to linear polystyrene standards are similar (using either chloroform or tetrahydrofuran as solvent), much higher values are obtained when either the universal calibration or the RALLS detector is used. This suggests that use of conventional linear polystyrene standards for SEC greatly under estimates the average molecular weight of the hyperbranched polymers. We expect the results obtained using the RALLS detector to be the most reliable since light scattering is an absolute measurement technique. Nevertheless, it is clear that regardless the SEC technique used, the molecular weight of the products reach a plateau value.

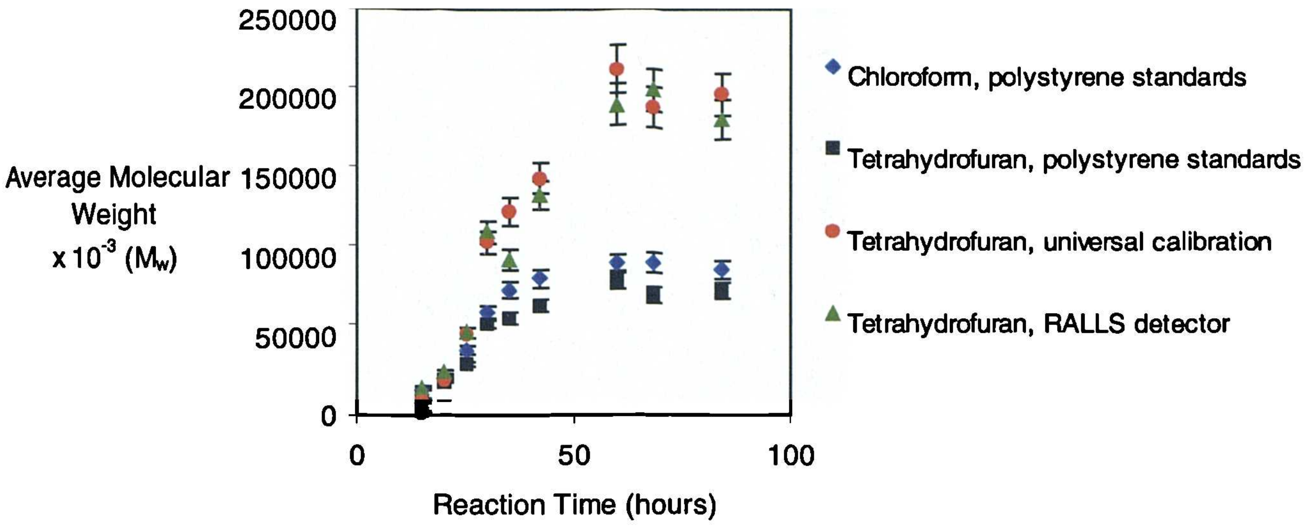


Figure 5.1.4: Graph to show the change in weight average molecular weight, versus reaction time for hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophthalates), obtained using different SEC techniques

By comparing the SEC results obtained using different solvents (chloroform and tetrahydrofuran) but the same calibrant (linear polystyrene), it can be seen that the observed average molecular weights of the polymer samples obtained using tetrahydrofuran are slightly less than those obtained using chloroform, see Figure 5.1.5. This phenomenon has been observed in other hyperbranched systems[4, 5] and can be rationalised by considering SEC which effects separation according to molecular volume rather than molecular mass, therefore making the hydrodynamic volume of a polymer in solution an important factor when determining molecular weight by SEC. With tetrahydrofuran as the solvent the hyperbranched polyester is contracted into a smaller more globular shape with a correspondingly smaller hydrodynamic volume. As a result, the polymer can penetrate the smaller pore sizes, spending a longer time in the column and thus has a longer retention time, with the assignment of lower average molecular weight. The effect is small, and the calibration is subject to some uncertainty, but suggests that chloroform is a better solvent for these systems than THF.

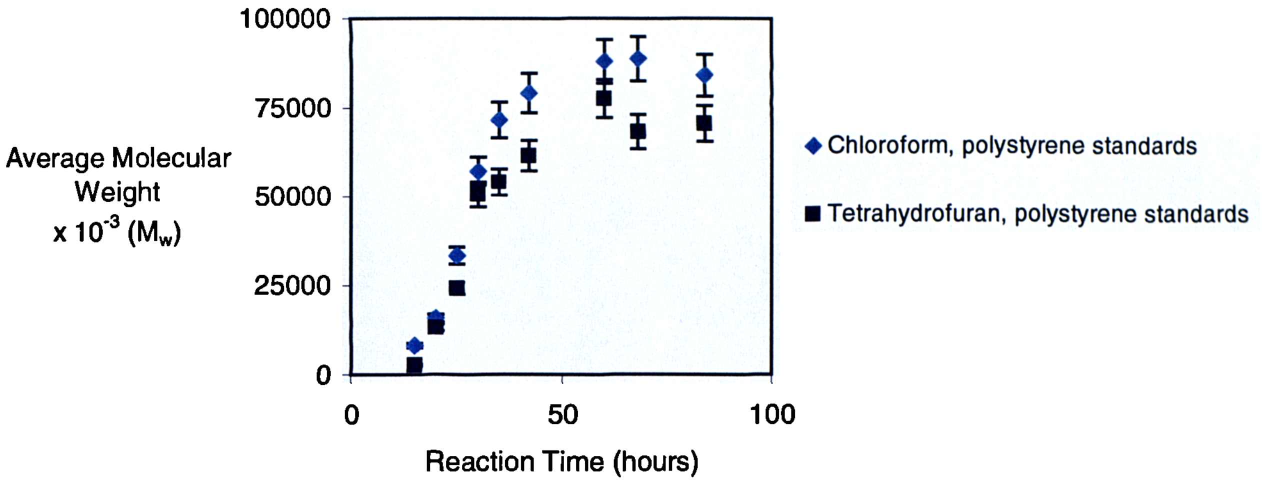


Figure 5.1.5: Change in M_w with reaction time for hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophthalates): measurements obtained by SEC using either THF or $CHCl_3$ as the solvent and linear polystyrene as the calibrant

5.1.4 SEC results from the variation of catalyst in the polymerisation of the AB_2 monomer dimethyl-5- (4-hydroxybutoxy)isophthalate

In order to investigate the effect of the catalyst on the polymerisation of the AB_2 monomers, a series of polymerisations of the AB_2 monomer, dimethyl 5- (4-hydroxybutoxy)isophthalate, were carried out using a range of catalysts as discussed in section 3.4. The SEC results obtained from these experiments are shown in Figure 5.1.6a, and are expanded further for simplification in Figure 5.1.6b shown overleaf. Average molecular weights were obtained using chloroform as the solvent and calibrated using linear polystyrene standards.

Figure 5.1.6a

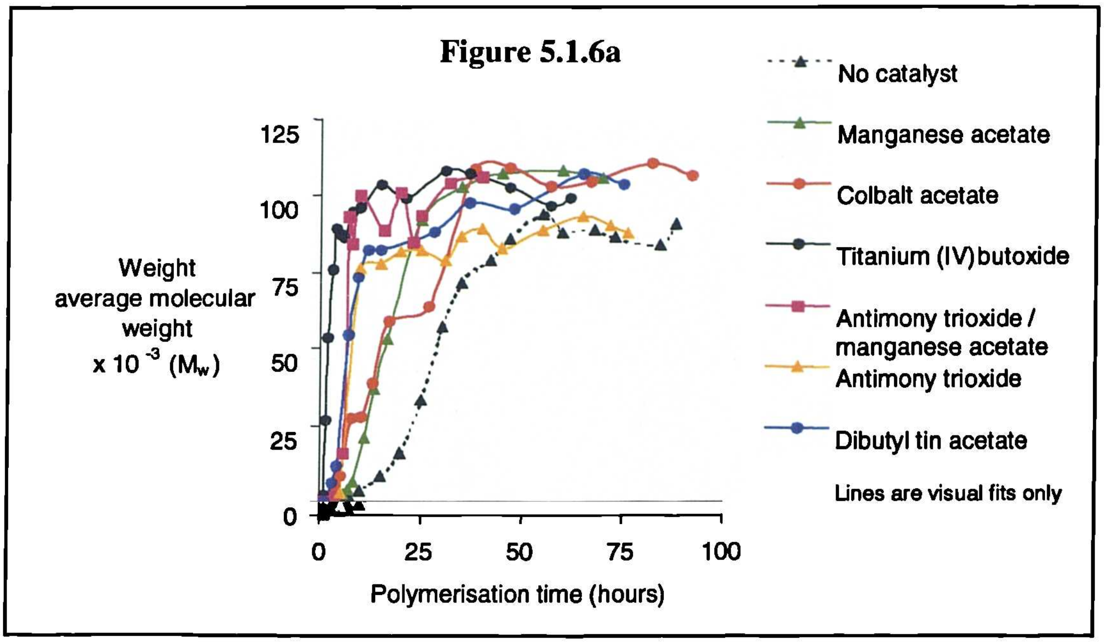
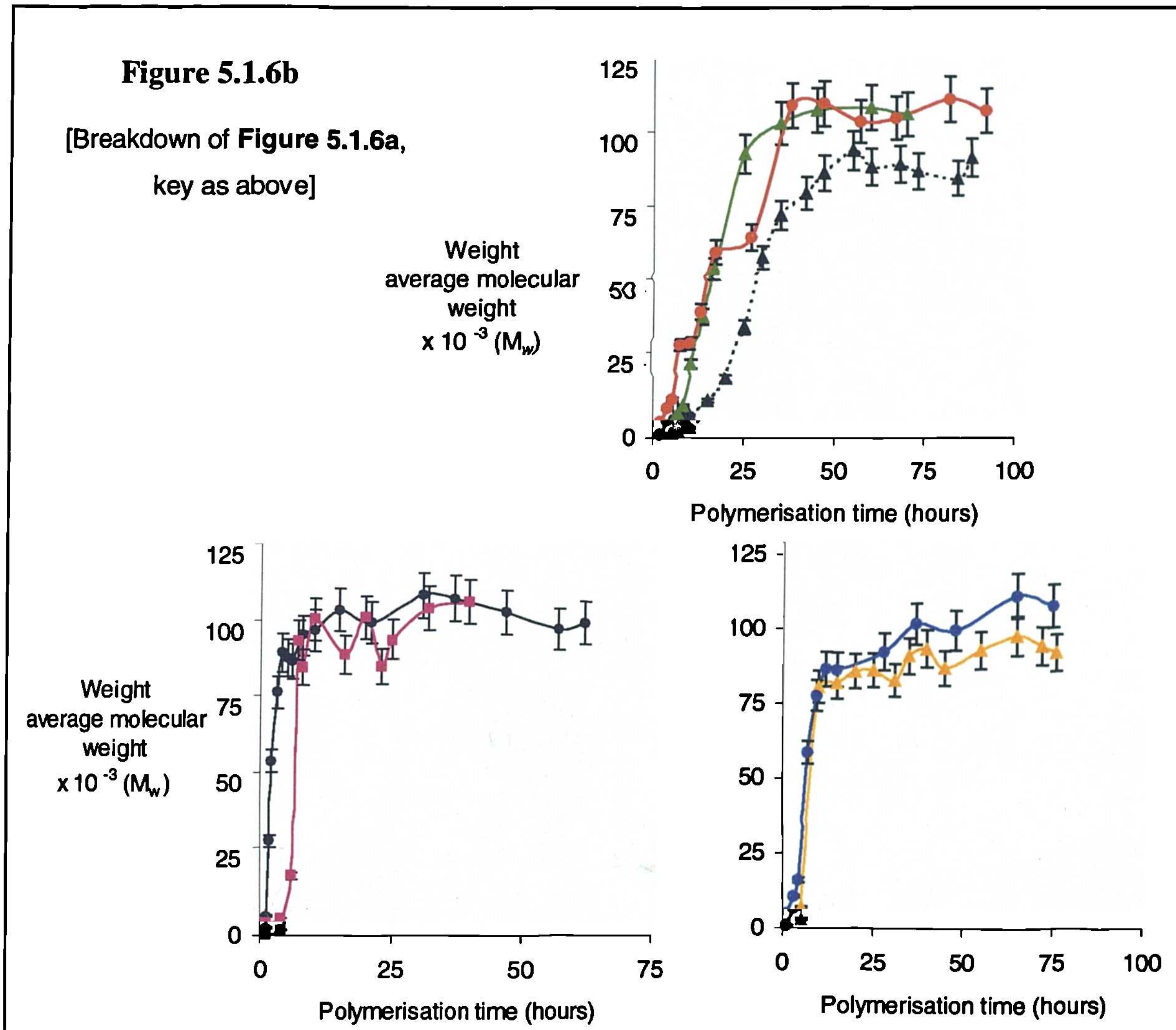


Figure 5.1.6b

[Breakdown of **Figure 5.1.6a**, key as above]



No catalyst < $Mn(OAc)_2$ ~ $Co(OAc)_2$ < $Bu_2Sn(OAc)_2$ ~ Sb_2O_3 < $Sb_2O_3/Mn(OAc)_2$ ~ $Ti(OBu)_4$

Figures 5.1.6a and b: The effect of the catalyst on the growth of molecular weight (M_w) for the polymerisation of dimethyl 5-(4-hydroxybutoxy)isophthalate

It can be seen from the SEC results shown in Figure 5.1.6 a and b that in all the polymerisations the weight average molecular weight reaches a plateau value between approximately 80000 and 100000. The $Ti(OBu)_4$, $Sb_2O_3/Mn(OAc)_2$, $Mn(OAc)_2$ and $Co(OAc)_2$ catalysed systems all reach higher plateau M_w values than the uncatalysed reaction and the $Bu_2Sn(OAc)_2$, Sb_2O_3 catalysed systems. The initial rate of the polymerisation is dependent on the catalyst used as shown below:

$$\text{No catalyst} < Mn(OAc)_2 \sim Co(OAc)_2 < Bu_2Sn(OAc)_2 \sim Sb_2O_3 < Sb_2O_3/Mn(OAc)_2 \sim Ti(OBu)_4$$

$$\xrightarrow{\hspace{6cm}}$$

Increasing rate of polymerisation

Clearly titanium (IV) butoxide and the combined antimony trioxide and manganese acetate catalyst system are the most effective catalysts for this polycondensation reaction since they reach the higher M_w values fastest. It is interesting to note that the addition of the manganese acetate, an ineffective catalyst, to the antimony trioxide, a moderately effective catalyst, gives a catalyst which is more effective than either.

In contrast to the low average molecular weight hyperbranched aliphatic polyesters obtained by Hawker and co-workers,[6] when dibutyl tin acetate was utilised as the catalyst in the polymerisation of 4, 4(4'-hydroxyphenyl) pentanoic acid, we have obtained relatively high average molecular weight polymer using the same catalyst. This suggests that the most appropriate catalyst to use for a particular polymerisation may be dependent on the AB_2 monomer system under consideration.

5.2 Determination of structure using matrix assisted laser desorption ionisation time of flight (MALDI-TOF) mass spectroscopy

5.2.1 Experimental

Mass spectra were obtained using a Kratos Kompact MALDI IV mass spectrometer equipped with a 337nm nitrogen laser. The instrument was operated in the linear mode to generate positive ion spectra at a non-variable accelerating voltage of 18kV. The apparatus was calibrated externally with a poly(ethylene glycol) standard obtained from Polymer Laboratories ($M_p = 1470$, M_w / $M_n = 1.04$).

Generally all solutions were prepared at a concentration of 10mg ml^{-1}. The poly(ethylene glycol) standard was dissolved in H_20. The matrix 2, 5-dihydroxybenzoic acid (DHB) was dissolved in a mixture of water/acetonitrile [40:60]. The alkali metal salts (LiCl, NaCl, KCl, RbCl, CsCl) were dissolved in water, whilst silver trifluoroacetate was dissolved in tetrahydrofuran. The hyperbranched polymers were dissolved in tetrahydrofuran (2mg ml^{-1}).

The DHB matrix and salt solution were deposited on the sample slide first (0.5µl each) and dried at ambient temperature (5 minutes) before depositing a sample of the hyperbranched polymer solution (0.5µl), which was dried as a before. Salt solutions, generally NaCl or KCl, were added to the sample to generate clearer spectra, this is referred to as doping the sample. Without doping ions are picked up from the martrix and solvents and can make interpretation of spectra difficult. During acquisition of spectra, the laser power was varied in order to obtain the best resolved spectra and the collected spectra were averaged over 100 shots, where one shot is defined as one pulse of laser irradiation.

5.2.2 Results and discussion

MALDI-TOF mass spectrometry has been used to investigate the structure of the polymers, **12** (n = 3), **13** (n = 4), **14** (n = 5) and **15** (n = 6). An example of a typical MALDI-TOF mass spectrum is shown for polymer **12** in Figure 5.2.1, a series of peaks are observed corresponding to degrees of polymerisation ranging from 2 to 18. This sample was not doped with alkali metal solution and ions were observed predominately as their $[M+K]^+$ species, with a small amount of the $[M+Na]^+$ adduct observed 16 mass units behind the main potassium series. Each peak in the main ion series corresponds to oligomers resulting from 1 to 17 simple condensation steps, where the mass of an oligomer of *n* units is [*n* x (monomer mass) – (*n* - 1) x (mass of MeOH)].

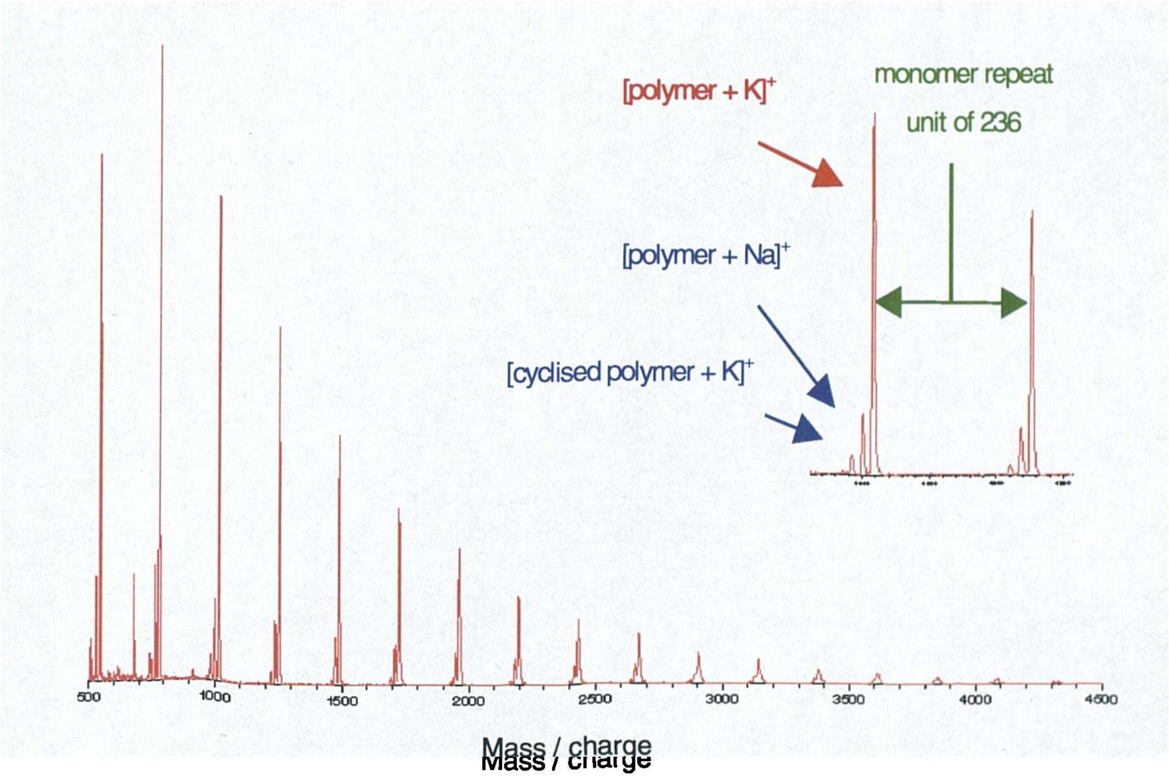


Figure 5.2.1: MALDI-TOF mass spectrum of hyperbranched poly(dimethyl 5-(3-hydroxypropoxy)isophthalate), **12** (n = 3), undoped, Mn = 1250, Mw = 2716 ($CHCl_3$ SEC)

A minor series of peaks is observed 32 mass units behind the main $[M+K]^+$ series. This is attributed to the loss of a further single methanol moiety to form a cyclic polymer.

For higher molecular weight polymers produced at longer reaction times only cyclic oligomers are observed. This is illustrated in Figure 5.2.2, which shows the spectra obtained for polymer **12** (n = 3) at different reaction times. Similar observations were made for the spectra obtained at different reaction times for polymers **13** (n = 4) and **15** (n = 6), their MALDI-TOF mass spectra are recorded in Appendix 3.

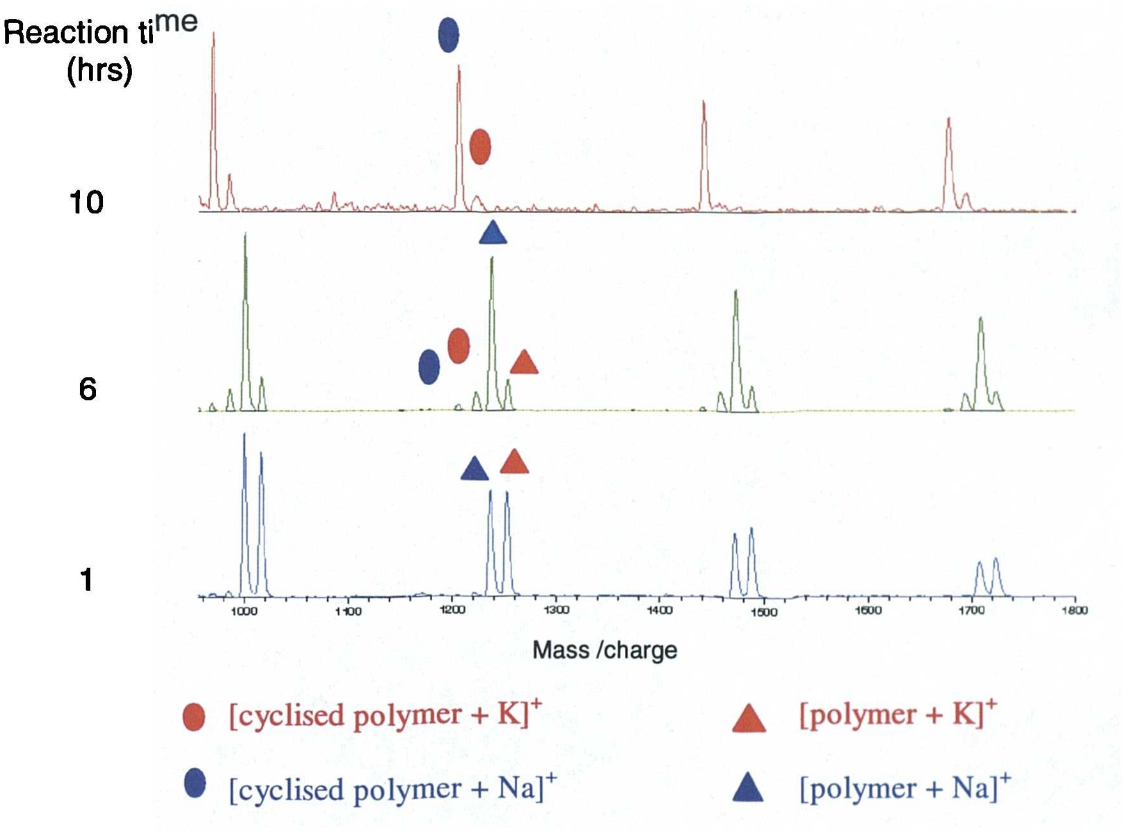
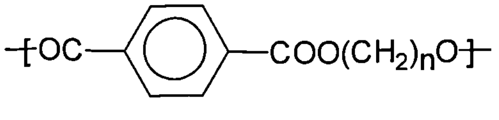


Figure 5.2.2: MALDI-TOF mass spectra obtained at different reaction times for hyperbranched poly(dimethyl 5-(3-hydroxypropoxy)isophthalate)s, **12** (n = 3)

This confirmation of the formation of cyclised hyperbranched polymer from MALDI-TOF mass spectroscopy indicates that this could be responsible for the plateau values reached for M_n and M_w identified by SEC and discussed in Section 5.1. Surprisingly, the same observations were made in the MALDI-TOF mass spectra of the analogous hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalate)s; after reaction times of 15 hours only cyclised hyperbranched polymer is observed although from SEC the M_w for this polymer continues to grow. It appears that the hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalate) is continuing to grow after cyclisation via a trans-esterification mechanism which is not observed for the polymers **12** ($n = 3$), **13** ($n = 4$), **14** ($n = 5$) and **15** ($n = 6$). Why trans–esterification occurs in the polymers where $n = 2$ and not in those where $n \geq 3$ is not easily understood, one can postulate that as the length of the alkylene chain is increased the inherent increase in mobility of the polymer structure does not favour trans-esterification. Consequently, after all the hyperbranched polymer has cyclised, there is no further mechanism available by which the polymer can continue to grow. This is an unexpected result since if we consider the linear polymers poly(ethylene terephthalate) and poly(butylene terephthalate), which have a structurally similar monomer repeat unit to the hyperbranched polyesters discussed in this work, trans-esterification is known to occur in both these systems regardless of the length of the alkylene chain in the monomer unit, see Figure 5.2.3 below.[7]



n = 2 poly(ethylene terephthalate)

n = 4 poly(butylene terephthalate)

Figure 5.2.3: Repeat unit in poly(ethylene terephthalate) and poly(butylene terephthalate)

Evidence of the formation of cyclised hyperbranched polymer is consistent with the results of Percec and co-workers,[8] who reported cyclisation in their hyperbranched liquid crystalline polyesters. These results however can be contrasted to those reported by Hamilton[9] and Hawker.[10] Both authors found no evidence for cyclised material in their hyperbranched polyesters. Therefore it can be concluded that cyclisation is extremely system specific, even within the single class of hyperbranched polymers considered.

One anomaly in the MALDI-TOF mass spectra of the hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s is observed for polymer **14** (n =5), see Figure 5.2.4 below.

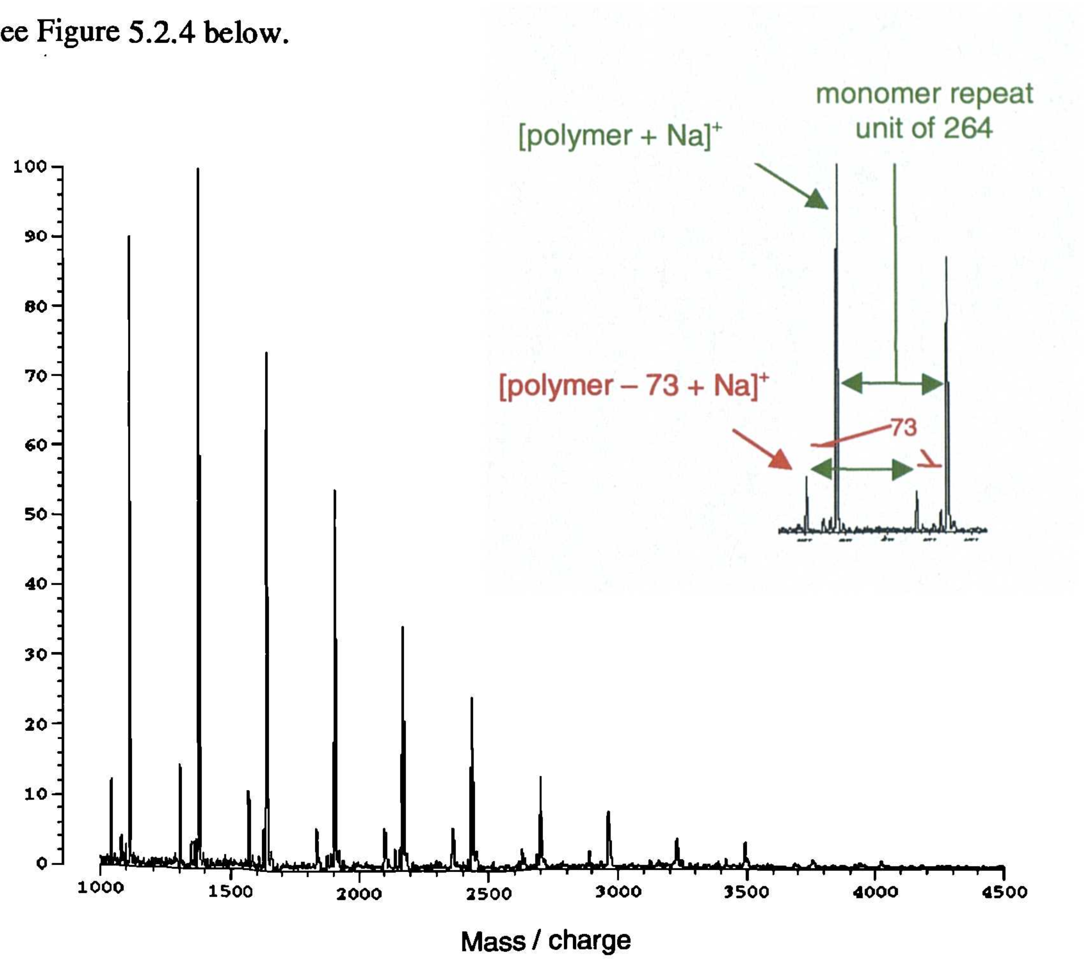


Figure 5.2.4: MALDI-TOF mass spectrum for hyperbranched poly(dimethyl 5-(5-hydroxypentoxy)isophthalate), **14** (n =5)

As expected, for low molecular weight polymer produced at short reaction times we observe uncyclised oligomers as the [M + Na]$^+$ adducts, whilst for higher molecular weight polymer produced at longer reaction times we observe cyclised oligomers. However, an extra ion series 73 mass units behind the main uncyclised series is observed, this is attributed to the loss of a single tetrahydrofuran moiety. This extra series could be a consequence of fragmentation occurring within the MALDI-TOF process since the C-C bonds next to a heteroatom are frequently cleaved in EI mass spectroscopy, leaving the charge on the fragment containing the heteroatom whose nonbonding electrons provide resonance stabilisation, see Figure 5.2.5.

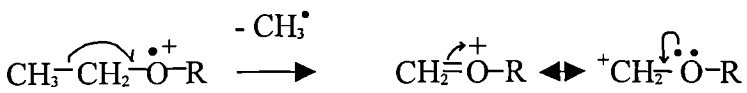


Figure 5.2.5: Fragmentation in EI mass spectrometry of ethers due to cleavage of the C-C bond next to the oxygen atom.

However the relative proportion of this extra ion series present in the spectrum, compared to the amount of uncyclised or cyclised oligomers, increases as the reaction proceeds indicating that this series is formed during the reaction (see Figure 5.2.6 overleaf). Furthermore, this ion series did not increase as the laser power was increased which one would expect for a fragmentation series.[11] Thus, this extra ion series is explained by a loss of a stable tetrahydrofuran unit from the focal unit of the polymer structure, which increases as the reaction proceeds. Isolation of tetrahydrofuran from the reaction mixture was attempted but without success since the loss of methanol always outweighs the amount of tetrahydrofuran eliminated from the reaction. This competing elimination reaction could account for the lower weight average molecular weight averages obtained for polymer **14** ($n = 5$, plateau $M_w \sim 30K$) as compared to polymer **12** ($n = 3$, plateau $M_w \sim 50K$).

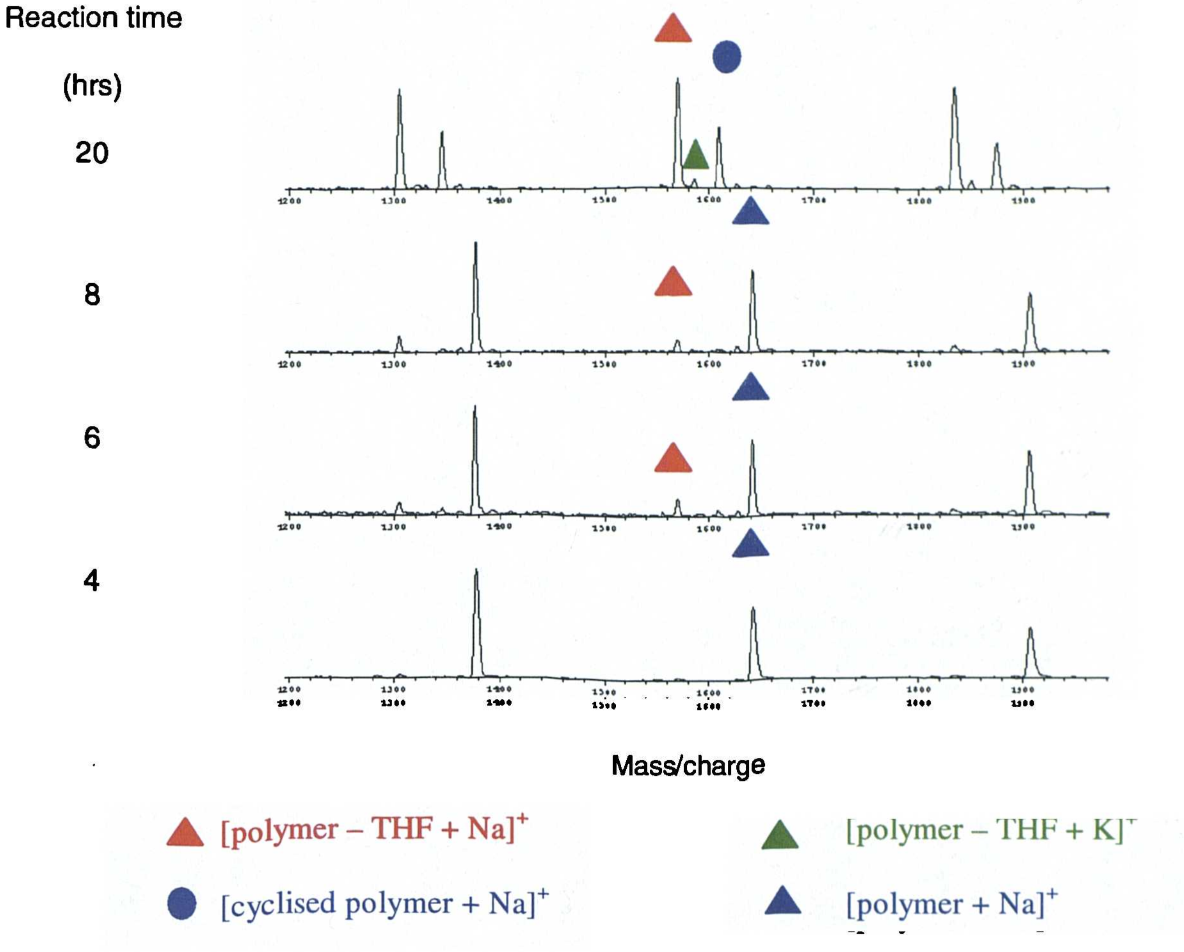


Figure 5.2.6: The change in the observed MALDI-TOF mass spectra with reaction time for polymer **14**, (n = 5)

2, 5-Dihydroxybenzoic *acid (DHB) was chosen as the matrix since it had been* used successfully in a MALDI-TOF MS study carried out on a linear polymer[12] with a similar monomer repeat unit to the hyperbranched polyesters being analysed in this study. Our initial studies of the application of MALDI-TOF mass spectroscopy to the hyperbranched polyesters also found that the use of this matrix gave clear, well resolved spectra. The difference in spectra obtained from a sample doped with an alkali metal salt compared to those where no ions are added is shown in Figure 5.2.7 overleaf. In the KCl doped sample (Fig. 5.2.7a) we observed predominantly the uncyclised oligomers detected as their potassium adducts, with two minor series corresponding to the uncyclised oligomers detected as their sodium adducts and the cyclised oligomers detected as their potassium adducts. Where no ions were added to the matrix (Fig.

5.2.7b), we observed predominantly the uncyclised oligomers detected as their sodium adducts. Three minor ion series are observed corresponding to the uncyclised oligomers detected as their potassium adducts, and the cyclised oligomers detected as both their sodium and potassium adducts. It is difficult to determine whether there is any ion selectivity occurring within the polymer samples or whether naturally there is a greater concentration of sodium ions present in the matrix and polymer solutions.

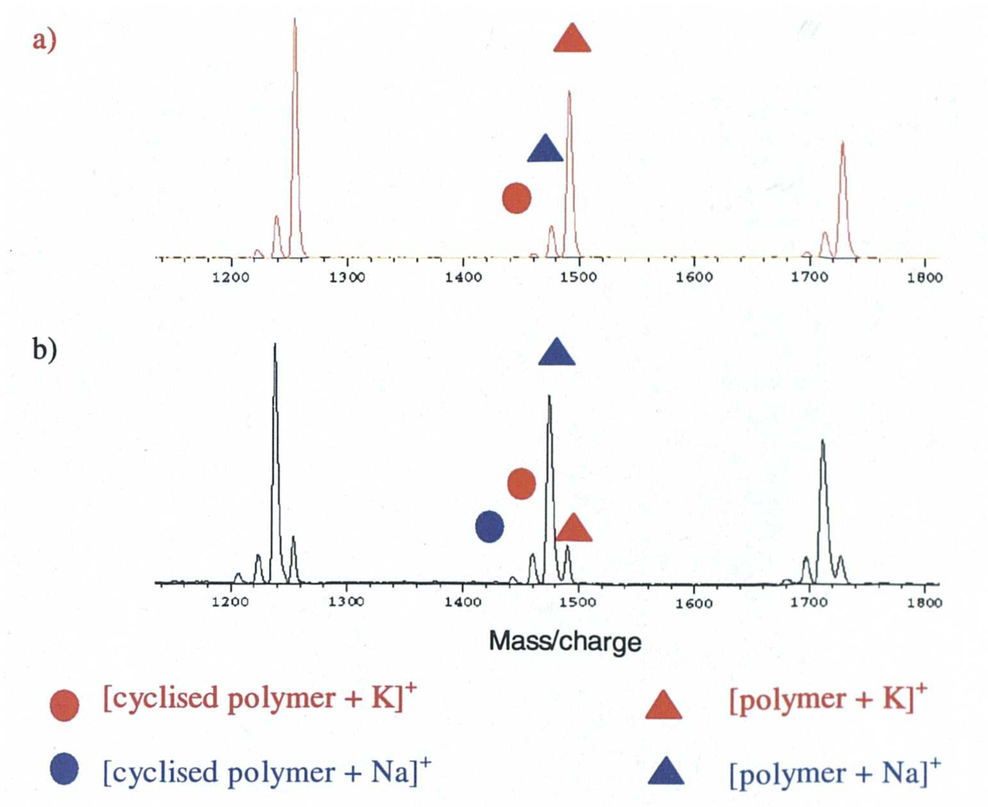


Figure 5.2.7:

MALDI-TOF spectra obtained for polymer **12** (a) doped with KCl, and (b) undoped

However, Figure 5.2.2 shows the change in MALDI-TOF spectra with reaction time for samples where no alkali metal salts were added. At one hour reaction time we observed the uncyclised oligomers detected as both their sodium and potassium adducts in equal amounts whilst at 10 hours reaction time we observed predominantly the cyclised oligomers detected predominantly as their sodium adducts. Since exactly the same matrix solutions and solvent for the polymer solutions were used, this would suggest that the cyclised polymer does exhibit ion selectivity with respect to the sodium ion. Such ion selectivity might be related to the ring size of the cyclised polymer.

Recent literature reports suggest that significant variations in the MALDI-TOF spectra can be obtained by changing the alkali metal cation. Scrivens and co-workers[13] found that spectra obtained for linear synthetic polymers with broad distributions, such as poly(ethylene terephthalate), could be manipulated by doping the polymer samples with different alkali metal cations, so as to narrow the observed distribution and molecular weight range observed. However when a range of alkali metal salts (LiCl, NaCl, KCl, RbCl and CsCl) were used in the generation of MALDI-TOF spectra for the hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalates), there was little change in the observed data as the size of the added cationic species was increased. Generally spectra generated with NaCl and KCl were found to be better resolved and thus in our studies we used these alkali metal salts. It appears that although the selective cation doping can effect the MALDI-TOF spectra obtained for linear polymers, this phenomenon is not observed in our hyperbranched systems and hence is system specific. Hobson[14] has made similar a observation in the MALDI-TOF mass spectroscopic analyses of hyperbranched poly(amidoamine)s.

It has been reported that MALDI-TOF spectra are highly dependent on the laser power incident on the sample in both linear and hyperbranched systems.[15, 16, 17] Belu *et al*[15] found that in linear polymers the spectrum obtained from the laser at the threshold power (the lowest power where a spectrum may be generated) is the most representative of the polymer distribution. A slight increase in power gives a skewed distribution which is shifted to lower mass. It has been suggested that this is due to degradation (scissions) of the polymer by the laser. However, MALDI-TOF mass spectrometry carried out by Hamilton[16] on low molecular weight aliphatic hyperbranched polyesters showed that at the threshold laser power, the low mass peaks were most intense. As the laser power was increased the distribution changed and peaks at higher m/e were observed with a peak in the distribution. Although the observation of larger oligomers at higher powers is intuitively expected the observed decrease in the lower mass species in the spectrum is surprising. If higher laser power results in fragmentation of all species one would expect the presence of more, not less, low mass peaks in the spectrum.

In an attempt to investigate the dependence of the quality of the observed MALDI-TOF mass spectra of hyperbranched poly(dimethyl-5-(6-hydroxyhexoxy)isophthalate) on the laser power, a series of spectra were collected at different laser powers and examined. The laser power was increased from 55 to 69% of the available laser power of the instrument. On inspection of the spectra shown in Figure 5.2.8, it is clear that the recorded spectrum is dependent on laser power, although it is difficult to explain the correlation between laser power and the form of the distribution in the spectrum. At lower laser powers the distribution is skewed towards lower mass, with a peak in the distribution observed at 1418 m/e (Fig 5.2.8 spectrum no. 3). As the laser power is increased the distribution changes and peaks at higher m/e are observed with a peak in the distribution observed at 2553 m/e (Fig.5.2. 8 spectrum no. 4). Again this is surprising, as one would expect that for a step-growth polymerisation the low molecular weight species to be the most abundant. However, by increasing the laser power further we observe an increase in the number of low mass species in the spectrum, with a peak in the distribution observed at 1975 m/e (Fig.5.2. 8 spectrum no. 5). Such a shift to lower masses could indicate fragmentation at higher laser powers resulting in the presence of more low mass peaks in the spectrum. If fragmentation of the hyperbranched polyester was occurring, one would expect to observe an additional ion series which is different to the intact polymer, however this is not the case.

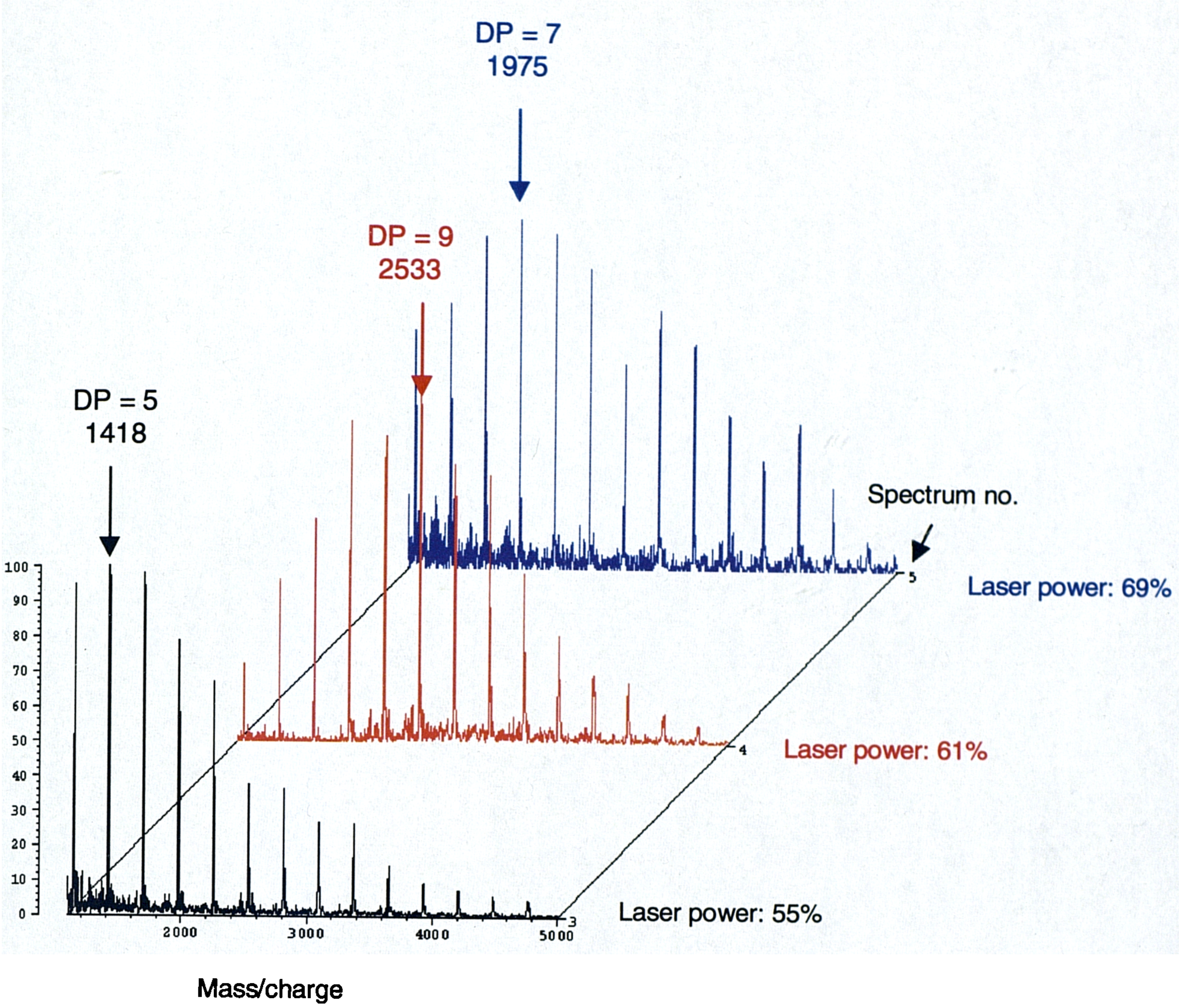


Figure 5.2.8: Variation in MALDI-TOF mass spectra obtained at different laser powers for the hyperbranched poly(dimethyl-5-(6-hydroxyhexloxy)isophthalate)

This work, and results reported by other workers in this field, show that the spectra are highly dependant on the laser power and therefore one should treat detailed interpretation of 'one off' spectra with considerable reserve. Since there are many other factors which determine the form of the distribution observed in MALDI-TOF spectra it is difficult to conclusively state that these observations are entirely due to the laser power, for example sample preparation[12] is also known to influence the spectra obtained considerably. Clearly there is still much to learn in the application of this comparatively new technique, including the effect of different experimental parameters on the observed spectra.

Regardless of these limitations, MALDI-TOF MS has been an invaluable tool in the characterisation of the polymers discussed here. It allowed the author to confirm the formation of the hyperbranched polyesters and prove the occurrence of cyclisation in these systems, as well as identifying the occurrence of side reactions in the case of hyperbranched poly(dimethyl 5-(5-hydroxypentoxy)isophthalate)s. However, the technique in our hands could not be regarded as a reliable indicator of the molecular weight and its distribution for any but the lowest molecular weight samples.

5.3 The intrinsic viscosity of hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s

5.3.1 Introduction

Dilute solution viscosity measurements for the hyperbranched poly(ω-dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s have been used to investigate the configuration of the polymers in solution. One of the simplest methods to measure the viscosity of a dilute polymer solution is by use of a capillary type viscometer, which measures the time taken for a fluid to flow through capillary of a specific length. The ratio of the time of flow of a polymer solution, t, to that of the pure solvent, t_o, is equal to the ratio of their viscosities (η / η_o) and is known as the relative viscosity η_{rel}:

$$\eta_{rel} = (t / t_o) = (\eta / \eta_o) \qquad \text{Equation 5.1}$$

The relative viscosity assumes that the density of the polymer solution and solvent are equal, this approximation is valid for dilute solutions. For infinitely dilute solutions (where η approaches η_o) the value of η_{rel} approaches unity and it becomes more useful to define the specific viscosity, η_{sp}, which is a measure of the increase in viscosity (η-η_o) brought about by the addition of the polymer to the solvent:

$$\eta_{sp} = t\text{-}t_o / t_o = \eta\text{-}\eta_o / \eta_o = \eta_{rel} - 1 \qquad \text{Equation 5.2}$$

The ratio η_{sp}/c, where c is the concentration of the polymer solution, is a measure of the capacity of the polymer at a given concentration to increase the viscosity. At the limit of infinite dilution (where c approaches 0) this is known as the intrinsic viscosity [η].

$$[\eta] = (\eta_{sp} / c)_{c\rightarrow 0} \qquad \text{Equation 5.3}$$

Alternatively, the intrinsic viscosity can be obtained by dividing $\ln(\eta_{rel})$ by the concentration of the polymer solution, c.

$$[\eta] = [\ln(\eta_{rel})/c]_{c\to 0} \qquad \text{Equation 5.4}$$

The evaluation of the intrinsic viscosity at zero concentration simplifies the interpretation of experimental results by eliminating polymer – polymer interactions, which occur even in dilute solutions. The intrinsic viscosity can then be obtained from the intercept of the plot of (η_{sp}/c) or $[\ln(\eta_{rel})/c]$ versus c.

In 1940 Mark and Houwink[18] derived an empirical relationship between the molecular weight of a polymer (M) and its intrinsic viscosity, shown below:

$$[\eta] = KM^{a} \qquad \text{Equation 5.5}$$

where K and a are constants for a given polymer, solvent and temperature.

A graph of log[η] *vs* log[M] is plotted where K and a can be evaluated from the intercept and gradient, respectively. The value of a provides an insight into the polymer configuration. Generally for flexible polymer molecules a lies between approximately 0.5 and 0.8, higher values of a are observed for less flexible (rodlike) molecules, whilst lower values are obtained for branched, compact systems ($a \leq 0.5$).

It is well known that linear polymers follow the Mark-Houwink equation given above, and therefore their intrinsic viscosity increases with increasing molecular weight. However, dendritic polymers do not obey this relationship ($\eta \propto M$) over the full range of molecular weights. This is illustrated in Figure 5.3.1, which shows the molecular weight-intrinsic viscosity relationship for different types of polymer architecture including linear, statistical hyperbranched (i.e. DB = 0.5) and dendritic polymers. For the polyether dendrimers prepared by Fréchet[19] and Tomalia's poly(amidoamine) dendrimers (PAMAM)[20] in both cases the intrinsic viscosities are reported to reach a maximum and decrease thereafter with increasing molecular weight.

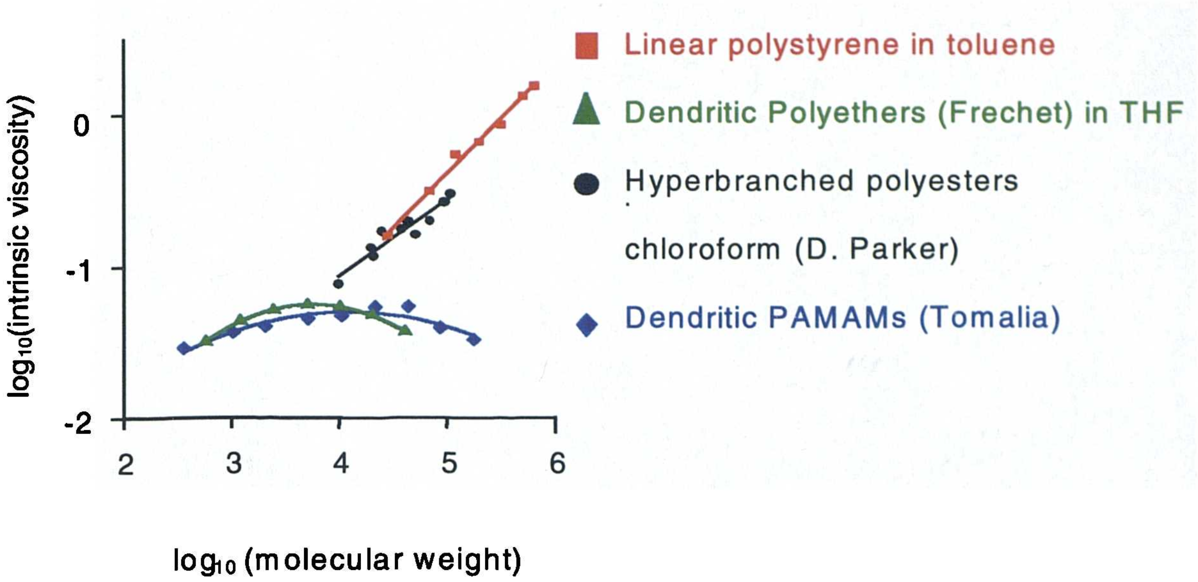


Figure 5.3.1: Graph of the log$_{10}$ [intrinsic viscosity] *vs.* log$_{10}$ [molecular weight], for a range of polymer architectures including linear, hyperbranched and dendritic systems

This unique behaviour can be explained by considering the conformational changes that dendrimers undergo through increasing in generation. At low generations the dendrimer adopts a relatively mobile conformation and, in terms of hydrodynamic volume, will show behaviour similar to that of a linear polymer. Therefore at low generations dendrimers will have a molecular weight/viscosity relationship which is qualitatively similar to that defined by the Mark-Houwink equation. However, as the dendrimer increases in size the structure gradually becomes more rigid and eventually approximates to a hard sphere. During this change the density increases since the molecular mass of the dendrimer increases faster than its hydrodynamic volume. The relationship between the molecular mass and intrinsic viscosity of hard spheres is described by Einstein's hard spheres relationship:

$$[\eta] \propto V_h/M$$

where V_h is the hydrodynamic volume, M is the mass and $[\eta]$ is the intrinsic viscosity.

Since dendrimers of higher generations approximate to hard spheres, this expression is more appropriate for accounting for trends in their intrinsic viscosity. As their hydrodynamic volume increases more slowly than their mass, their intrinsic viscosity will decrease with increasing mass.

Generally, dilute solution viscometry studies of hyperbranched systems[1,2] have found that these polymers obey the Mark Houwink equation, so that their intrinsic viscosity increases with increasing molecular weight, this is illustrated in Figure 5.3.1 for the hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalates).[3] Although no direct comparison has been made between the solution viscosity properties of a linear and hyperbranched polymer composed of the same or similar repeat motif, generally it has been found that hyperbranched polymers have a lower solution viscosity when compared with similar linear polymers.

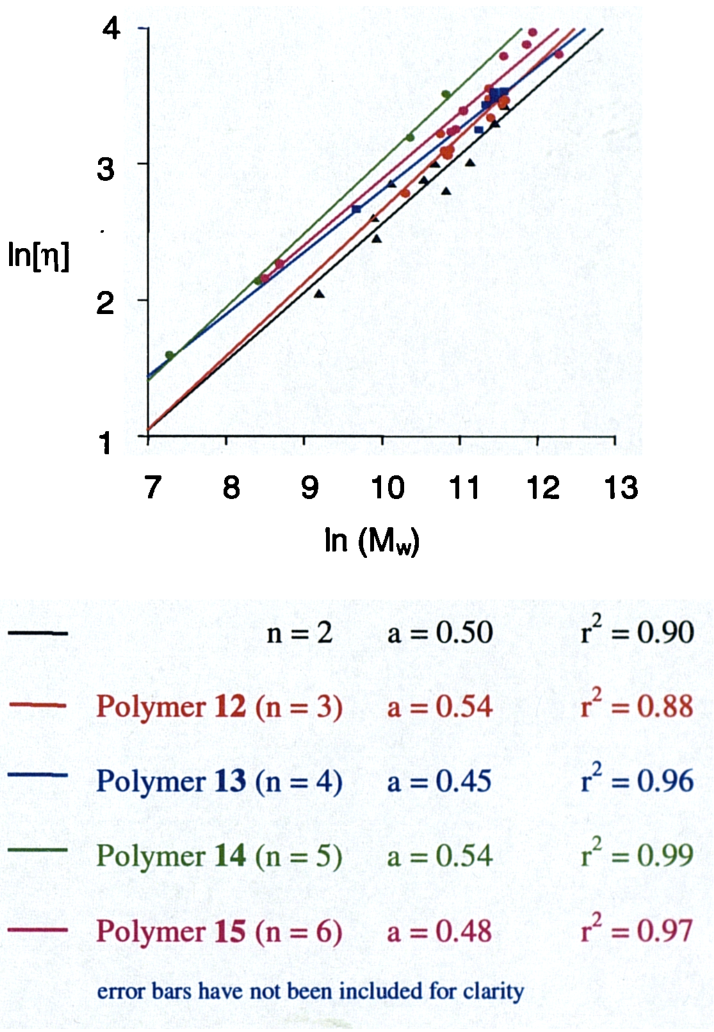
Recently Hobson *et al*[21,22] reported that core terminated hyperbranched poly(amidoamine)s, with a degree of branching ≥ 0.9, exhibited a molecular weight/intrinsic viscosity relationship similar to that shown by dendrimers i.e. the intrinsic viscosity passes through a characteristic maximum and then decreases with increasing molecular weight. This result suggests that the topology in these systems resembles that of dendrimers rather than statistical hyperbranched systems, and that for hyperbranched structures the intrinsic viscosity/molecular weight relationship is dependent on the specific system under consideration, in particular the degree of branching. This result could be a turning point in hyperbranched polymer science, since it suggests that a hyperbranched polymer with a similar degree of branching to a dendrimer can replicate dendritic solution viscosity properties, an observation which has been confirmed also in a computational study of intrinsic viscosity of hyperbranched polymers.[23] Although a thorough investigation of how the degree of branching in hyperbranched polymers effects the solution viscosity properties of the materials has not been carried out to date, such work might be valuable in predicting the viscosity/molecular weight relationship for such materials as a function of their molecular structures. It might subsequently be possible for synthetic chemists to design routes to hyperbranched polymers with 'tailor-made' viscosity/molecular weight relationships, such an achievement might be technologically valuable.

5.3.2 Dilute solution viscometry measurements of hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s

Intrinsic viscometry measurements were made using a Schott-Gerate automated viscometer system (AVS), in which the polymer solution or solvent was contained in a Schotte-Gerate Ubbelohde viscometer (bore size 0.46mm), immersed in a constant temperature water bath at 25°C. The AVS system allowed flow times to be measured to an accuracy of 0.01seconds by means of an opto-electronic sensor. All polymer solutions (0.01g ml^{-1} in chloroform) were filtered at least twice through a Whatman 0.2μm filter and their concentrations calculated accurately in order to obtain accurate solution viscometry results.

The polymer solution (20ml) was transferred to an Ubbelohde viscometer thermostated at 25°C, where the temperature of the polymer solution was allowed to equilibrate for 20 minutes. Up to 9 time of flow readings were then recorded until a suitable standard deviation had been obtained ($\leq 0.1\%$) for at least 5 readings. The polymer solution was diluted using chloroform (10ml) and the procedure repeated, a total of 5 dilutions were made. Using this method the time of flow for the pure solvent was obtained.

The measurements obtained for the time of flow of the solvent and of the polymer solutions at different concentrations, were used to calculate the reduced (η_{sp}/c) and inherent ($\ln(\eta_{rel})/c$) viscosity for each polymer. By plotting η_{sp}/c or $\ln(\eta_{rel})/c$ versus concentration, the intrinsic viscosity of each polymer was obtained from the intercept. This procedure was carried out for all the hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalates)s, over a range of weight average molecular weights determined by SEC (solvent:$CHCl_3$, calibrant: linear polystyrene). This allowed a plot of log[η] versus log[molecular weight] to be constructed and is shown in Figure 5.3.2. The viscometry results for the hyperbranched poly(dimethyl 5-(2-hydroxyethoxy) isophthalate)s are also included for comparison.[3]



—	n = 2	a = 0.50	$r^2 = 0.90$
—	Polymer **12** (n = 3)	a = 0.54	$r^2 = 0.88$
—	Polymer **13** (n = 4)	a = 0.45	$r^2 = 0.96$
—	Polymer **14** (n = 5)	a = 0.54	$r^2 = 0.99$
—	Polymer **15** (n = 6)	a = 0.48	$r^2 = 0.97$

error bars have not been included for clarity

Figure 5.3.2: Graph of ln[M_w] *vs* ln[η] for the hyperbranched poly(ω-dimethyl 5-(hydroxyalkoxy)isophthalate)s

The hyperbranched poly(dimethyl 5-(hydroxyalkoxy)isophthalates) showed a linear intrinsic viscosity/weight average molecular weight relationship. The increase in the number of methylene units in the alkylene chain of the AB_2 monomer does not appear to effect the gradient of the slopes substantially, with *a* values obtained between 0.45 and 0.54, thus indicating a branched and compact structure in all these hyperbranched polyesters.

A similar linear dependence has been shown by Turner *et al*[2] for aromatic hyperbranched polyesters synthesised from 3, 5-diacetoxybenzoic acid. Values of *a* between 0.3 – 0.4 were obtained, again indicating a branched and compact structure for this hyperbranched system. It should be noted that qualitative comparisons of *a* values between different polymers are only strictly correct when referring to viscometry measurements carried out at the same temperature and in the same solvent. The weight average molecular weight values should be born in mind when examining ln[η] *vs* ln[M_w] plots, since the M_w values reported in the results presented here are linear polystyrene equivalent masses, obtained by SEC, and are therefore subject to some uncertainty.

5.4 Thermal analysis of hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s

5.4.1 Introduction

The glass transition, defined as the onset of chain segmental motion in a polymer, is well understood for linear polymers. Factors affecting the glass transition include chain flexibility, branching and cross-linking, molecular structure, and molecular weight. For linear polymers the glass transition, T_g, increases with increasing molecular weight up to a limiting value, $T_{g\infty}$. This relationship has been described in terms of a chain-end free volume theory by Fox and Flory. The following equation was established:

$$T_g = T_{g\infty} - K/M_n \qquad \text{Equation 5.6}$$

where K is a constant.

However, it appears from the literature that the factors governing the glass transition temperature in dendrimers or hyperbranched polymers are not understood fully. The glass transition in a number of hyperbranched and dendritic systems has been found to be affected by both the nature of the backbone and the terminal groups in the polymer. Kim and Webster found, through modification of the end groups of their hyperbranched poly(phenylene)s,[24] that the T_gs were highly dependent on the structure and polarity of the end groups in the polymer. Since the internal structures and linkages remained the same within the set of polymers compared, they proposed that the glass transition of the hyperbranched polymers was a function of the motion of the end groups. This follows logically as hyperbranched polymers do not possess the same long unbranched segments required for segmental motion and thought to be the determinant of the glass transition of linear polymers. This dependence of the glass transition on the nature of the end groups in dendrimers and hyperbranched polymers has been demonstrated by a number of groups, examples are given below.[24,25,26]

Effect of terminal groups on the glass transition of hyperbranched polyethers (M_w~7000, M_n ~ 5000)

Terminal groups	H	C_6H_5	$OCOCH_3$	$OSi(CH_3)_3$
T_g (°C)	43	51	70	70

Effect of terminal groups on the glass transition of dendritic polyether monodendrons (generation 4)

Terminal groups	H	Br	CN
T_g (°C)	39	52	76

The internal structure of hyperbranched polymers has been found to effect the glass transition in a similar manner to that of linear polymers; thus, increasing the flexibility of the polymer structure decreases the T_g. For example, the T_g of hyperbranched polyurethanes, prepared by Kumar *et al*,[27] was lowered by increasing the length of the oligoethyleneoxy spacer segments between the branch points in the polymer. In contrast, an increase in T_g was observed for hyperbranched poly(amidoamine)s prepared by Hobson *et al*,[28] when the methylene spacer length was increased between the branch points in the polymer; no explanation was given for this surprising effect.

The influence of the degree of branching upon the glass transition of hyperbranched poly(ether-ketone)s has been studied by Hawker *et al.*[29] Fluoro-terminated hyperbranched poly(ether ketone)s were prepared with varying degrees of branching (DB = 0.39, 0.49 and 0.71). The polymers were found to have the same T_g (162°C) demonstrating that in this hyperbranched system the glass transition temperature was independent of the degree of branching.

Stutz carried out a detailed theoretical study of the glass transition of dendritic polymers[30] and postulated that the presence of a large number of end groups in dendrimers decreases the glass transition temperature, whilst the large amount of branching within the structure increases it. Thus, these two opposing effects will cancel each other resulting in little difference in the glass transition for linear polymers and analogous dendrimers. This has been demonstrated experimentally by Wooley,[31] who showed that dendritic, hyperbranched and linear macromolecules, based on the 3, 5-dihdroxybenzoic acid building block, were all found to have similar glass transitions of approximately 200°C.

The effect of molecular weight upon the glass transition of dendritic macromolecules has received little attention to date. In Fréchet's study of the glass transition of dendritic polyesters and polyethers, the glass transition temperature in these systems increased with molar mass up to a certain limit, above which it remained virtually constant.[25] Fréchet found that existing theories did not apply to these dendritic polyesters and polyethers and therefore proposed a modified version of the Fox and Flory equation (Equation 5.6) to account for the large number of chain ends in the dendritic structures. This expression, shown in Equation 5.7, relates the glass transition to both the molecular weight (M) and the number of end groups within the dendrimer (n_e), and has been found to provide a reasonable fit for the dendritic polyesters and polyethers.

$$T_g = T_{g\infty} - K' \, n_e / M \qquad \text{Equation 5.7}$$

where $K' = \rho N \theta / \alpha$.

(n_e is the number of chain ends, ρ is the chain end density, N is Avagadro's number, θ is the chain-end free volume and α is the free volume expansion coefficient).

For hyperbranched polymers the situation is more complex with different T_g/molecular weight relationships reported. For example, in the hyperbranched poly(phenylene)s reported by Kim and Webster,[32] the T_g remained at approximately 240°C in the M_n range of 2000 to 35000, whilst for hyperbranched polyesters prepared by Stainton,[4] a linear relationship between the glass transition and the reciprocal number average molecular weight was reported for a relatively narrow molecular weight range. Parker[3] examining a much broader molecular weight range of the same hyperbranched polyester has shown a much better correlation with the reciprocal weight average molecular weight. Clearly more work is required before we can understand the factors effecting the glass transition in hyperbranched structures, and explain the contrasting results reported so far.

5.4.2 Experimental

Thermogravimetric analysis (TGA) was performed on a Stanton Redcroft TG760 thermobalance, at a heating rate of 10°Cmin^{-1} in a nitrogen atmosphere.

Differential scanning calorimetry (DSC) measurements were recorded using a Perkin Elmer DSC 7, under a nitrogen atmosphere. Each polymer was annealed at 200°C for 2 minutes, the sample was cooled at a rate of 200°Cmin^{-1} to 25°C where it was held for a further 5 minutes. A DSC trace was recorded at a heating rate of 10°Cmin^{-1} from 0°C to 200°C. This procedure was repeated at least twice for each polymer sample. Representative DSC traces for each of the hyperbranched polymers, **12**, **13**, **14** and **15** are included in Appendix 3.

5.4.3 Thermogravimetric analysis and differential scanning calorimetry of hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s: results and discussion

Thermogravimetric analysis has shown all hyperbranched polymers to be thermally stable, retaining 98% of their mass up to 320°C ±10°C. DSC failed to reveal any crystalline melting points for any of the hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s. No melting points were detected by DSC which is consistent with the formation of amorphous polymer. This lack of crystallinity, due to disruption of packing by branched segments, has been observed in a number of other dendritic and hyperbranched polymers.[33, 34]

The glass transition for the hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s was found to vary between approximately 24 and 88°C depending on the length of the alkylene chain in the polymer. This is illustrated in the table overleaf which shows that as the methylene spacer length between the branch points in the polymer is increased, the T_g of the hyperbranched polymer is lowered. The T_g for the hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalate) has been included for comparison.[3]

The effect of the increasing the length of the methylene spacer on the glass transition of the hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s.

Number of methylene units in the alkylene chain	2	3	4	5	6
T_g (°C)	78-88	61-66	45-51	34-36	24-28

In order to investigate whether the molecular weight had any effect on the glass transition of the hyperbranched polyesters, the glass transition temperatures over a range of average molecular weights were obtained for the hyperbranched poly(dimethyl 5-(4-

hydroxybutoxy)isophthalate)s. These results, shown in Figure 5.4.1 below, show clearly that the T_g of the hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophthalate)s is effected by the molecular weight, both M_n and M_w, showing a similar T_g/molecular weight relationship to that found in linear systems. An increase in the T_g is observed with increasing M_n and M_w until a maximum T_g is obtained. To confirm conclusively that the glass transition has reached a plateau value more T_gs would be required at higher molecular weights, however, since SEC has shown that in this system the M_n and M_w reach a plateau value, only glass transitions for polymer samples up to ~100 000 M_w and 15 000 M_n could be obtained.

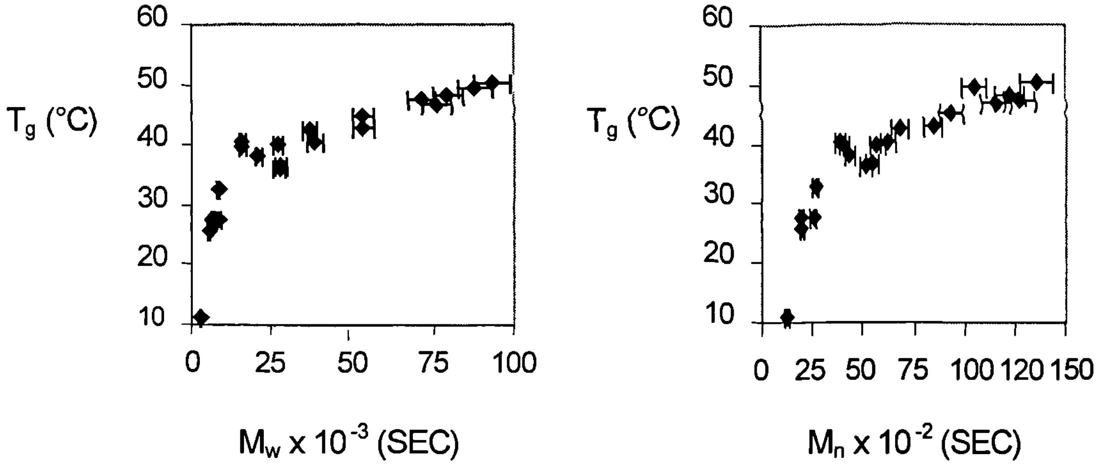


Figure 5.4.1: Change in glass transition temperature with average molecular weight (SEC) for hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophthalate)s

SEC results were obtained using chloroform as the solvent and calibrated using linear polystyrene. Therefore it should be born in mind when examining these plots that the M_w and M_n values reported in Figure 5.4.1 are linear polystyrene equivalent masses and are subject to some uncertainty.

According to the Fox and Flory equation for linear polymers (Equation 5.6), and Fréchet's modified version of the Fox and Flory equation for dendritic polymers (Equation 5.7), the glass transition in these systems is inversely proportional to the molecular weight (i.e. $T_g \propto 1/M$). In order to determine if a similar relationship could be found between T_g and the molecular weight for hyperbranched polymers, the data given in Figure 5.4.1 was plotted as $1/M_n$ and $1/M_w$ *vs* T_g, (see Figure 5.4.2). In linear systems oligomers and very low molecular weight polymer are known not to follow the $T_g \propto 1/M_n$ relationship, and thus only T_gs of polymer samples where Mw >8 000 and Mn > 3000 were included in these plots.

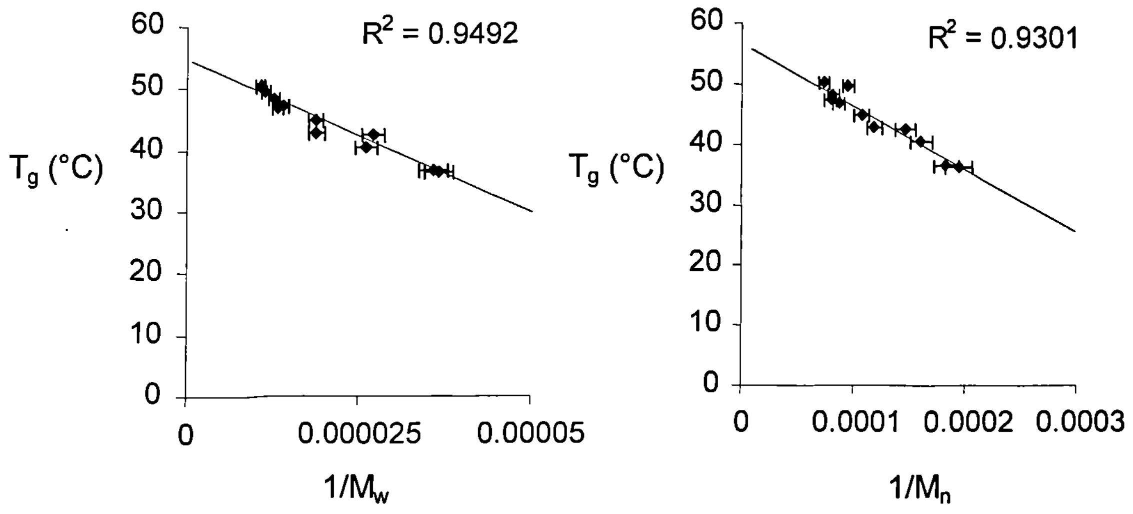


Figure 5.4.2: Change in the glass transition temperature with reciprocal average molecular weight for hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophthalate)s

As shown in Figure 5.4.2, we observe a linear relationship between the T_g and the reciprocal molecular weight (M_n and M_w) for the hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophthalate)s. Thus it appears in this system that a similar trend is observed between the T_g and molecular weight as is found in linear and dendritic polymers.

While this result corresponds well with similar results by reported Hamilton,[5] for aliphatic hyperbranched polyesters, and by Stainton,[4] for the analogous hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalate)s, other hyperbranched systems have found little effect of the molecular weight on the glass transition.[32] These contrasting results suggest that the T_g/molecular weight relationship for hyperbranched polymers is system specific.

Generally for linear polymers the T_g/molecular weight relationship is best described in terms of molecular weight by their M_n. It was anticipated that due to the large polydispersities of the hyperbranched polyesters the M_w may provide a better description of the molecular weight, therefore for comparison both $1/M_n$ and $1/M_w$ *vs* T_g were plotted. However it is interesting to note that both M_n and M_w can be used to describe the relationship in this hyperbranched system, giving reasonable straight line fits to the data.

Another interesting feature of these results is that although hyperbranched polymers and linear polymers have vastly different structures, they show a very similar T_g/reciprocal molecular weight relationship. This could be accounted for using the same approach used to describe the differences in T_g between linear and dendritic polymers proposed by Stutz, that is, the presence of a large number of end groups decreases the T_g, whilst the large amount of branching within the structure increases it. Thus, these two opposing effects will cancel each other resulting in little difference in the T_g for linear polymers and analogous hyperbranched polymers. However, as yet no work has reported how molecular weight effects the T_g for linear, dendritic and hyperbranched systems, constructed from similar or the same building blocks. Results from these experiments would be useful in establishing if there are any differences between the different types of architecture and their T_g/molecular weight relationship.

To conclude, TGA has confirmed the hyperbranched polymers to be thermally stable materials. DSC analysis has shown that these materials are amorphous, which is consistent with data reported for other hyperbranched polymers. The T_g has been found to be dependent on the internal structure of the polymer, therefore as the alkylene chain length is increased, the T_g is lowered.

For the hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophth late)s, the effect of the molecular weight on the T_g is similar to that found in linear p lymers; it appears from the plot of T_g versus M_n or M_w that the glass transition incre ses with increasing molecular weight with a maximum T_g obtained at high molecu r weights, in addition, a linear relationship between the T_g and the reciprocal average m lecular weight (M_n and M_w) is observed in this system.

5.5 Spectroscopic characterisation of hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s

5.5.1 Experimental

Infrared spectra were recorded using a Perkin-Elmer 1600 series FTIR spectrometer. The spectra were recorded as KBr discs or in the solid state. ^{1}H and ^{13}C nmr spectra were recorded using a Varian VXR 400 nmr spectrometer at 399.953 MHz (^{1}H) and 100.577 MHz (^{13}C). Quantitative ^{13}C nmr spectra were recorded using a Bruker AMX 500 nmr spectrometer at 124.67 MHz. Deuterated chloroform and deuterated toluene were used as solvents with tetramethylsilane as an internal reference.

5.5.2 Infrared spectroscopic analysis of hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s

Infrared spectroscopic analysis was consistent with the formation of polymer for the hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalates). Representative infrared spectra for each of the hyperbranched polyesters, **12**, **13**, **14** and **15**, are recorded in Appendix 3.

It was anticipated that infrared spectroscopy could be used to monitor the decrease in hydroxyl groups as the polymerisation progressed. However, no correlation could be made between reaction time and the intensity of the hydroxyl peak, and generally no hydroxyl peak was observed in the infrared spectra of the polymers. This observation agrees well with the identification of cyclised hyperbranched material by MALDI-TOF mass spectroscopy, since cyclised polymer would no longer contain their hydroxyl functionality. A comparison of the infrared spectrum for an AB_2 monomer (**9**, n = 4) and the corresponding hyperbranched polymer (**13**) is shown in Figure 5.5.1, overleaf highlighting the absence of a hydroxyl peak at ~3300cm^{-1} in the polymer.

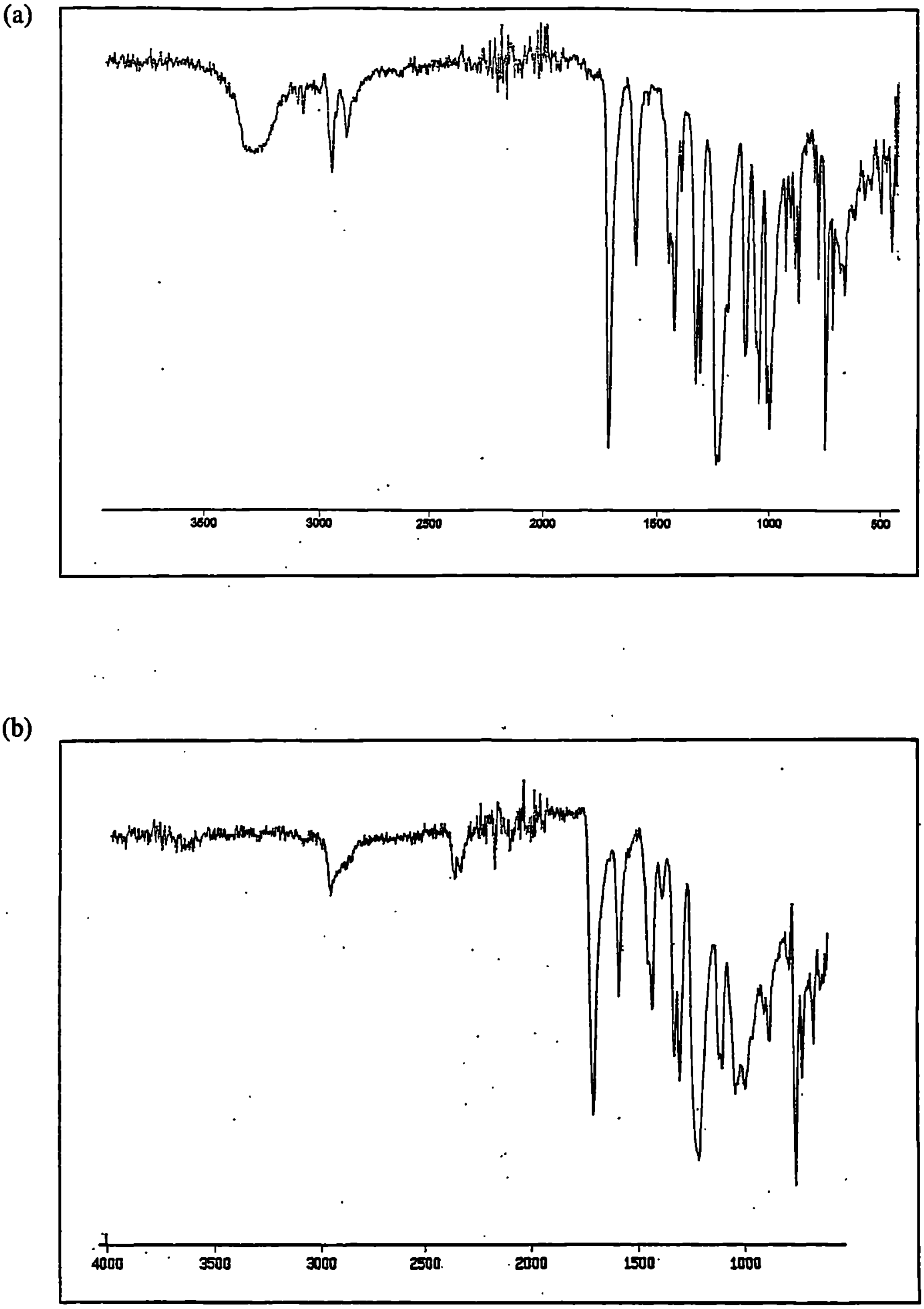


Figure 5.5.1:

Infrared spectrum of (a) the AB_2 monomer dimethyl 5-(3-hydroxypropoxy)isophthalate and (b) the hyperbranched poly(dimethyl 5-(3-hydroxypropoxy)isophthalate)

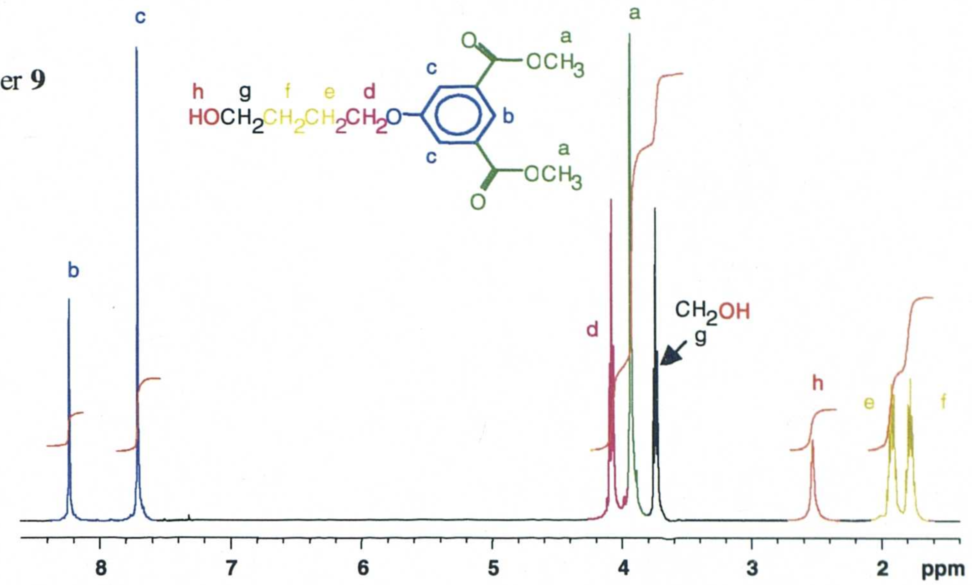
5.5.3 ^{1}H and ^{13}C nuclear magnetic resonance (nmr) spectroscopic analysis of hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s

^{1}H and ^{13}C nmr spectroscopic analysis was consistent with the formation of polymer for the hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s. The peaks in both ^{1}H and ^{13}C nmr spectra can be readily assigned with reference to the monomer spectra. Representative ^{1}H and ^{13}C nmr spectra for each of the hyperbranched polyesters, **12**, **13**, **14** and **15**, are recorded in Appendix 3.

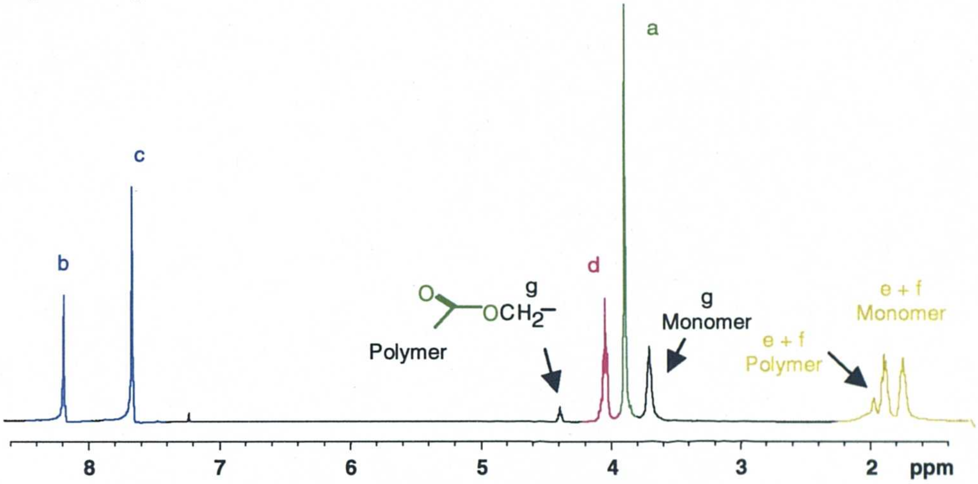
The broad nature of the peaks in the ^{1}H nmr spectra is characteristic of polymeric materials due to overlapping resonances from protons in very similar, but unique environments. The peaks in the ^{13}C nmr spectra show only slight broadening and in some cases reveal a degree of fine structure arising from the linear, branched, and terminal monomer residue units within the polymer, this matter will be discussed in more detail in Section 5.6.

^{1}H Nmr spectroscopy can be used to monitor the progression of the reaction. The chemical shift of the CH_2 protons bonded to the hydroxyl group in the monomer changes from ~δ3.8 ppm to ~δ4.5 ppm in the polymer, where they are bonded to an aryl ester. This is illustrated in Figure 5.5.2 which compares the ^{1}H nmr spectrum obtained for the AB_2 dimethyl 5-(4-hydroxybutoxy)isophthalate monomer, **9**, with that of the corresponding hyperbranched polymers **13a,** obtained after 2 hours reaction time, and **13b**, obtained after 8 hours reaction time.

c) AB$_2$ monomer **9**



b) Polymer **13a** [2 hours]



a) Polymer **13b** [8 hours]

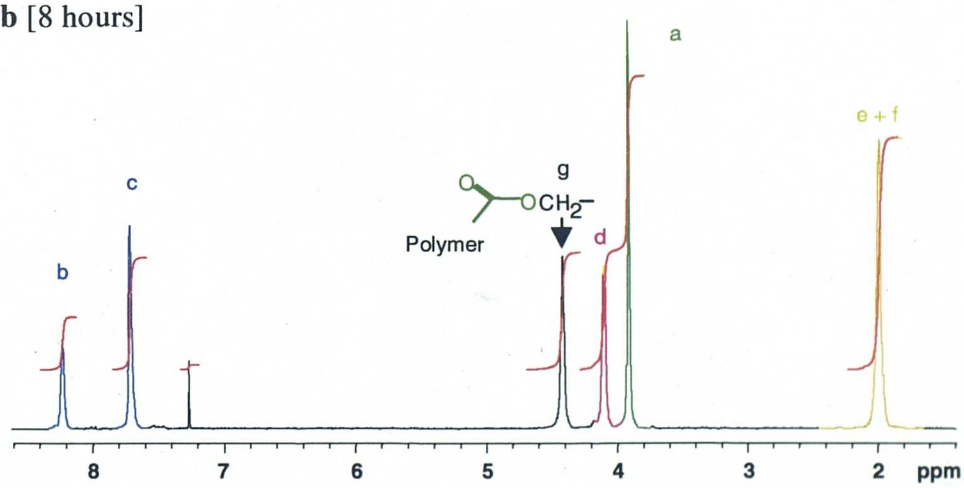


Figure 5.5.2: Change in the ^{1}H nmr spectrum with reaction time for the hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophthalate)

5.6 Determination of the degree of branching in hyperbranched polymers

5.6.1 Introduction

Since the first reports describing the preparation and characterisation of hyperbranched polymers, the determination of the degree of branching in these three dimensional, randomly branched structures has been an ongoing feature in hyperbranched polymer science. The amount of branching in a polymer is directly related to the relative abundance of the four different monomer residue units located within the structure, as highlighted in Figure 5.6.1 below.

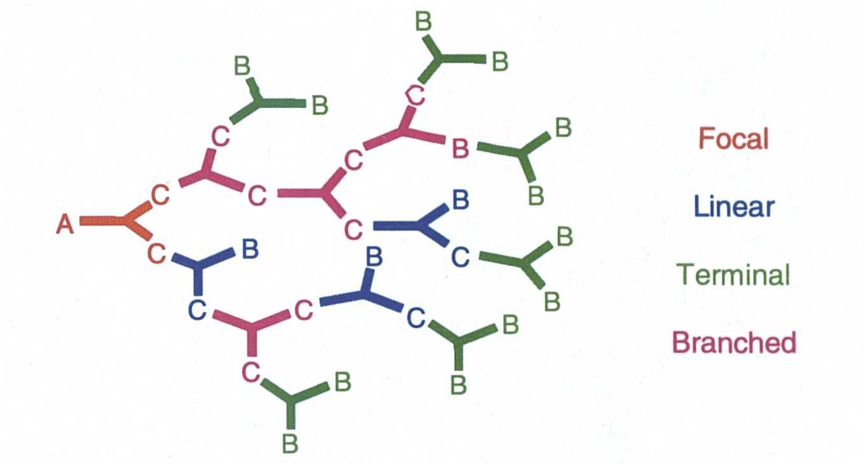


Figure 5.6.1: The four types of units present within a hyperbranched polymer.

The concept of the degree of branching (DB) was introduced by Fréchet[35] in order to define hyperbranched polymers better and to allow their comparison with dendritic and linear polymers. The degree of branching was defined as the ratio of the sum of branched and terminal units, to the total number of repeat units, and is shown in Equation 5.8 overleaf:

$$DB = \frac{N_B + N_T}{N_B + N_L + N_T} \qquad \text{Equation 5.8}$$

where N_B, N_L and N_T refer to the number of branched, linear and terminal units located in the hyperbranched polymer respectively.

However, this term was reconsidered by Frey *et al*[36] whose calculations take into account that unreacted monomer units have terminal groups and hence, under Fréchet's definition contribute towards the number of terminal units resulting in misleading values for the degree of branching. Their new definition is shown in Equation 5.9.

$$DB = \frac{2N_B}{2N_B + N_L} \qquad \text{Equation 5.9}$$

Using this equation, a linear polymer would have a degree of branching equal to zero (containing no branched units), whilst perfectly branched dendritic polymers would have a degree of branching equal to one (containing no linear units). Hyperbranched polymers are expected to have a degree of branching between zero and one depending on the proportion of linear units present in the polymer structure. Although it is theoretically possible to form hyperbranched structures which resemble those of linear polymers or of dendrimers, Frey and co-workers have shown in their theoretical treatment of an AB_2 polymerisation that the expected degree of branching for a hyperbranched polymer, with a statistical distribution of the different units, is 0.5.

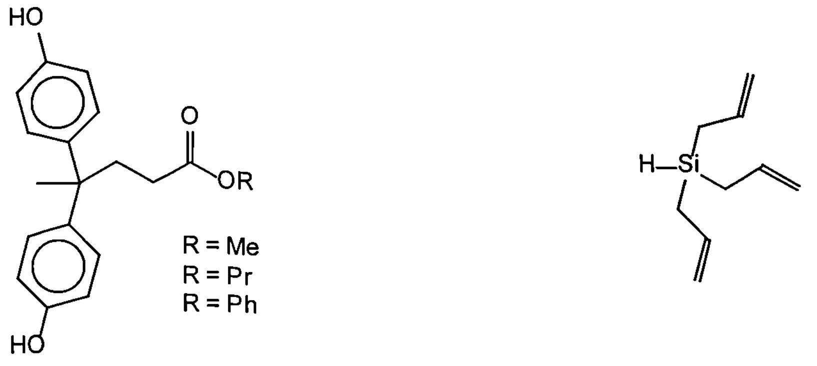
Since it has been demonstrated that the differences in architecture between linear and dendritic polymers result in differing physical properties of these materials, it is thought that large variations in physical properties could exist for hyperbranched polymers with varying degrees of branching. It is postulated that hyperbranched polymers with low degrees of branching would be expected to have physical properties similar to those of linear polymers, and similarly hyperbranched polymers with degrees of branching closer to one would be expected to have physical properties similar to those of dendritic polymers. Consequently, determination and manipulation of the degree of branching in hyperbranched structures is important in order to understand both the effect of branching on the polymer properties, and to devise methods for manipulating the degree of branching in an effort to control these properties in the future.

The development of techniques to determine the degree of branching in hyperbranched polymers has greatly facilitated the structural characterisation of these materials. The degree of branching in most cases is determined using nmr spectroscopy, where the different units present in the macromolecule possess different chemical shifts. Integration of these peaks allows the relative percentage of each unit to be determined and hence the degree of branching can be calculated. A combination of ^{1}H, ^{13}C and ^{19}F nmr spectroscopy have been used in numerous cases to determine the degree of branching in hyperbranched macromolecules, typical values ranging from 0.5 to 0.7.[35, 37]

However, in a number of hyperbranched systems degrees of branching cannot be obtained using nmr spectroscopy due to either broadness and lack of resolution of the relevant peaks, or the absence of any significant differences in the chemical shifts for the different units. Therefore Kambouris and Hawker[38] have devised an alternative technique which does not rely on spectroscopic methods. This method involves chemical modification of the end groups followed by cleavages of the bonds between the repeat units to produce 'monomer-like' fragments. By determining the relative percentages of the different 'monomer-like' fragments the degree of branching can be calculated. The degradation reaction must be highly selective to retain the distinct units of the hyperbranched structure. This technique has been used to determine the degree of branching in hyperbranched polyesters[38] (DB = 0.49) and hyperbranched polycarbonates[39] (DB = 0.53).

Attempts to vary the degree of branching by changing the polymerisation conditions, and by minor changes in the monomer structure met with little success. For example, the hyperbranched aromatic polyester prepared from 3, 5-bis(trimethylsiloxy)benzoyl chloride, was found to have a degree of branching between 0.55-0.6 regardless of the temperature of reaction, the catalyst used, or the presence of a solvent.[40] In Hawker's[6] study of the effect of monomer structure and catalyst on the degree of branching of hyperbranched polyesters, based on 4, 4(4'–hydroxyphenyl) pentanoic acid, the nature of the ester group and catalyst were found to have no effect on the degree of branching for these materials, with values obtained between 0.46-0.51.

Recently however Frey and co-workers[36] have studied the degree of branching in hyperbranched systems extensively, with both theoretical and experimental work reported. Frey and co-workers derived expressions to describe the degree of branching in AB_2 (Equation 5.9), AB_3 and AB_m systems (where $m \geq 2$), and concluded that the maximum value for the degree of branching achievable in a statistical AB_2-type polymerisation is 0.5 (independent of the presence of a core molecule), and in an AB_3 system 0.44. Such findings have already been confirmed experimentally, for example degrees of branching between 0.46 and 0.51 were reported for AB_2 type hyperbranched polyesters prepared by Hawker, while a degree of branching of 0.48 ± 0.05 was obtained for the AB_3 based hyperbranched polycarbosilanes prepared by Frey,[41] see Figure 5.6.2 overleaf.



AB_2 monomer used to prepare hyperbranched polyesters with a DB = 0.46 -0.51

AB_3 monomer used to prepare hyperbranched polycarbosilanes with a DB = 0.44

Figure 5.6.2: Examples of degrees of branching obtained for AB_2 and AB_3 based polymers

Frey and coworkers have continued their investigations of the degree of branching in hyperbranched macromolecules by examining techniques which enhance the degree of branching.[42, 43] Three techniques were outlined which will theoretically enhance the DB:

(1) Different reactivities of linear and terminal units.

(2) Use of prefabricated dendrons for the synthesis of hyperbranched polymers.

(3) Slow AB_m monomer addition to B_f core molecules in solution ("core-dilution/slow addition technique").

To date no systematic studies of slow AB_m monomer addition have been reported, although it appeared that Malmstrom and Hult's[44] stepwise addition of discrete amounts of AB_2 monomers to a polyfunctional core (B_f) enhanced the degree of branching as expected; however, the high degrees of branching (DB = 0.8) claimed have since been corrected to ≤ 0.5.[45] Frey and co-workers have confirmed this theoretical result using a computer simulation of slow AB_m monomer addition to B_f core molecules in solution. This work showed that the "core-dilution/slow addition technique" leads to higher degrees of branching than the random one-pot polymerisation,[43] hence for an AB_2 based hyperbranched polymer a degree of branching of 0.67 was predicted.

Chu and Hawker[46] have already demonstrated the use of prefabricated dendrons for the synthesis of their hyperbranched poly(ether-ketones). In this work Chu and Hawker successfully manipulated the degree of branching in hyperbranched polymers by the deliberate insertion of either a dendritic or linear fragment into an AB_2 monomer, to produce an AB_4 or AB_3 monomer respectively. Polymerisation of the AB_2 monomer 3, 5-difluro-4'-hydroxybenzophenone yields the hyperbranched poly(ether ketone), which was shown by ^{19}F nmr to have a degree of branching of 0.5. Modification of the AB_2 monomer by insertion of a dendritic fragment leads to an AB_4 monomer, in which the presence of a pre-existing dendritic fragment in the monomer unit effectively enhances branching during polymerisation. In this case a hyperbranched poly(ether ketone) with a degree of branching of 0.72 was obtained. Conversely, in the polymerisation of the AB_3 monomer, the introduction of a linear fragment in the monomer effectively lowers the degree of branching in the resulting hyperbranched poly(ether ketone), which displayed a degree of branching of 0.39.

Frey[47] recently demonstrated a universal method for enhancing the degree of branching of hyperbranched structures by postsynthetic modification, see Figure 5.6.3. After formation of the hyperbranched structure, a B-protected molecule Ab_m is added to the reaction mixture, which leads to complete or nearly complete consumption of B groups. Subsequent deprotection of the terminal b groups ($b \rightarrow B$) leads to the modified hyperbranched polymer with a DB close to 1. This procedure has been used to prepare hyperbranched polycarbosilanes.

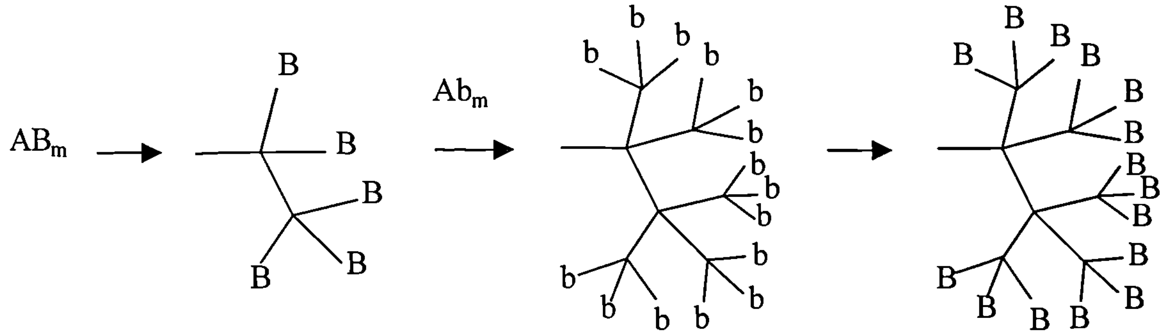


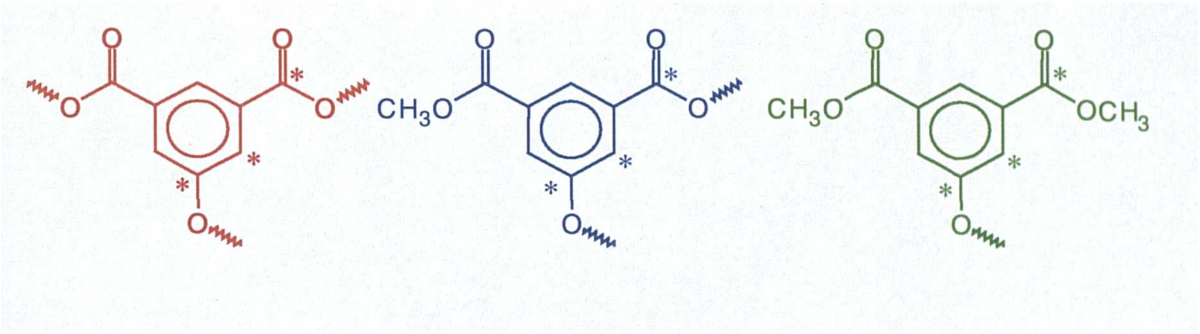
Figure 5.6.3: General concept for enhancement of the degree of branching by postsynthetic modification

Recently degrees of branching approaching one have been reported in two hyperbranched systems. Hobson *et al*[11] prepared the hyperbranched analogues of Tomalia's poly(amidoamine)dendrimers via the melt polymerisation of *N*-acryloyl-1, 2-diaminoethane hydrochloride. Using quantitative ^{15}N nmr spectroscopy, this hyperbranched system was found to have a degree of branching >0.9. Interestingly these systems were found to exhibit dendritic solution viscosity behaviour. Fomine *et al*[48] have reported for their hyperbranched coumarin-containing polymers degrees of branching equal to 1(± 5-10%). It was postulated that the high degrees of branching are due to the high temperature of the polymerisation (330°C). Under these conditions it was claimed that the high mobility of the polymer chains diminishes steric hindrances, thus promoting the complete reaction between functional groups. It should be noted that near perfect branching in AB$_m$ systems does not imply the formation of materials with a dendritic topology, since it is possible for a hyperbranched polymer with irregular growth to have a perfect branching and a DB = 1.

It can be seen from the literature that determination and manipulation of the degree of branching in hyperbranched structures is being addressed theoretically and experimentally by a number of research groups. However, for the future development of these highly branched materials, control of the degree of branching is a crucial condition for the systematic study of the physical properties of hyperbranched polymers. Therefore it is evident that more research is required before conclusive structure/property relationships can be determined for hyperbranched polymers.

5.6.2 Determination of the degree of branching in hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s, by quantitative ^{13}C nuclear magnetic resonance spectroscopy

It was anticipated that the degree of branching could be determined using quantitative ^{13}C nmr spectroscopy, since this technique had been employed successfully in the determination of DB in the analogous hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalate)s.[4] To determine DB, it is necessary to assign signals in the spectrum to those arising from terminal, linear and branched units, see Figure 5.6.4 below.



Branched Linear Terminal

Figure 5.6.4: Three different units in the hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s

Typically within a monomer residue unit there will be only one or two carbon atoms which will be influenced sufficiently by their immediate environment for the degree of branching to be calculated. In the hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s examined in this work, only the carbonyl carbon and certain aromatic carbon atoms (marked with an asterisk in Figure 5.6.1) were influenced by their surrounding environment, and since this effect was small a partially resolved multiplet was observed for the different units rather than separate peaks. Therefore a curve fitting procedure was necessary to separate the multiplet into its constituent signals (i.e. linear, branched and terminal). An example is given for polymer **12** (n = 3), in which an expansion of the ^{13}C nmr spectrum for the aromatic carbon 3 is shown in Figure 5.6.5 below.

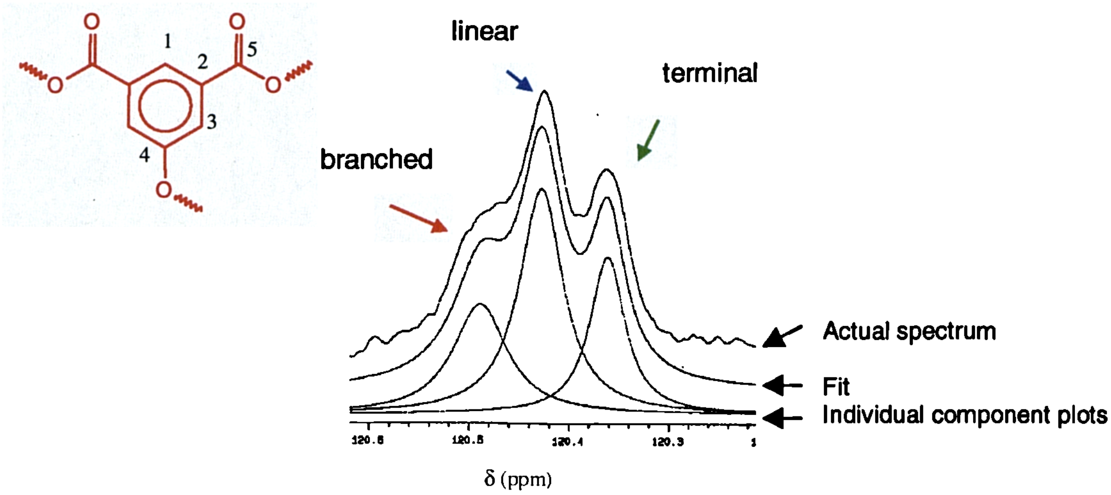


Figure 5.6.5: ^{13}C nmr expansion of the multiplet due to the aromatic carbon (3) associated with linear, terminal and branched units present in hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophthalate), and its Laurentzian deconvolution

A Laurentzian deconvolution is performed to separate the multiplet into the individual components and to allow integration of the areas beneath each of the signals. The relative integrated areas give a direct method of calculating the amount of each of the monomer residue units present in the polymer sample, thus once the peaks have been assigned to terminal, linear and branched units the degree of branching can be calculated using Equation 5.9. This analysis requires that the spectrum is recorded under quantitative conditions, that is that differences in relaxation time have no effect on the relative integrated intensities. Quantitative ^{13}C nmr spectra have been recorded using a relaxation delay of 2 and 10 seconds for the hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy) isophthalate)s. It should be noted that generally the focal unit is not observed in the ^{13}C nmr spectrum since it is present in such small amounts compared to the other units. Additionally, in the hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s the occurrence of cyclisation, identified by MALDI-TOF MS, will remove the focal unit (i.e. the focal unit has reacted and is now a branched unit).

Assignment of the different monomer units was made in a similar manner to that used for hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalate).[4] If we consider the aromatic or carbonyl carbon under consideration, when located in a terminal unit one would expect it to have a greater freedom of movement than the same carbon located in a branched unit. In terms of ^{13}C nmr spectroscopy, the relaxation time of the carbon in the terminal environment will be shorter than that of a carbon in a branched environment, hence the line width of a terminal unit will be narrower than a branched unit, with the line width of a linear unit expected to be intermediate between the two.

After investigating several nmr solvents, it was found the best resolved spectra were obtained using deuterated toluene at 95°C. For each of the hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s, where peaks which were resolved sufficiently for degrees of branching to be calculated, the line widths, integrals and degrees of branching are summarised in Table 5.6.1. The peak numbers given in Table 5.6.1 correspond to the peak number in the spectra which are recorded in Appendix 3.

Table 5.6.1: Summary of line widths, integrals and possible degrees of branching from quantative ^{13}C analysis of polymers **12** (n =3), **13** (n = 4), **14** (n = 5) and **15** (n = 6)

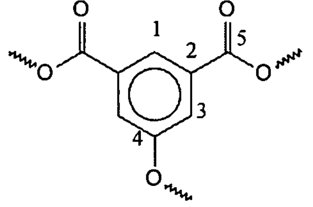
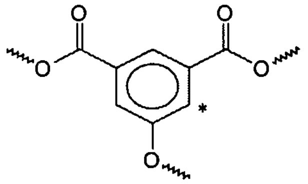
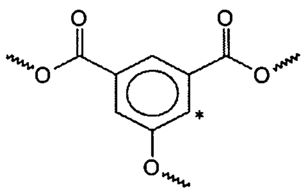
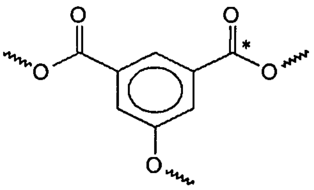
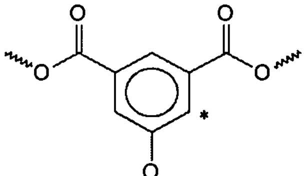
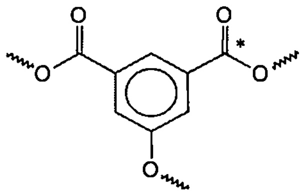
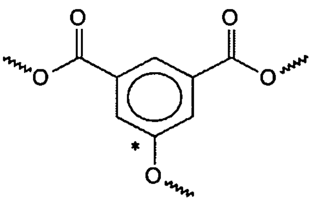
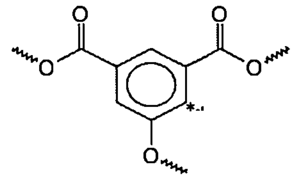
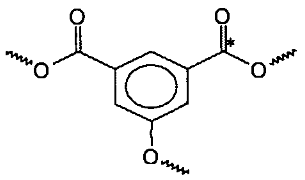
Polymer	^{13}C nmr peak assignment	Peak Number (from deconvolution, see spectra in Appendix 3)	Line Width (Hz)	Integral	DB (±5°o) with line width assignment		DB (±5°o) with integral assignment	
	 * Asterisk denotes carbon atom under consideration							
12		1	8.16	616	B			
(n = 3)		2	6.55	1015	L	0.55		
		3	5.3	574	T			
13		1	8.39	323	T		T	
(n = 4)		2	11.37	879	B		L	0.51
		3	9.49	456	L		B	
13		1	2.19	201	T		L	
(n = 4)		2	6.63	1034	B		B	0.79
		3	2.22	337	L		L	
		4	5.2	954	L		T	
14		1	6.28	582	L		T	
(n = 5)		2	5.39	701	L		L	0.47
		3	7.42	612	B		B	
		4	5.28	672	T		L	
14		1	1.7	242	T		L	
(n =5)		2	5.39	978	B		B	0.74
		3	1.81	430	L		L	
		4	3.51	824	L		T	
14		1	5.22	311	T			
(n = 5)		2	7.35	848	L	0.50		
		3	8.87	420	B			

Table 5.6.1: Continued...

Polymer	^{13}C nmr peak assignment	Peak Number (see spectra in Appendix 3)	Line Width (Hz)	Integral	DB with line width assignment		DB with integral assignment	
15 (n = 6)		1	5.47	230	T		T	
		2	6.87	510	B		L	0.53
		3	6.6	290	L		B	
15 (n = 6)		1	2.29	247	L		L	
		2	5.78	804	B		B	0.79
		3	2.26	328	T		L	
		4	4.74	778	L		T	

Although it would have been preferential to confirm that the degrees of branching were independent of the region of the spectrum from which they were calculated, this was not possible. However, all the data has been included to demonstrate that determination of the degree of branching is not a trivial problem, and, that in the case of these hyperbranched polyesters interpretation of data is difficult given the inconsistency of results.

For polymer **12** (n = 3), a DB could be determined only from one of the aromatic carbons (3), shown in Figure 5.6.5. The different units were assigned on the basis of line width obtaining a DB of 0.55, agreeing well with the expected statistical DB of 0.5. This assignment of units in this case also correlates well with the integral values, since in a hyperbranched polymer the number of terminal units is always equal to the number of branched units plus one ($N_T = N_B + 1$), therefore one would expect these peaks to have similar integrals. In the same way, where we observe 2 peaks for the linear units, these integrals should be of a similar value. In this spectrum we assume the peaks attributed to the 2 linear units are superimposed on each other thus producing one peak.

For polymer **13** (n = 4), DBs were calculated from two different regions of the ^{13}C nmr spectrum with differing results. Examining the 3 peaks obtained for the aromatic carbon (3), it is clear that assignment of the units on line width does not correlate with values obtained for the integrals, with vastly different integrals obtained for the terminal and branched units (i.e. $N_T \neq N_B + 1$). However, by assuming that the peaks for the two linear units have overlapped, but not directly on top of each other, this would produce a peak with a much larger line width than expected. We can then assign the branched unit to having the intermediate line width, and the terminal unit is still assigned the narrowest line width. Using this approach the integrals for the terminal and branched units are similar satisfying $N_T = N_B + 1$. Determination of the degree of branching on the basis of the integral values gives a DB of 0.51, again agreeing well with the expected statistical DB of 0.5.

If we consider the 4 peaks obtained for the carbonyl carbon (5) in the same polymer, we can see again that by assigning solely on line width this does not satisfy the integral constraints. Indeed, not only are the integrals for the terminal and branched units drastically different, but also those of the 2 linear units. If we assume that the terminal units are embedded in the polymer therefore restricting their mobility more than the linear units, we can then assign the intermediate line width to the terminal unit, with the two narrower line widths assigned to the 2 linear units, and the widest line width assigned to the branched unit. This assignment gives similar integrals for both the terminal and branched units, and for the 2 linear units, with a DB of 0.79 obtained. Clearly, this is much higher than the expected statistical DB of 0.5 and does not correlate with the DB determined from the carbonyl carbon peak in the same polymer (DB = 0.51).

For polymer **14** (n = 5), DBs were calculated from three different regions of the ^{13}C nmr spectrum with differing results. Examining the 4 peaks obtained for the aromatic carbon (3), it is clear that assignment of the units solely on line width again does not correlate with values obtained for the integrals. As was found for polymer **13**, integrals for the terminal and branched units and those of the 2 linear units are different. If the same assumption is made as for polymer **13**, that the terminal units are embedded in the polymer thus restricting their mobility more than the linear units, and we assign the units as before, a DB of 0.47 is obtained.

However, if we consider the 4 peaks obtained for the carbonyl carbon (5) we can see that by assigning solely on line width again does not satisfy the integral constraints. In fact, we observe a very similar pattern to that found for the same carbonyl carbon in polymer **13** (n = 4). Therefore we have made the same assumption as before, that the terminal units are embedded in the polymer therefore restricting their mobility more than the linear units, and we have assigned the units correspondingly and obtained a DB of 0.74. A much higher DB is obtained than the expected statistical DB of 0.5, but one that is similar to the DB obtained in polymer **13** (n = 4), from the same region of the ^{13}C nmr spectrum.

If we consider the second aromatic carbon (4), only 3 peaks are observed. The units can be assigned on the basis of line width and a DB of 0.5 is obtained. In this assignment both the line widths and the integral values correlate with each other. Here we are also making the same assumption made for polymer **12** (n = 3), that the peaks attributed to the 2 linear units are superimposed on each other thus producing one peak.

For polymer **15** (n = 6), DBs were calculated from two different regions of the ^{13}C nmr spectrum again with differing results. Examining the 3 peaks obtained for the aromatic carbon (3) it is clear that assignment of the units solely on line width does not correlate with values obtained for the integrals. The same assumptions were made for the same carbon peak in polymer **13** (n = 4), assuming that the peaks for the two linear units have overlapped but not directly on top of each other, producing a peak with a much larger line width than expected. Hence, the branched unit is then assigned as having the intermediate line width, and the terminal unit is still assigned the narrowest line width. In this way the integrals for the terminal and branched units are similar satisfying $N_T = N_B + 1$. Determination of the degree of branching on the basis of the integral values gives a DB of 0.53, again agreeing well with the expected statistical DB of 0.5 and similar to those degrees of branching obtained from the same carbon in polymers **12**, **13** and **14**.

Finally, if we consider the 4 peaks obtained for the carbonyl carbon (5) we can see that by assigning solely on line width again does not satisfy the integral constraints. In fact, we observe a very similar pattern as was found for the same carbonyl carbon in polymers **13** (n = 4) and **14** (n = 5). Therefore, we have made the same assumption as before, that the terminal units are embedded in the polymer therefore restricting their mobility more than the linear units, and we have assigned the units correspondingly obtaining a DB of 0.79. This is interesting as we have obtained a higher DB than the expected statistical DB of 0.5, but one that is similar to the DBs obtained from the same carbon in polymers **13** (n =4) and **14** (n = 5).

Overall, upon examination of the data we do find that we obtain similar DBs for the same region of the spectrum for the different hyperbranched polyesters. So for example, for polymers **12** (n = 4), **13** (n = 5) and **14** (n = 6), DBs were obtained between 0.74 and 0.79, determined from the aromatic carbon (3), and between 0.51 and 0.55, determined from the carbonyl carbon (5). Ideally one should obtain similar degrees of branching from different regions of the ^{13}C nmr spectrum for each polymer. However this has not been possible for any of the hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalates) and therefore it is difficult to confirm a degree of branching for these hyperbranched polyesters using quantitative ^{13}C nmr spectroscopy. This could be attributed partly to the technique used to determine the DB, which is subject to errors particularly in the curve fitting procedure and in the subsequent evaluation of the integrals for each peak in the multiplet, however, it appears that this technique is unsuitable for the determination of DB in this hyperbranched system. The possibility of determining the degree of branching by chemical degradation of the polymers into the different monomer residue units was investigated, however no chemical reaction was found to be selective enough to retain the difference between the units.

Intuitively the author expects that the DB for these systems will be found to be 0.5, i.e. statistical, which is consistent with all of the DBs determined from the aromatic ^{13}C nmr analyses, but inconsistent with those determined from the carbonyl resonances. Furthermore, degrees of branching close to the statistical value of 0.5 have been unambiguously determined for the analogous hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalates), where $n = 2$, thus it seems reasonable to suggest that similar DBs might be obtained in the analogous hyperbranched polyesters where $n \geq 3$, since all these polymers ($n = 2$ to 6) have been shown to display similar values of the constant a in the Mark-Houwink relationship(~0.5), which is related to the polymer configuration, i.e. where $a \leq 0.5$ this indicates a branched, compact structure for the polymer.

5.7 References

[1] Turner, S. R., Voit, B. I. and Mourey, T. H., *Macromolecules*, 1993, **26**, 4617-4623.

[2] Turner, S. R., Walter, F., Voit, B. I. and Mourey, T. H., *Macromolecules*, 1994, **27**, 1611-1616.

[3] Parker. D., *unpublished results*.

[4] Stainton, N. M., Ph.D. Thesis, University of Durham, 1994.

[5] Hamilton, L. H., Ph.D. Thesis, University of Durham, 1996.

6 Chu, F. K., Hawker, C. J., Pomery, P. J. and Hill, D. J. T., *J. Polym. Sci., Part A, Polym. Chem.*, 1997, **35**, 1627-1633.

[7] Pilati, F., "*Comprehensive Polymer Science*," Pergamon Press, Oxford, 1989, **5**, 294.

[8] Percec, V., Chu, P. W. and Kawasumi, M., *Macromolecules*, 1994, **27**, 4441-4453.

[9] Feast. W. J., Hamilton, L. M., Hobson, L. J., Rannard, S., *J. Mat. Chem.* 1998, **8(5)**, 1121.

[10] Chu, F., Hawker, C. J., Pomery, P. J. and Hill, D. J. T., *J. Poly. Sci., Part A, Polym. Chem.*, 1997, **35**, 1627.

[11] Hobson, L. J., Kenwright, A. M. and Feast, W. J., *J. Chem. Soc., Chem. Commun.*, 1997, 1877-1878.

[12] Blais, J. C., Tessier, M., Bolbach, G., Remaud, B., Rozes, L., Guittard, J., Brunot, A., Marechal, E., Tabet, J. C., *Int. J. Mass. Spectrom. and Ion Proc.*, 1995, **144**, 131.

[13] Jackson, A. J., Yates, H. T., MacDonald, W. A., Scrivens, J. H., Critchley, G., Brown, J., Deery, M. J., Jennings, K. R., Brookes, C., *J. Am. Soc. Mass Spectrom.*, 1996, **8**, 132.

[14] Hobson, L., *unpublished results.*

[15] Belu, A. M., deSimone, J. M., Linton, R. W., Lange, G. W. and Friedman, R. M., *J. Am. Soc. Mass Spectrom.*, 1996, **7**, 11.

[16] Feast. W. J., Hamilton, L. M., Rannard, S., *Polymer Bull.*, 1997, **39(3)**, 347.

[17] Martin, K., Spickermann, J., Rader, H. J., and Mullen, K., *Rapid Commun. Mass Spectrom.*, 1996, **10**, 801.

[18] Lovell. P. A., "*Comprehensive Polymer Science*," Pergamon Press, Oxford, 1989, **1**, 192.

[19] Mourey, T. H., Turner, S. R., Rubinstein, M., Fréchet, J. M. J., Hawker, C. J. and Wooley, K. L., *Macromolecules*, 1992, **25**, 2401-2406.

[20] Tomalia, D. A., Hall, M. and Wilson, L. R., *Encyclopaedia of Polymer Science and Engineering*, Wiley, 1990, 2nd Ed., **Index Vol.**, 46.

[21] Hobson, L. J. and Feast, W. J., *J. Chem. Soc., Chem. Commun.*, 1997, 2067-2068.

[22] Hobson, L. J., Kenwright, A. M. and Feast, W. J., *J. Chem. Soc., Chem. Commun.*, 1997, 1877-1878.

[23] Widmann, A. H. and Davies, G. R., *Comput. Theor. Polym. Sci.* 1998, **8**, 191-199.

[24] Kim, Y. H. and Beckerbauer, R., *Macromolecules*, 1994, **27**, 1968-1971.

[25] Wooley, K. L., Hawker, C. J., Pochan, J. M. and Fréchet, J. M. J., *Macromolecules*,1993, **26**, 1514-1519.

[26] Uhrich, K. E., Hawker, C. J., Fréchet, J. M. J. and Turner, S. R., *Macromolecules*, 1992, **25**, 4583-4587.

[27] Kumar, A. and Ramakrishnan, S., *J. Chem. Soc., Chem. Commun.*, 1993, 1453-1454.

[28] Hobson, L. J. and Feast, W. J., *personal communication.*

[29] Hawker, C. J. and Chu, F. K., *Macromolecules*, 1996, **29**, 4370-4380.

[30] Stutz, H., *J. Polm. Sci: Part B-Polym. Phy.,* 1995, **33**, 333.

[31] Wooley, K. L., Fréchet, J. M. J. and Hawker, C. J., *Polymer,* 1994, **35**, 4489-4495.

[32] Kim, Y. H. and Webster, O. W., *Macromolecules*, 1992, **25**, 5561-5572.

[33] Kricheldorf, H. R. and Lohden, G., *Macromol. Chem. Phy.*, 1995, **196**, 1839-1854.

[34] Miller, T. M., Kwock, E. W. and Neenan, T. X., *Macromolecules*, 1992, **25**, 3143.

[35] Hawker, C. J., Lee, R. and Fréchet, J. M. J., *J. Am. Chem. Soc.*, 1991, **113**, 4583-4588.

[36] Holter, D., Burgath, A. and Frey, H., *Acta Polymerica*, 1997, **48**, 30-35.

[37] Kim, Y. H. and Webster, O. W., *J. Am. Chem. Soc.*, 1990, **112**, 4592-4593.

[38] Kambouris, P. and Hawker, C. J., *J. Chem. Soc., Perkin Trans. 1*, 1993, 2717-2721.

[39] Bolton, D. H. and Wooley, K. L., *Macromolecules*, 1997, **30**, 1890-1896.

[40] Wooley, K. L., Hawker, C. J., Lee, R. and Fréchet, J. M. J., *Polymer J.*, 1994, **26**, 187-197.

[41] Lach, C., Muller, P., Frey, H. and Mulhaupt, R., *Macromol. Rapid Commun.*, 1997, **18**, 253-260.

[42] Holter, D. and Frey, H., *Acta Polymerica*, 1997, **48**, 298-309.

[43] Hanselmann, R., Holter, D. and Frey, H., *Macromolecules*, 1998, **31**, 3790-3801.

[44] Malmström, E., Johansson, M. and Hult, A., *Macromolecules*, 1995, **28**, 1698-1703.

[45] Malmström, E. and Hult, A., *PMSE Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1997, **77**, 151.

[46] Hawker, C. J. and Chu, F. K., *Macromolecules*, 1996, **29**, 4370-4380.

[47] Lach, C. and Frey, H., *Macromolecules*, 1998, **31**, 2381-2383.

[48] Fomine, S., Rivera, E., Fomina, L., Ortiz, A. and Ogawa, T., *Polymer*, 1998, **39**, 3551-3558.

CHAPTER SIX

THE SYNTHESIS AND CHARACTERISATION OF HYPERBRANCHED COPOLYESTERS AND POLYESTER BLENDS

6.0 Introduction

The aim of the work reported in this chapter was to investigate differences observed in molecular weight growth for the hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s, where the number of methylene units (n) in the alkylene chain is increased from 2 to 6. As discussed in Chapter 5, for the polymerisation of the dimethyl 5-(ω-hydroxyalkoxy)isophthalates, where the duration of the reaction was varied between 1 and 40 hours, SEC of the resulting hyperbranched polymers **12** (n = 3), **13** (n= 4), **14** (n = 5) and **15** (n = 6) showed that a plateau value for M_n and M_w was reached fairly early in the reaction, whilst in the analogous hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalate), where n = 2, the M_w continues to increase throughout the reaction. Furthermore, MALDI-TOF MS confirmed the presence of cyclised material in <u>all</u> these hyperbranched polymers (where n = 2, 3, 4, 5 and 6). After cyclisation trans-esterification is the only other mechanism by which these polymers could continue to increase in molecular weight. Trans-esterification is a well known phenomenon in linear polyesters.[1] It appears that the hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalate) continued to grow after cyclisation via a trans-esterification mechanism which was not observed for the polymers **12** (n = 3), **13** (n = 4), **14** (n = 5) and **15** (n = 6). It is not easy to understand why trans–esterification is observed in the n = 2 case and not where n = 3, 4, 5 and 6. However, it was postulated that as the length of the alkylene chain is increased the inherent increase in mobility of the polymer structure is the factor which inhibits trans-esterification. In an attempt to investigate this hypothesis studies have been carried out where pairs of selected hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s, from n = 2, 3, 4, 5 and 6, have been blended in the melt and the resulting materials analysed to determine if trans-esterification had occurred in these systems. In addition, the corresponding hyperbranched copolyesters were prepared from the appropriate pair of dimethyl 5-(ω-hydroxyalkoxy)isophthalate monomers, it was anticipated that these materials would provide analytical data similar to that which would be expected in the hyperbranched polymer blends where substantial trans-esterification had occurred, therefore making a useful comparison with the results obtained from the blending studies.

This chapter describes the synthesis and characterisation of these hyperbranched copolyesters and polyester blends. Only polymer samples, which appeared from their MALDI-TOF mass spectra to be cyclised, were used in the blending studies. This ensured that trans-esterification was the only mechanism available to the polymer to continue growing. The DSC and MALDI-TOF MS results provide valuable information regarding the occurrence of trans-esterification in these systems and will be discussed in detail in Section 6.2.

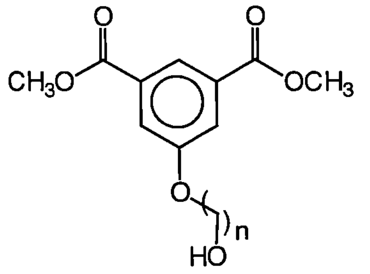
6.1 Preparation of hyperbranched copolyesters and polymer blends

6.1.1 Synthesis of hyperbranched copolyesters derived from the AB_2 dimethyl 5-(ω-hydroxyalkoxy)isophthalate monomers

The AB_2 dimethyl 5-(ω-hydroxyalkoxy)isophthalate monomers containing between 2 and 6 methylene units in the alkylene chain were used in this study.[2]

The copolyesters were prepared from two of the AB_2 monomers (1:1 molar equivalents) with the total mass of the two monomers at ~4g. The general polymerisation procedure described in Section 3.1 was used to prepare the hyperbranched copolyesters using titanium butoxide as the catalyst at 0.1 weight %. A reaction temperature of 210°C was maintained for 25 hours. The copolyesters prepared are shown below, **CP 16-22**.

The range of hyperbranched copolyesters prepared from AB_2 dimethyl 5-(ω-hydroxyalkoxy)isophthalate monomers:



n = 2/3: Hyperbranched copolyester **CP16**
n = 2/4: Hyperbranched copolyester **CP17**
n = 2/5: Hyperbranched copolyester **CP18**
n = 2/6: Hyperbranched copolyester **CP19**
n = 4/3: Hyperbranched copolyester **CP20**
n = 4/5: Hyperbranched copolyester **CP21**
n = 4/6: Hyperbranched copolyester **CP22**

MALDI-TOF mass spectroscopic analyses of these hyperbranched copolyesters were consistent with the formation of copolymers. MALDI- TOF mass spectra obtained for the copolyesters are discussed in more detail in Section 6.2.

Spectroscopic analyses by ^1H and ^{13}C nmr of these hyperbranched copolyesters were consistent with the formation of polymer, however no information regarding the arrangement of the different monomer units within the polymer chains was revealed.

Representative ^{1}H and ^{13}C nmr spectra for each of the copolymers (**CP16-22**) are recorded in Appendix 4.

Thermogravimetric analysis has shown the hyperbranched copolymers to be thermally stable, retaining 98% of their mass up to 320°C.

A well-defined glass transition was observed by DSC for each of the copolyesters. No melting points were detected by DSC in any of the copolymers which is consistent with the formation of amorphous polymers. Representative DSC traces for the each of the hyperbranched copolyesters are recorded in Appendix 4. The DSC results are discussed in more detail in Section 6.2.

6.1.2 Synthesis of hyperbranched polymer blends derived from the hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s

The hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s, containing between 2 and 6 methylene units in the alkylene chain (i.e. where n = 2, 3, 4, 5 and 6), were used in this blending study.[2] For the hyperbranched polymers **12** (n = 3), **13** (n= 4), **14** (n = 5) and **15** (n = 6), samples where a plateau M_w and M_n value had been reached were chosen for blend preparations (as identified by SEC using $CHCl_3$ as the solvent and calibrated using linear polystyrene). A moderately high molecular weight hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalate) sample, where n = 2, was chosen for this study (SEC: M_w = 106 000, Mn = 21 000).

The hyperbranched polymer blends were prepared from two of the hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s, (approximately 1:1 mass equivalents), with the total mass of the two polymers at ~1.5g. The individual polymers were first ground to a powder using a pestle and mortar, polymer samples were prepared by mixing a 1:1 mass ratio of two different polymers. The polymer sample, contained in the reaction vessel under a flow of nitrogen gas, was heated at a rate of 10°Cmin^{-1} to 210°C, and then held at this temperature for up to 25 hours. Although stirring of the polymer blend was attempted using a magnetic stirrer, it is thought that this had little effect due to the viscous nature of the polymers in the melt. Since the blending experiments were carried out on a smaller scale (~1.5g) compared to previous polymerisations (~4-5g), a smaller reaction vessel was used, see Figure 6.1 below.

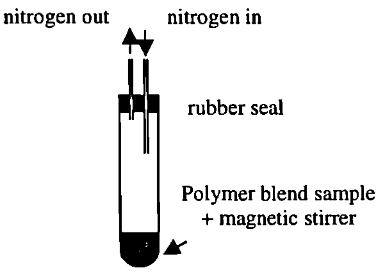
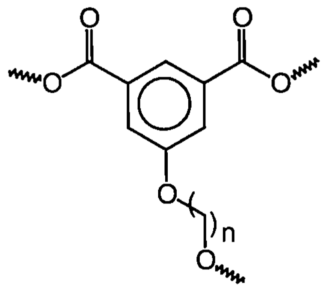


Figure 6.1: Reaction vessel used for the preparation of hyperbranched polymer blends

The polymer blends prepared are shown below, **PB16-22**.

The range of hyperbranched polymer blends prepared from the hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s:



n = 2/3: Hyperbranched polymer blend **PB16**
n = 2/4: Hyperbranched polymer blend **PB17**
n = 2/5: Hyperbranched polymer blend **PB18**
n = 2/6: Hyperbranched polymer blend **PB19**
n = 4/3: Hyperbranched polymer blend **PB20**
n = 4/5: Hyperbranched polymer blend **PB21**
n = 4/6: Hyperbranched polymer blend **PB22**

Spectroscopic analyses by ^{1}H and ^{13}C nmr of these hyperbranched polymer blends showed the presence of polymer although no information regarding the arrangement of the different monomer units within the polymer chains was revealed. Representative ^{1}H and ^{13}C nmr spectra for each of the hyperbranched polymer blends (**PB16-22**) are recorded in Appendix 4.

Glass transitions were observed by DSC for the polymer blends. No melting points were detected by DSC in any of the polymer blends confirming the presence of amorphous polymers. These DSC results are discussed in more detail in Section 6.2. Representative DSC traces for the each of the hyperbranched polymer blends (**PB16-22**) are recorded in Appendix 4.

Thermogravimetric analysis has shown all hyperbranched polymer blends to be thermally stable, retaining 98% of their mass up to 160°C, with higher temperatures obtained for the onset of decomposition for high conversion products (~320°C).

Where MALDI-TOF mass spectra were obtained, these were consistent with the presence of hyperbranched polymer and will be discussed in more detail in Section 6.2.

6.2 Structural and physical characterisation of the hyperbranched copolyesters and polymer blends

Structural and physical characterisation of the hyperbranched copolyesters and polymer blends has been conducted using DSC, MALDI-TOF MS and SEC. Experimental details for the work reported in this chapter are given in Appendix 4.

6.2.1 Differential scanning calorimetry (DSC) and matrix assisted laser desorption ionisation time of flight mass spectroscopy (MALDI-TOF MS) of the hyperbranched copolyesters and blends: results and discussion

DSC was performed on the hyperbranched copolyesters and polymer blends, the results are summarised in Table 6.1 overleaf. For comparison, the glass transition temperatures of the original homopolymers used in blend preparations have been included. Using the Fox equation (Equation 6.0), the calculated glass transition temperatures ($T_{g(calc)}$) were obtained for the polymer blends, based on the weight fractions of the original homopolymers (ω_1, ω_2) and their respective glass transition temperatures (T_{g1}, T_{g2}). This $T_{g(calc)}$ corresponds to the T_g expected for a blend prepared from two miscible homopolymers.

$$\frac{1}{T_{g(calc)}} = \frac{\omega_1}{T_{g1}} + \frac{\omega_2}{T_{g2}} \qquad \text{Equation 6.0}$$

Glass transitions were calculated for the copolyesters using the above expression, where ω_1 and ω_2 are the weight fractions of the monomers, and T_{g1} and T_{g2} are the T_gs of the corresponding homopolymers.

Table 6.1: Summary of DSC results for the hyperbranched copolyesters and blends obtained after 25 hours at 210°C [**CP16-22** and **PB16-22**]

COPOLYMER			POLYMER BLEND			
Sample	Observed T_g /°C	Calculated $T_{g(calc)}$ /°C	Sample	Homopolymer T_g /°C	Observed T_g /°C	Calculated $T_{g(calc)}$ /°C
CP16 [n = 2/3]	73	73	**PB16** [n = 2/3]	n = 2: 84 n = 3: 65	73	73
CP17 [n = 2/4]	54	62	**PB17** [n = 2/4]	n = 2: 84 n = 4: 50	80 51	63
CP18 [n = 2/5]	54	47	**PB18** [n = 2/5]	n = 2: 84 n = 5: 34	77 37	59
CP19 [n = 2/6]	47	40	**PB19** [n = 2/6]	n = 2: 84 n = 6: 28	81 31	56
CP20 [n = 4/3]	52	56	**PB20** [n = 4/3]	n = 4: 50 n = 3: 65	53	58
CP21 [n = 4/5]	38	40	**PB21** [n = 4/5]	n = 4: 50 n = 5: 34	37	42
CP22 [n = 4/6]	32	35	**PB22** [n = 4/6]	n = 4: 50 n = 6: 28	46 29	36

For the hyperbranched polymer blends **PB16-22**, samples were removed during the blending experiments after 3 and 25 hours. DSC results on these samples are given in the table below. Where two T_gs were observed the difference between the two glass transition temperatures is given in brackets.

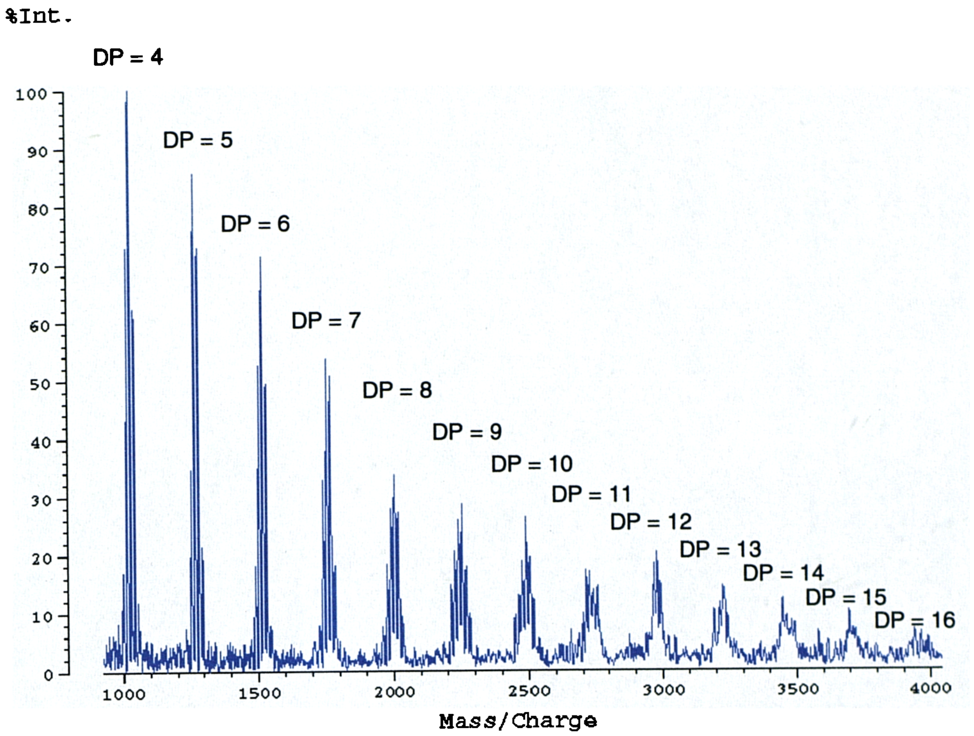
Table 6.2: Change in glass transition temperature with reaction time for hyperbranched polymer blends **PB16-22**

Sample	**PB16** [n = 2/3]	**PB17** [n = 2/4]	**PB18** [n = 2/5]	**PB19** [n = 2/6]	**PB20** [n = 4/3]	**PB21** [n = 4/5]	**PB22** [n = 4/6]
T_g /°C (@ 3 hours)	65	46 81 (35)	35 83 (48)	27 84 (57)	52	37	23 55 (32)
T_g /°C (@ 25 hours)	73	51 80 (29)	37 77 (40)	31 81 (50)	53	37	29 46 (17)

Examining the DSC results shown in Table 6.1, only one glass transition is observed for the copolymers **CP16-22**. As expected, the temperature at which this transition occurs is between the T_gs of the corresponding homopolymers. One exception is **CP17** ($n = 2/4$) which shows a T_g closer to one of the homopolymers (**13**, $n = 4$), this experiment was repeated with the same result, the author has no explanation for this surprising result. The presence of a single glass transition could indicate that two homopolymers have formed which are either miscible or have phase segregated into domains below the detection limits of DSC.[3] Alternatively the single glass transition could indicate that the different monomers have reacted and formed a copolymer. Since MALDI-TOF mass spectroscopic analyses of these polymers is consistent with the formation of hyperbranched copolymer, it is likely that the single glass transition observed in DSC is the result of the formation of copolymer.

An example of a typical MALDI-TOF mass spectrum obtained for **CP20** ($n = 3/4$) is shown in Figure 6.2 overleaf. This sample was doped with NaCl and ions were observed as their $[M+Na]^+$ species. A series of peaks were observed which correspond to low molecular weight uncyclised polymer with degrees of polymerisation (DP) between 4 and 16. Examining the spectrum in more detail, for each degree of polymerisation we observe peaks which correspond to the different ratios of the monomer units possible within the copolymer. For example, for a DP of 4 we observe 5 peaks which correspond to a 4:0, 3:1, 2:2, 1:3 and a 0:4 incorporation ratio of the two types of monomer residue units [$n = 3$: $n = 4$]. The relative intensities of the component peaks for each telomer are qualitatively as would be expected from statistical copolymer formation. However, the set of peaks for each telomer is not always complete and the data are not good enough to support quantitative analysis.

Full MALDI-TOF mass spectrum obtained for the copolymer **CP 20** (NaCl doped sample).



Expanded MALDI-TOF mass spectrum obtained for the copolymer **CP 20** (NaCl doped sample).
The ratios correspond to the ratio of the monomer residue units in the copolymer, i.e. **8**, n = 3: **9**, n = 4.
Only uncyclised polymers are observed as their Na adducts.

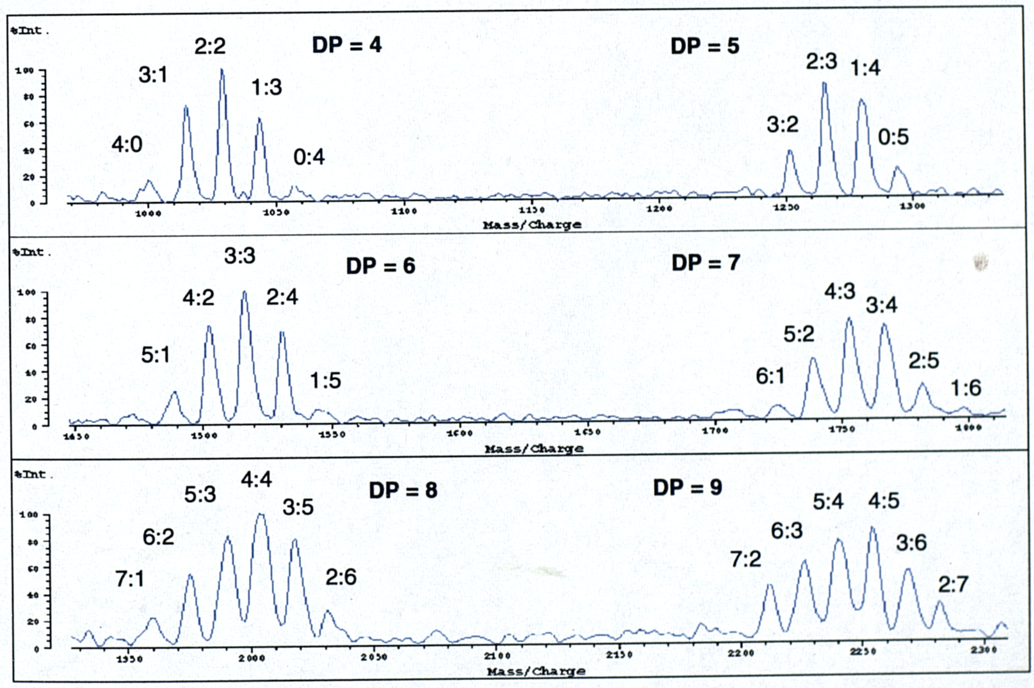


Figure 6.3: MALDI-TOF mass spectrum of the hyperbranched copolymer **CP 20**, derived from dimethyl 5-(3-hydroxypropoxy)isophthalate) and dimethyl 5-(4-hydroxybutoxy)isophthalate), after 3 hours at 210°C

Further MALDI-TOF mass spectra are provided in Appendix 4 which confirm the formation of hyperbranched copolyesters in **CP16-22**. Unfortunately no MALDI-TOF mass spectrum could be obtained for **CP19** (n = 2/5), this was surprising since clearly resolved spectra were generated for the other copolyesters.

DSC reveals differences in the thermal behaviour of the hyperbranched polymer blends **PB16-22**. Two glass transitions are observed for **PB17**, **PB18**, **PB19** and **PB22** (Table 6.1). These T_gs correspond closely to those of the original homopolymers, deviating by a maximum of 11°C. The presence of two T_gs in the polymer blends indicates that the two homopolymers are immiscible and that no appreciable reactions have occurred between the different homopolymers; at least none that can be detected using DSC. The two T_gs in each of these polymer blends appear to be converging with reaction time. This is shown clearly in Table 6.2 which shows the T_gs observed for the hyperbranched polymer blends after 3 and 25 hours at 210°C. Although this change in the T_gs indicates that a reaction is occurring between the two homopolymers, since the deviation of the T_gs from that of the original homopolymers is still only small, this suggests that this is a minor or very slow process occurring within the polymer blends.

In contrast, only one T_g is observed in the polymer blends **PB16**, **PB20** and **PB21**, indicating that either the two homopolymers are miscible and/or that a reaction has occurred between the two homopolymers to a significant extent. Where one T_g was observed in the hyperbranched polymer blends, this was found to be in close agreement with the expected T_g as calculated using the Fox equation (Equation 6.0).

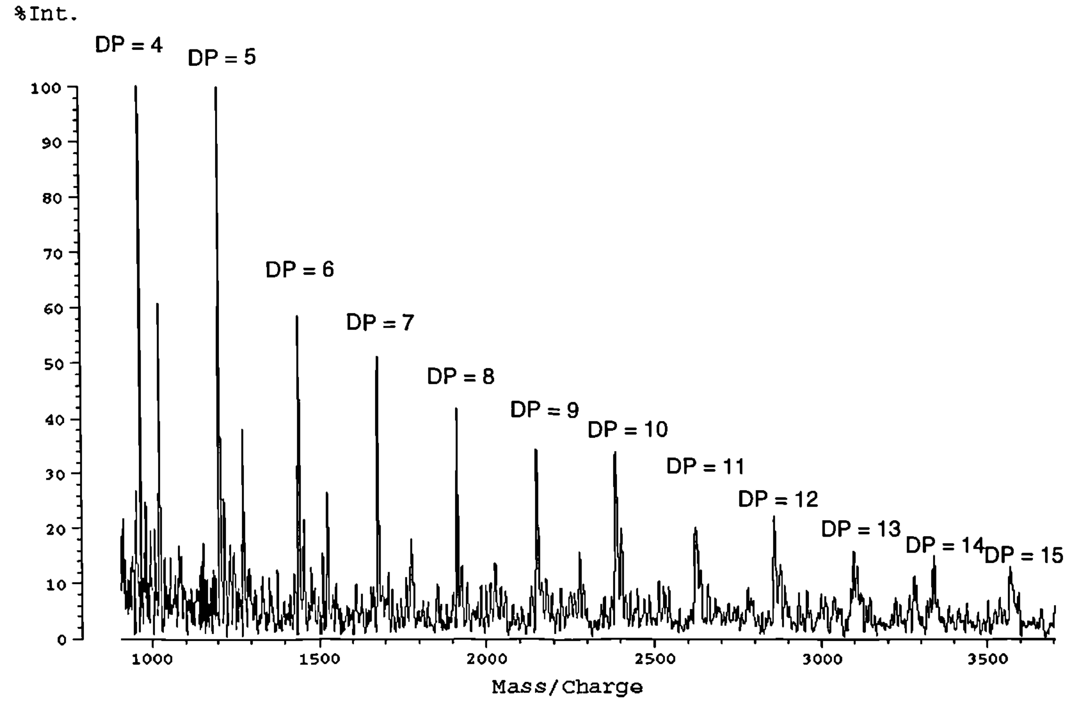
An interesting feature of these DSC results is that polymer blends prepared from two homopolymers which differ in the length of the alkylene chain by a single methylene unit (i.e. where n = 2/3, 4/3 and 4/5), appear to be miscible and hence only one T_g is observed. However, where the length of the alkylene chain varies by more than one methylene unit (i.e. where n = 2/4, 2/5, 2/6 and 4/6), the polymer blends are immiscible and two T_gs are observed. Thus it appears that the length of the alkylene chain influences the miscibility of the homopolymers in the polymer blend.

Although DSC has shown that trans-esterification occurs only to a minor extent in **PB17**, **PB18**, **PB19** and **PB22**, in which two T_gs were observed, no information can be gained regarding the occurrence of trans-esterification in **PB16**, **PB20** and **PB21** since only one T_g was observed. However further information can be extracted from the MALDI-TOF mass spectra of these hyperbranched polymer blends.

Generation of clearly resolved spectra for the polymer blends was only possible for **PB16**, **PB 19**, **PB 20** and **PB 21**. It is not known why we were unable to generate spectra for the other copolymers, whether it was due to shortcomings in experimental technique or to the nature of the polymer sample being analysed. This illustrates one of the limitations of MALDI-TOF MS in that spectra cannot be generated by a routine reliable protocol even in cases where polymers of similar structures are being analysed. In the authors experience a considerable empirical effort is sometimes required in order to generate any spectrum at all. The matrix, solution concentration, additives, drying method, laser power, location of sample on the sample holder all appear to be significant and are not always well controlled. In short, MALDI-TOF MS is an experimentally difficult technique but when good spectra are observed it is a very powerful characterisation tool.

An example of a MALDI-TOF mass spectrum obtained for **PB20** (n = 3/4) is shown in Figure 6.3 overleaf. This sample was doped with NaCl and ions were observed as their $[M+Na]^+$ species. A series of peaks were observed which correspond to low molecular weight cyclised polymer with DPs between 4 and 15. Examining the fine structure of the mass spectrum in detail, for each degree of polymerisation we observe two main peaks corresponding to the cyclised homopolymers which are separated by 14x units where x is the DP and 14 is the mass of a CH_2 unit.

Full MALDI-TOF mass spectrum obtained for the polymer blend **PB 20** (NaCl doped sample).



Expanded MALDI-TOF mass spectrum obtained for the polymer blend **PB 20** (NaCl doped sample). The ratios correspond to the ratio of the monomer residue units in the polymer blend, **9**:**10** i.e. n = 3: n = 4. Only cyclised polymers are observed as their Na adducts.

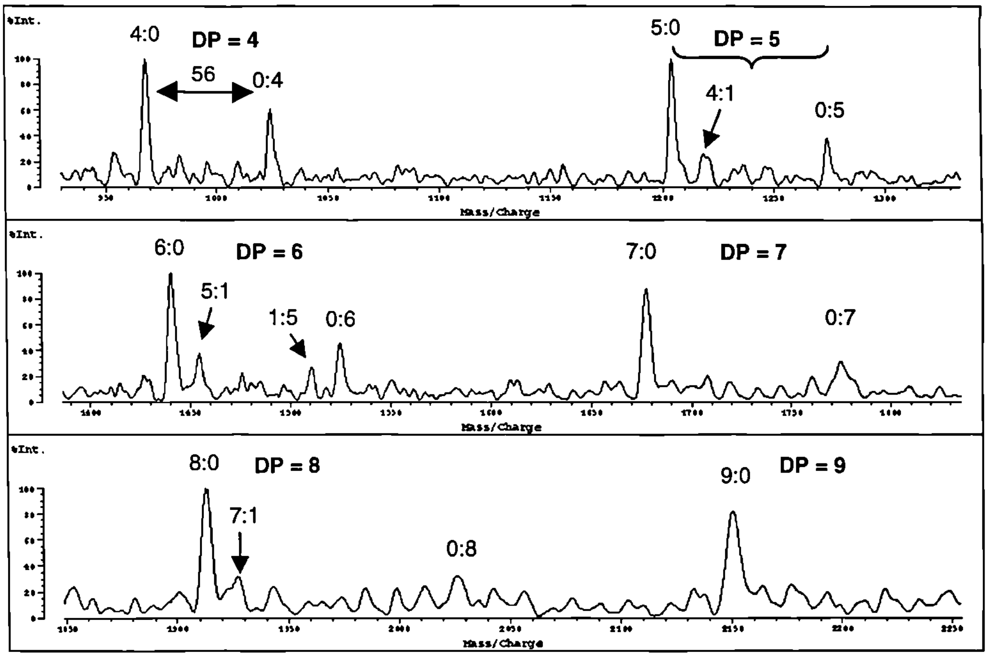
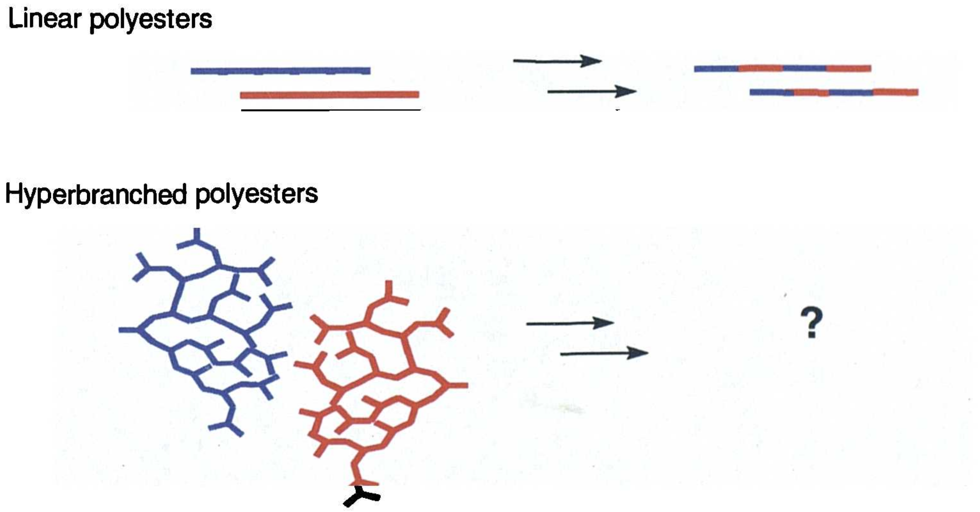


Figure 6.3: MALDI-TOF mass spectrum of the hyperbranched polymer blend **PB 20**, derived from hyperbranched poly(dimethyl 5-(3-hydroxypropoxy)isophthalate) and hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophthalate), after 25 hours at 210°C.

Between these two peaks, smaller peaks are observed which correspond to a telomer resulting from trans-esterification between the two different homopolymers. Thus for a DP of 5 we observe 3 peaks which correspond to a 5:0, 4:1, 0:5 ratio of the two monomer residue units (n = 3: n = 4), clearly the amount of trans-esterification appears to be small. Similar observations were made in the MALDI-TOF mass spectra obtained for the polymer blends **PB16** and **PB21**, which are recorded in Appendix 4. Unfortunately the assignment of peaks in the MALDI-TOF mass spectrum obtained for **PB19** (n = 2/6) is ambiguous, since peaks can be assigned more than one possible structure. For example the cyclised homopolymer (n = 2) with a DP of 7 has the same mass as a polymer blend resulting from trans-esterification between the original homopolymers to give a molecule with a 2:4 ratio of the two different monomer residue units (n = 2: n = 6), see Appendix 4 for spectra.

Since MALDI-TOF MS is not a quantitative technique with respect to relative abundance of ions, the extent of trans-esterification occurring in these systems cannot be calculated. However, the MALDI-TOF mass spectra of ***CP16-22*** have shown that copolymers can be identified easily using this technique, and that all the different copolymers possible for each degree of polymerisation can be observed. It seems reasonable to suggest that if trans-esterification was occurring in the polymer blends to a substantial degree and producing polymeric species of the same kind as those found in copolymers, then it should be possible to identify these species in the same way, using MALDI-TOF MS. However, where MALDI-TOF mass spectra were obtained for the polymer blends, the main ion series observed correspond to the cyclised homopolymers with a small number of minor peaks observed corresponding to a copolymer molecule resulting from trans-esterification of the two homopolymers. This suggests that in **PB16**, **PB 20** and **PB 21**, trans-esterification is occurring to a minor extent since only a small amount of the polymers observed in the spectra are the result of trans-esterification reactions.

By combining the results obtained from DSC and MALDI-TOF MS, it appears that although a small amount of trans-esterification is occurring in the hyperbranched polyester blends, this is not a significant process in these systems. This result supports the hypothesis that the plateau values reached for the M_n and M_w in the polymerisation of monomers **8**, **9**, **10** and **11**, is a consequence of the reluctance of the hyperbranched polymers to trans-esterify after cyclisation has occurred. For trans-esterification to occur in a polymer it is necessary for two ester groups from different molecules to come into contact. Generally in a linear polymer the ester groups are accessible and hence trans-esterification is a well-known phenomenon in linear polymers.[1] However, the three-dimensional, highly branched structures presented by hyperbranched polymers might not allow the polymer chains from different molecules to approach closely enough and with the appropriate stereochemistry for trans-esterification to occur, see Figure 6.4 below.


Linear polyesters

Hyperbranched polyesters

Figure 6.4: Illustration to show the differences in trans-esterification in linear and hyperbranched polyesters

Thus it seems reasonable to suggest that while the ester groups at the periphery of two hyperbranched polymer molecules will be able to participate in an ester-ester exchange reaction, ester groups located within the polymer are less likely to participate due to their inaccessibility. Consequently, not all the ester groups in the hyperbranched polyesters are available for intermolecular reactions and only a small degree of trans-esterification is observed in these systems.

If one considers trans-esterification in a linear system such as PET[4] which has a similar monomer structure to the AB_2 monomers used in this study, the OH end groups in PET are known to play an important role in trans-esterification; when the OH end groups of such linear polymers are capped the rate of trans-esterification is decreased. Although the exact mechanism for trans-esterification is uncertain, this feature of trans-esterification in linear PET suggests that in a cyclised hyperbranched polymer containing only methyl ester end groups, trans-esterification is less likely to occur and if occurs will be considerably slower than trans-esterification initiated by OH groups.

The occurrence of trans-esterification in these hyperbranched polymers might be related to the length of the alkylene chain in the polymer, so, for example in the hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalate) which has only two methylene units in the alkylene chain, this polymer might be expected to exhibit a stiffer structure compared with those polymers which have longer methylene sequences (**12**, **13**, **14** and **15**). This stiffness may produce a more open structure and allow the polymer chains between different molecules to come into contact with one another, allowing trans-esterification to occur in this system. As the length of the alkylene chain is increased the inherent mobility of the polymer structure might result in folding or collapsing of the polymer chain conformations within the molecule. As a consequence the chain ends may be buried within the polymer and less available for trans-esterification. Since it is the flexibility of the longer alkylene chains which will allow the polymer chains to fold, it follows that these alkylene chains will tend to reside at the surface of the polymer. The presence of these at the surface may prevent other polymer molecules from coming into contact with the ester groups and thus inhibit trans-esterification. In the case of n = 2, the alkylene chain is too short to allow this folding to occur, making the ester groups and linkages in the polymer more accessible for trans-esterification.

Further work is required in order to explain why the molecular weight in the hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalate)s continues to grow after all the polymer has cyclised. We have only prepared and analysed blends derived from the hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s. However, it would be interesting to blend these hyperbranched polymers with different polyesters, (e.g. linear polyesters) to determine if any trans-esterification is observed in these blends, and to investigate if there are any differences between the blends derived from the hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalate)s and the analogous hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s, containing more than two methylene units in the alkylene chain.

6.2.2 Size exclusion chromatography data of the hyperbranched copolyesters and polyester blends: results and discussion

SEC was a performed on the hyperbranched copolymers, **CP16-22**, and polymer blends, **PB16-22**, using chloroform as the solvent, and calibrated using linear polystyrene standards. These results were inconclusive but for the sake of completeness are summarised in Table 6.3. The plateau M_w, given in column 2, refers to the plateau M_w obtained for the hyperbranched polymers **12**, **13**, **14** and **15**, as identified by SEC and discussed in Chapter 5. The M_n and M_w of the original homopolymers used to prepare the polymer blends have been given in column 6. Due to the large polydispersities of the polymer blends no reliable information regarding the occurrence of trans-esterification can be deduced from the SEC data. SEC traces for each of the copolymers and polymer blends are recorded in Appendix 4.

A surprising feature of the SEC results is that for the copolymers and blends derived solely from monomers and polymers where the number of methylene units in the alkylene chain is greater than two, (i.e. where a plateau M_n and M_w is reached) one might have expected to obtain molecular weights between those obtained for the homopolymers. Clearly this is not the case for most of the copolymers and blends (**CP21**, **CP22**, **PB16**, **PB17**, **PB19**, **PB20**, and **PB22**). In addition, where DSC and MALDI-TOF MS data suggests that little trans esterification has occurred in the polymer blends, changes in the molecular weights for some of the polymer blends do not support this conclusion since large changes in M_w do occur (**PB16, PB17, PB19, PB20**, and **PB22**). The SEC data (Table 6.3) has been included for completeness, however the author is unable to explain these results and feels that further work is required before any useful attempt at secure interpretations of this data can be made. For example, SEC measurements for the copolymers and polymer blends at different reaction times would allow investigation of the growth of the molecular weight for these materials. Comparison of such data with that obtained for the homopolymers might be more informative than the single SEC measurements reported in Table 6.3.

Table 6.3: Summary of SEC results obtained for the hyperbranched copolymers after 25 hours at 210°C, **CP16-22,** and polymer blends after 25 hours at 210°C, **PB16-22.**

COPOLYMER				POLYMER BLEND			
1 Sample	**2** Maximum M_w	**3** M_n	**4** M_w	**5** Sample	**6** Homopolymers M_n;M_w	**7** M_n	**8** M_w
CP16 [n = 2/3]	n =3: 50 000	1600	91600	**PB16** [n = 2/3]	n = 2: 13000; 60000 n = 3: 9000; 53000	14500	77200
CP17 [n = 2/4]	n =4: 100 000	18200	131800	**PB17** [n = 2/4]	n = 2: 23000; 60000 n = 4: 21000; 106000	16900	145600
CP18 [n = 2/5]	n =5: 40 000	19300	112900	**PB18** [n = 2/5]	n = 2: 13000; 60000 n = 5: 6000; 32000	11900	53000
CP19 [n = 2/6]	n =6: 150 00	13200	78700	**PB19** [n = 2/6]	n = 2: 13000; 60000 n = 6: 28000; 153000	11700	163800
CP20 [n = 4/3]	n =4: 100 000 n =3: 50 000	18250	86300	**PB20** [n = 4/3]	n = 4: 21000; 106000 n = 3: 9000; 53000	16300	117400
CP21 [n = 4/5]	n =4: 100 000 n =5: 40 000	24000	134400	**PB21** [n = 4/5]	n = 4: 21000; 106000 n = 5: 6000; 30000	11800	60400
CP22 [n = 4/6]	n =4: 100 000 n =6: 150 000	27368	445825	**PB22** [n = 4/6]	n = 4: 21000; 106000 n = 6: 28000; 153000	12100	178000

6.3 Conclusions

To conclude, the DSC and MALDI-TOF results show that trans-esterification is a relatively unfavourable process in the hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s (**12**, **13**, **14** and **15**), this supports the hypothesis that the plateau values reached for the molecular weight (M_n and M_w) of the hyperbranched polymers is due to cyclisation and the reluctance of the polymers with more than two methylene units in the alkylene chain to trans-esterify. In addition from DSC of the hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s it appears that the miscibility of the polymers in the blends is influenced by the length of the methylene sequence in the polymer, thus, for polymer blends prepared from two homopolymers which differ in the length of the alkylene chain by a single methylene unit (i.e. where n = 2/3, 4/3 and 4/5), these appear to be miscible and hence only one T_g is observed. However, where the length of the alkylene chain varies by more than one methylene unit (i.e. where n = 2/4, 2/5, 2/6 and 4/6), these polymer blends are immiscible and two T_gs are observed.

6.4 References

[1] Pilati, F., "*Comprehensive Polymer Science*," Pergamon Press, Oxford, 1989, **5**, 294.

[2] The AB_2 dimethyl 5-(2-hydroxyethoxy)isophthalate monomer and hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalates) were obtained from Ian Anderson, the author wishes to thank Ian for allowing his materials to be used in this study.

[3] Richardson. M. J., "*Calorimetry and Thermal Analysis of Polymers*," Hanser, Munich, 1984, 180.

[4] Peace. S. K., Richards. R. W., MacDonald. W. A., presented at the 37th International Symposium on Macromolecules, Gold Coast, Australia, 12-17 July 1998.

CHAPTER SEVEN

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

7.0 Conclusions and suggestions for future work

A simple synthetic strategy has been developed which was used to prepare a range of hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalates). Dimethyl 5-(ω-hydroxyalkoxy)isophthalate AB_2 monomers, containing between 3 and 6 methylene units in the alkylene chain, have been synthesised on a scale of ≥ 75g, using simple chemistry and in reasonable yields. The hyperbranched polyesters derived from these monomers have been prepared in a simple one step condensation reaction, and materials with a range of molecular weights have been produced. The structural and physical characterisation of these materials has been carried out using a variety of analytical techniques including SEC, MALDI-TOF MS, quantitative ^{13}C nmr spectroscopy, dilution viscometry and DSC.

Although SEC using linear polystyrene standards as calibrants has been unable to provide absolute molecular weights, it has been possible to confirm that the hyperbranched materials are polydisperse. SEC of the hyperbranched polymers **12** ($n = 3$), **13** ($n= 4$), **14** ($n = 5$) and **15** ($n = 6$) showed that a plateau value for M_n and M_w was reached fairly early in the reaction, whilst in the analogous hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalate), where $n = 2$, the M_w continues to increase throughout the reaction. Furthermore, MALDI-TOF MS confirmed the presence of cyclised material in all these hyperbranched polymers (where $n = 2, 3, 4, 5$ and 6). Since after cyclisation trans-esterification is the only mechanism by which these polymers could continue to increase in molecular weight, it appeared that the hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalate) continued to grow after cyclisation via a trans-esterification mechanism, which was not observed for the polymers **12** ($n = 3$), **13** ($n = 4$), **14** ($n = 5$) and **15** ($n = 6$). Why trans-esterification was observed in the polymer where $n = 2$ and not where $n \geq 3$ is not easy to understand, however it was postulated that as the length of the alkylene chain is increased the inherent increase in mobility of the polymer structure is the factor which inhibits trans-esterification. This hypothesis was investigated by preparing a range of hyperbranched polymer blends derived from the cyclised hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalates), where n = 2, 3, 4, 5 and 6. DSC and MALDI-TOF MS of these materials showed that trans-esterification was a relatively unfavourable process in the hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s (**12**, **13**, **14** and **15**). Thus, this result supports the hypothesis that the plateau values reached for the molecular weight (M_n and M_w) of the hyperbranched polymers is due to cyclisation and the reluctance of the polymers with more than two methylene units in the alkylene chain to trans-esterify.

In this work MALDI-TOF MS was found to be an extremely useful analytical tool, identifying the presence of cyclised material in the hyperbranched polymers and in showing that the relative amount of the cyclised product, compared to the uncyclised polymer, increases with reaction time. The occurrence of a side reaction, which was otherwise undetected in the hyperbranched poly(dimethyl 5-(5-hydroxypentoxy)isophthalates), was identified and explained using MALDI-TOF MS analysis.

Although no conclusive degrees of branching could be determined using quantitative ^{13}C nmr spectroscopy for the hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalates), where n ≥ 3, a DB close to the statistical value of 0.5 was obtained for the analogous hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalate). It seems reasonable to suggest that the polymers where n ≥ 3 will have similar degrees of branching to the polymer where n = 2 (i.e. DB ~ 0.5), since solution viscometry studies have shown that all the hyperbranched polyesters, where n = 2, 3, 4, 5 and 6, display a similar value for the constant *a* in the Mark-

Houwink relationship (~ 0.5), indicating that all the polymers have a similar polymer configuration (i.e. a branched, compact structure).

Thermal analysis has shown these polymers to be amorphous with no melting points detected by DSC. The glass transition temperature of the hyperbranched polymers was found to be affected by the internal structure of the polymers, thus as the length of the methylene spacer between the branch points in the polymer was increased, the glass transition temperature was lowered. Further studies on the thermal behaviour of the hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophthalates) showed a linear relationship between the glass transition and the reciprocal molecular weight (both M_n and M_w) which is similar to the T_g/M_n relationship observed in linear polymers.

Overall, the synthesis of the hyperbranched polymers has been successful, with some very interesting results obtained whilst conducting structural and physical characterisation of these materials. However, the same problems arise in relation to characterisation of these hyperbranched polyesters, as has been recognised by the hyperbranched community in general. Thus, although we are able to probe different aspects of the hyperbranched structure using different analytical techniques, we are still unable to characterise these novel topology polymers fully, even by collating the information gained from all the different techniques used. Consequently extensive work is required before we can begin to understand the 'structure/property' relationships exhibited by these materials.

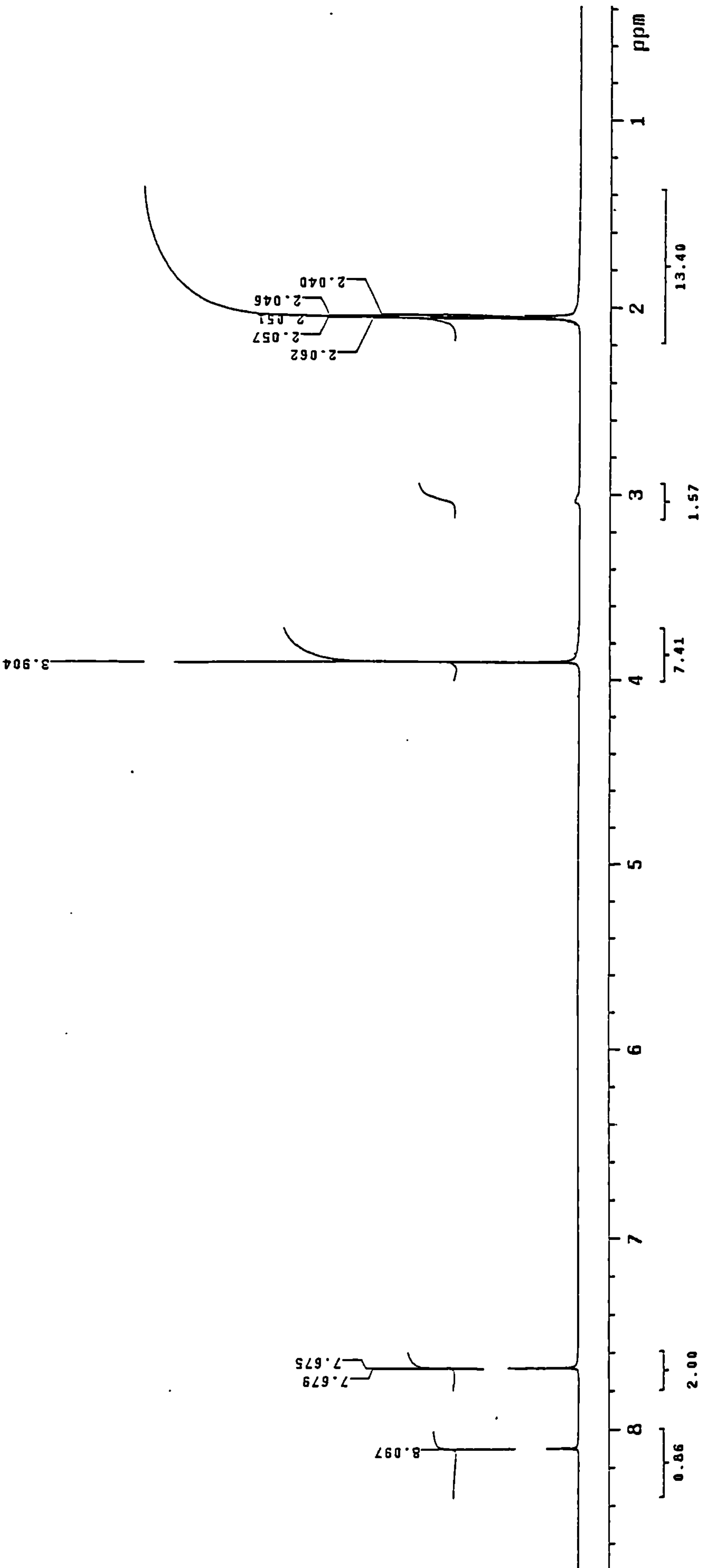
Fractionation of these hyperbranched polyesters would be an extremely valuable exercise since the molecular weight and structure of the individual fractions could be examined and compared in detail. For example, if in the future the degrees of branching for the hyperbranched polyesters could be determined unambiguously, it would be possible to investigate if there is any relationship between the molecular weight of a polymer fraction and its degree of branching.

Although we have confirmed the formation of cyclised material in the hyperbranched systems discussed in this work, the size of the cyclic is unknown. Modelling studies of these hyperbranched polyesters might be useful in predicting if cyclics of a certain size have a greater probability of forming. This information might explain the ion selectivity observed in the MALDI-TOF MS study of the hyperbranched poly(dimethyl 5-(3-hydroxypropoxy)isophthalate)s. In addition, information regarding the configuration of the hyperbranched polyesters might be gained from modelling studies to support the claim that the length of the alkylene chain is the factor which inhibits trans-esterification.

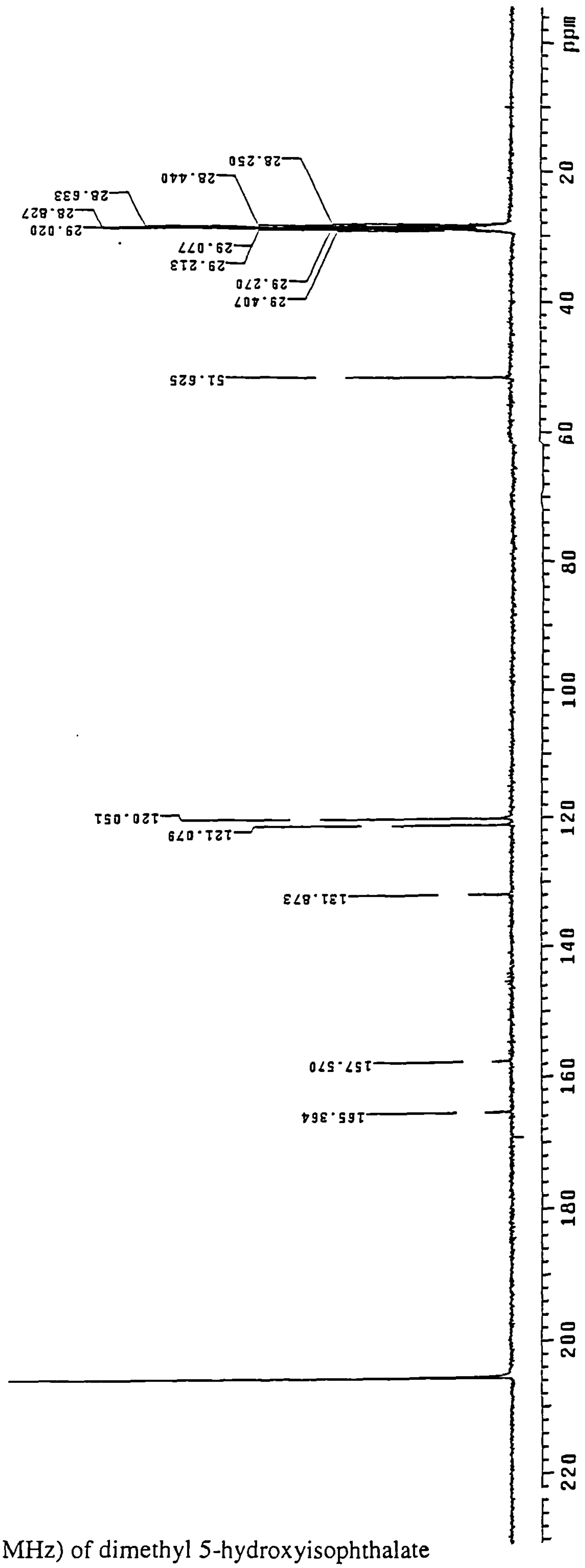
As discussed in Chapter 6, although we have shown that trans-esterification was a relatively unfavourable process in the hyperbranched poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s, (**12**, **13**, **14** and **15**), further blending studies are required in order to confirm the occurrence of trans-esterification in the hyperbranched polyester where n = 2. Since the SEC data obtained for the copolyesters and blends was inconclusive, SEC measurements for the copolymers and polymer blends at different reaction times might be useful as this would allow investigation of the growth of the molecular weight for these materials. Comparison of such data with that obtained for the homopolymers might be more informative than the single SEC measurements reported so far.

APPENDIX ONE

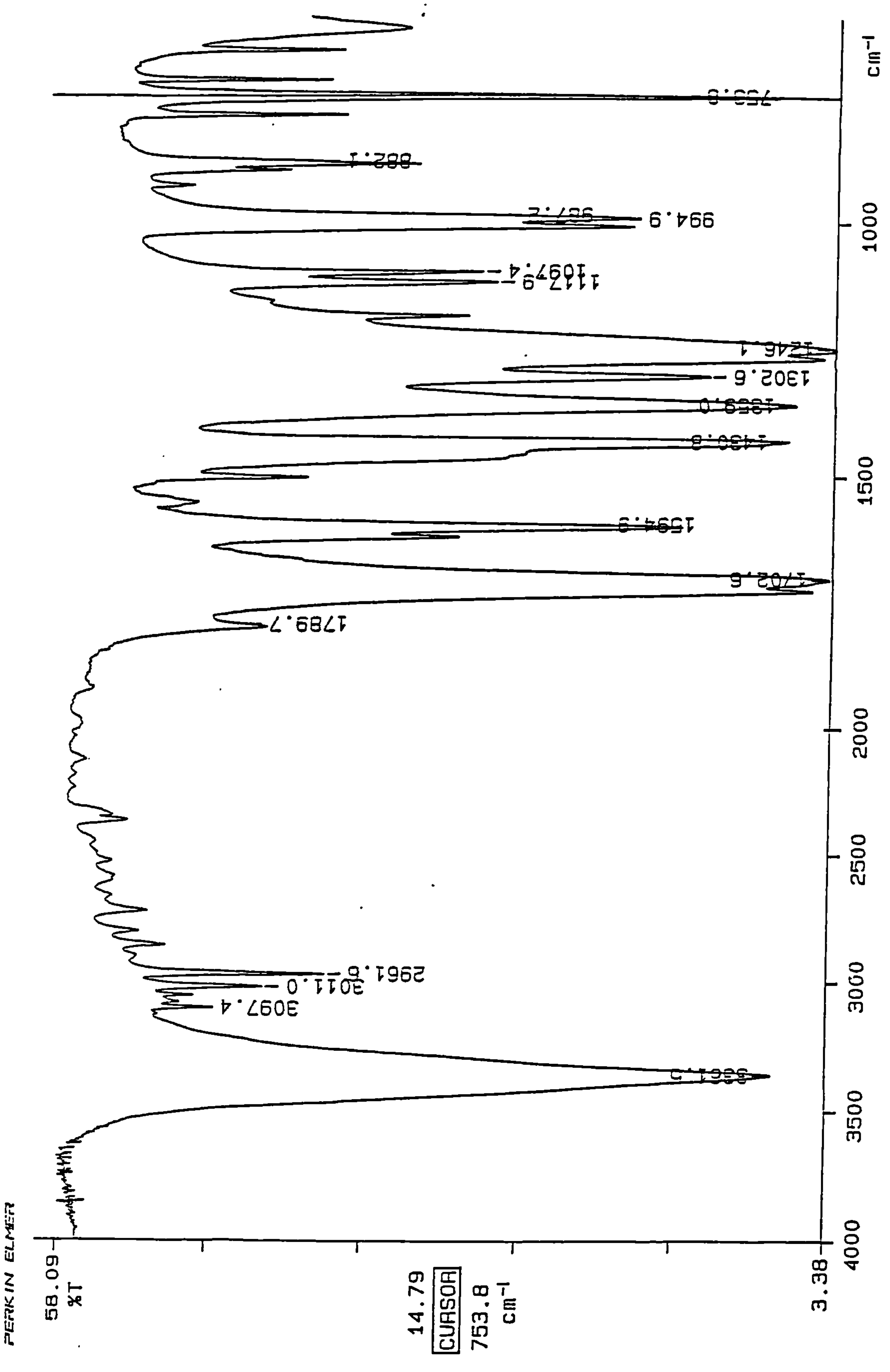
CHARACTERISATION DATA FOR CHAPTER 2



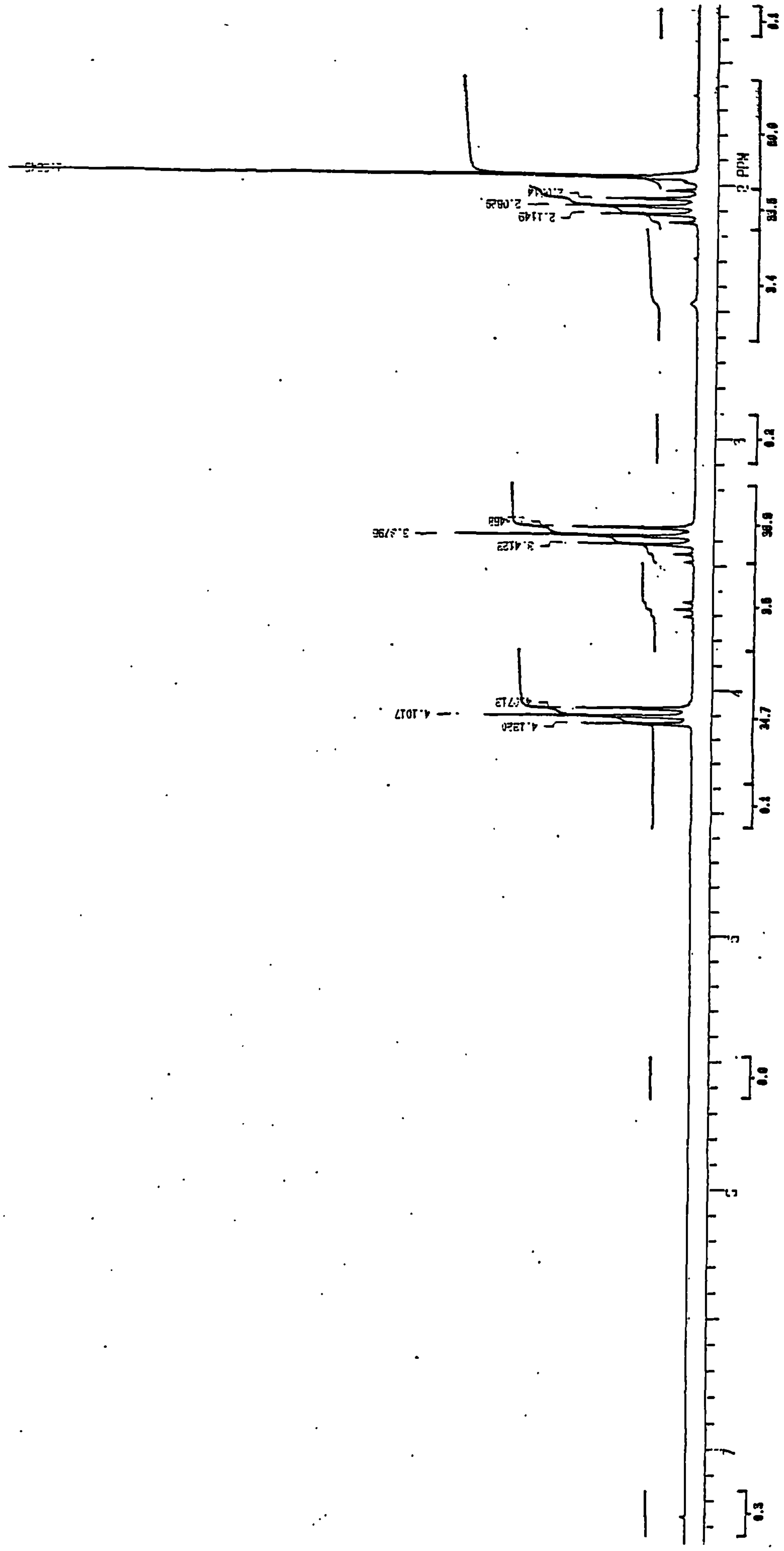
Appendix 1. 1: ^{1}H nmr spectrum (400 MHz) of dimethyl 5-hydroxyisophthalate



Appendix 1. 2: ^{13}C nmr spectrum (100 MHz) of dimethyl 5-hydroxyisophthalate

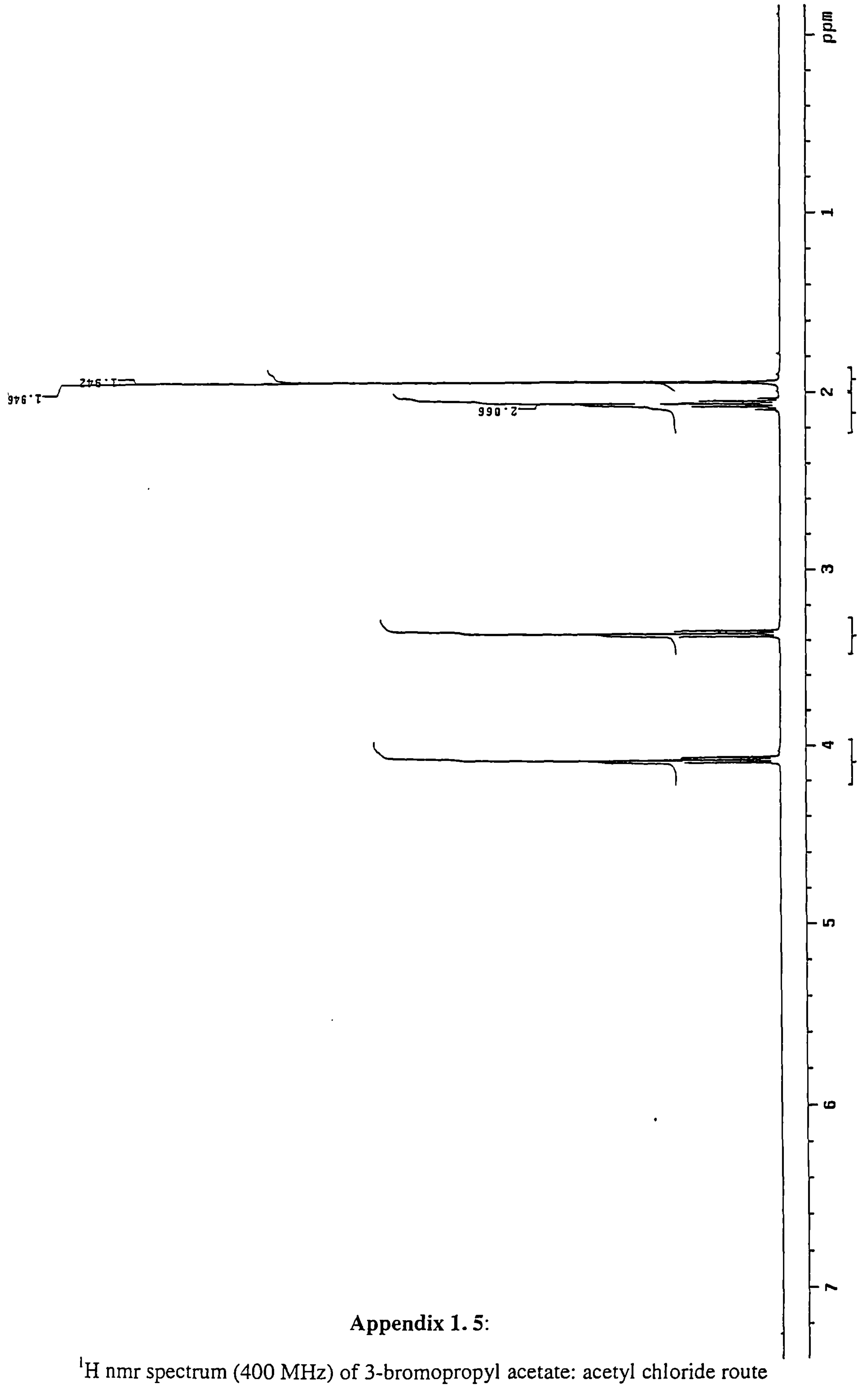


Appendix 1. 3: FTIR (KBr disc) spectrum of dimethyl 5-hydroxyisophthalate



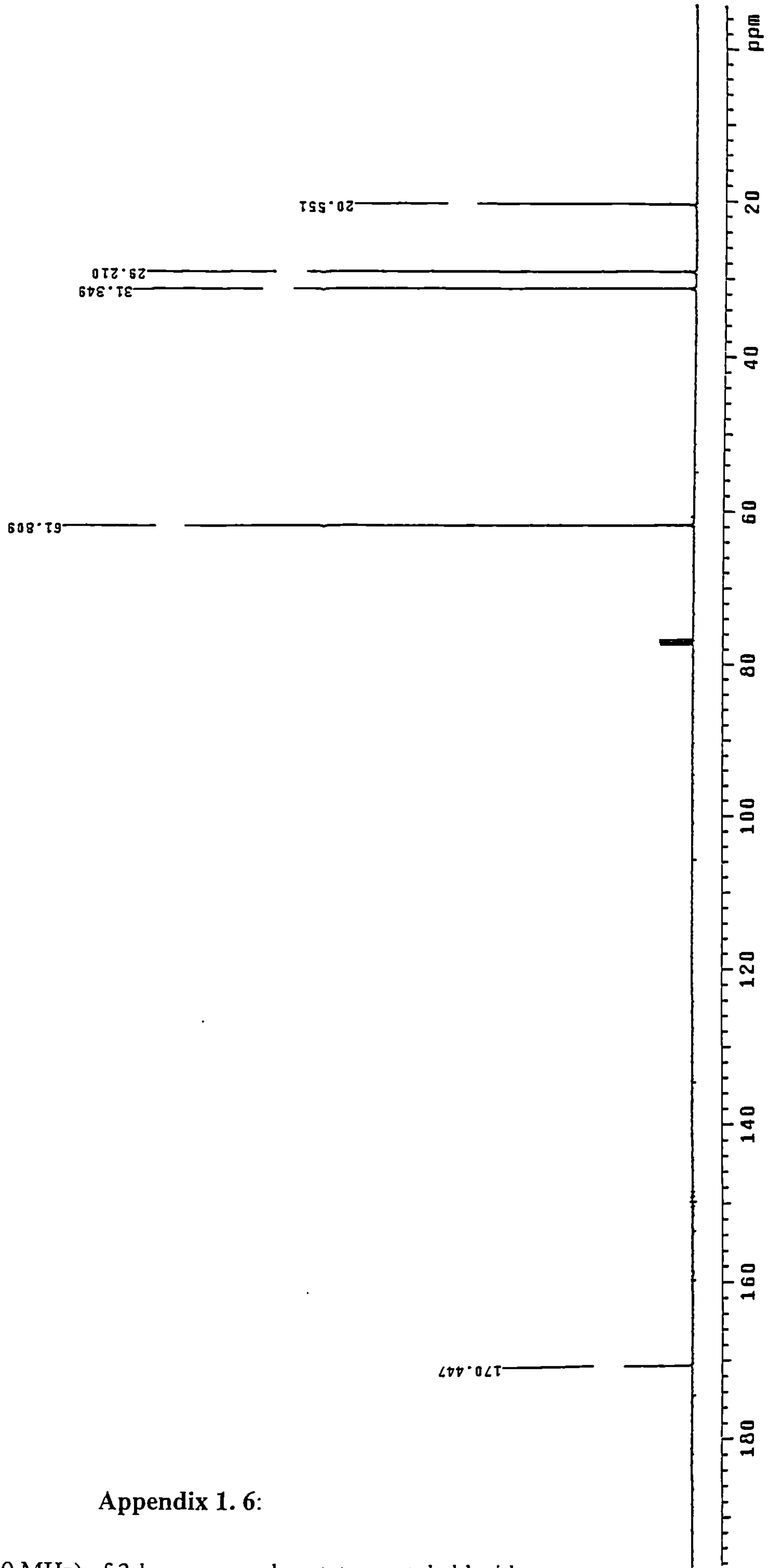
Appendix 1. 4:

^{1}H nmr spectrum (400 MHz) of 3-bromopropyl acetate: acetic anhydride route



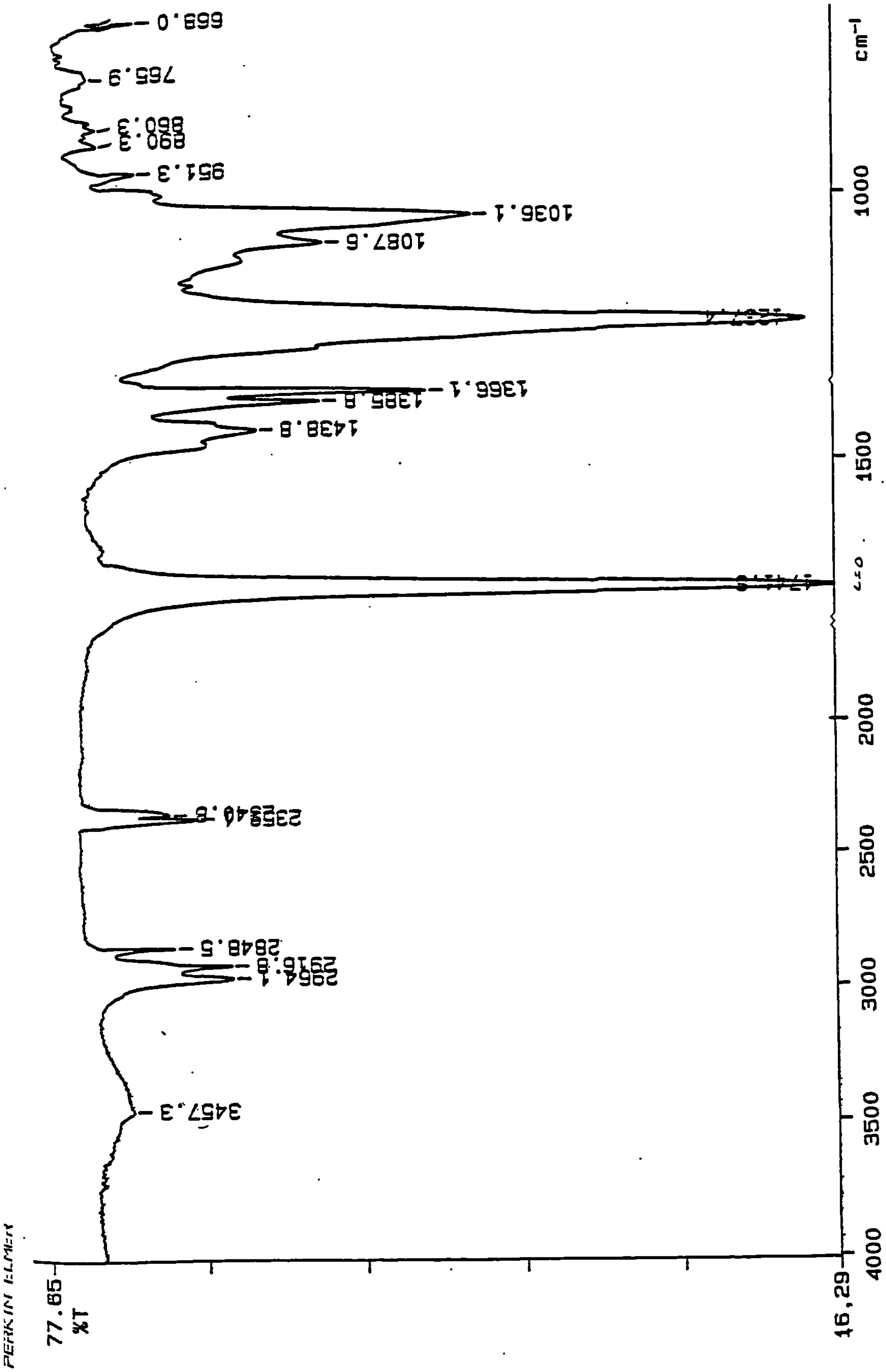
Appendix 1. 5:

^{1}H nmr spectrum (400 MHz) of 3-bromopropyl acetate: acetyl chloride route



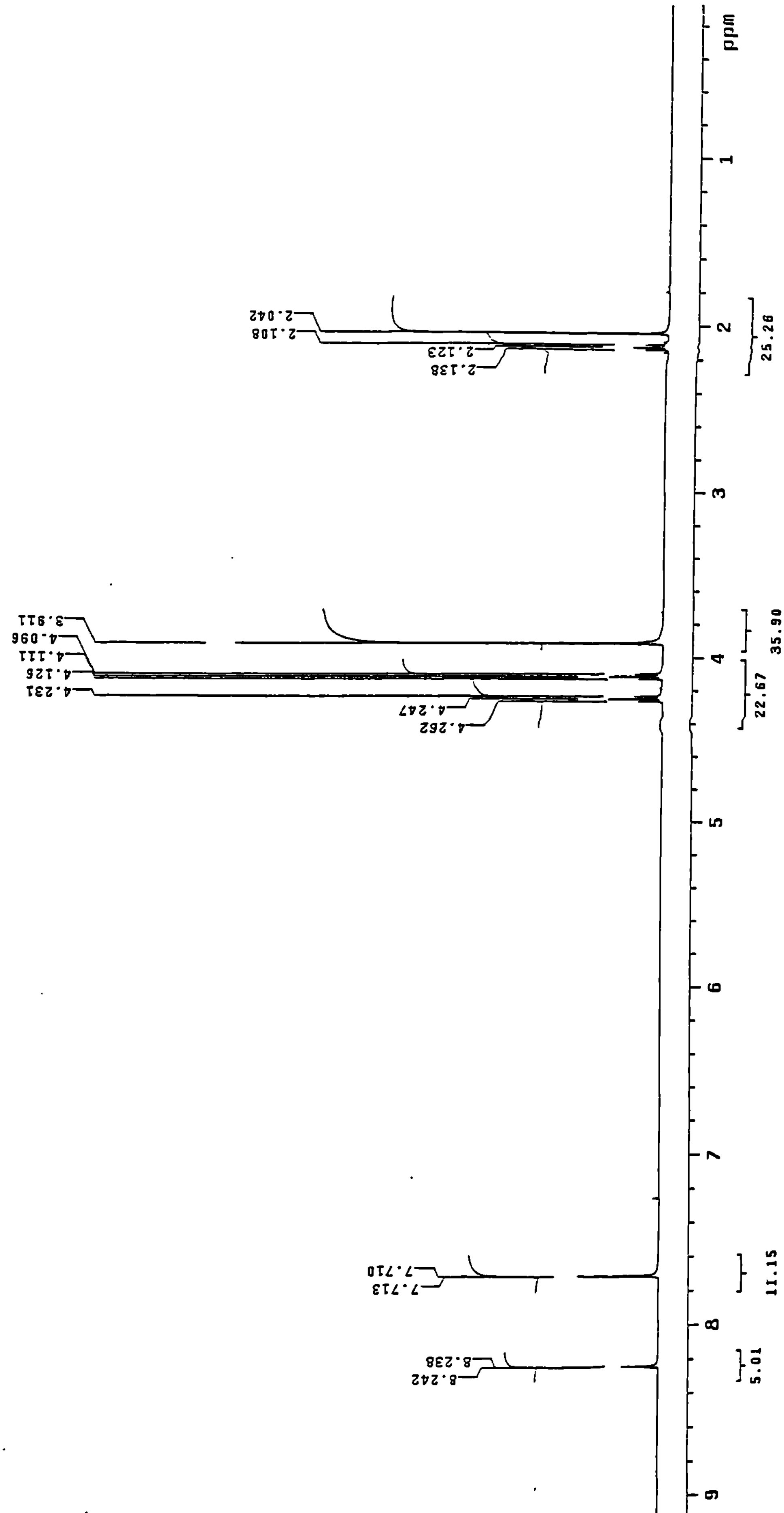
Appendix 1. 6:

^{13}C nmr spectrum (100 MHz) of 3-bromopropyl acetate: acetyl chloride route

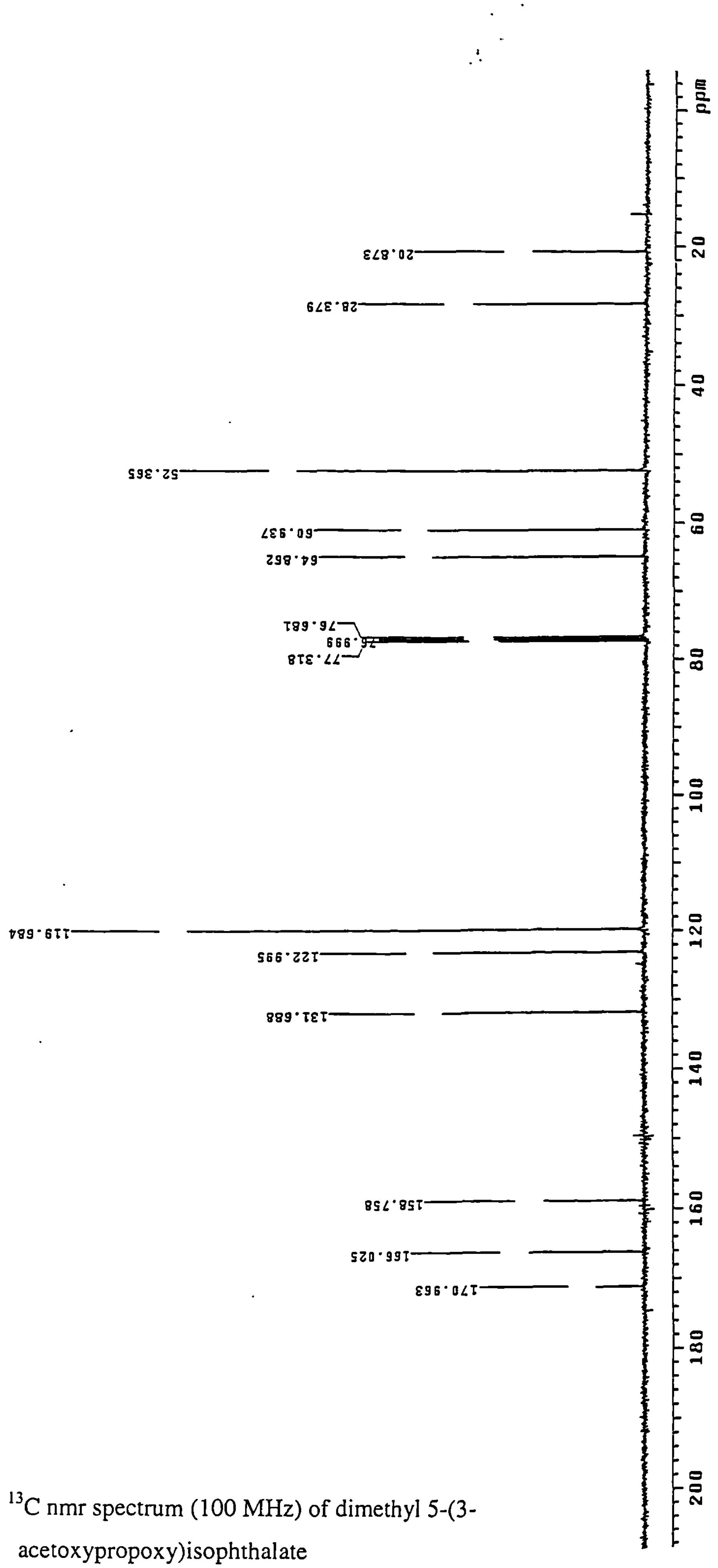


Appendix 1. 7:

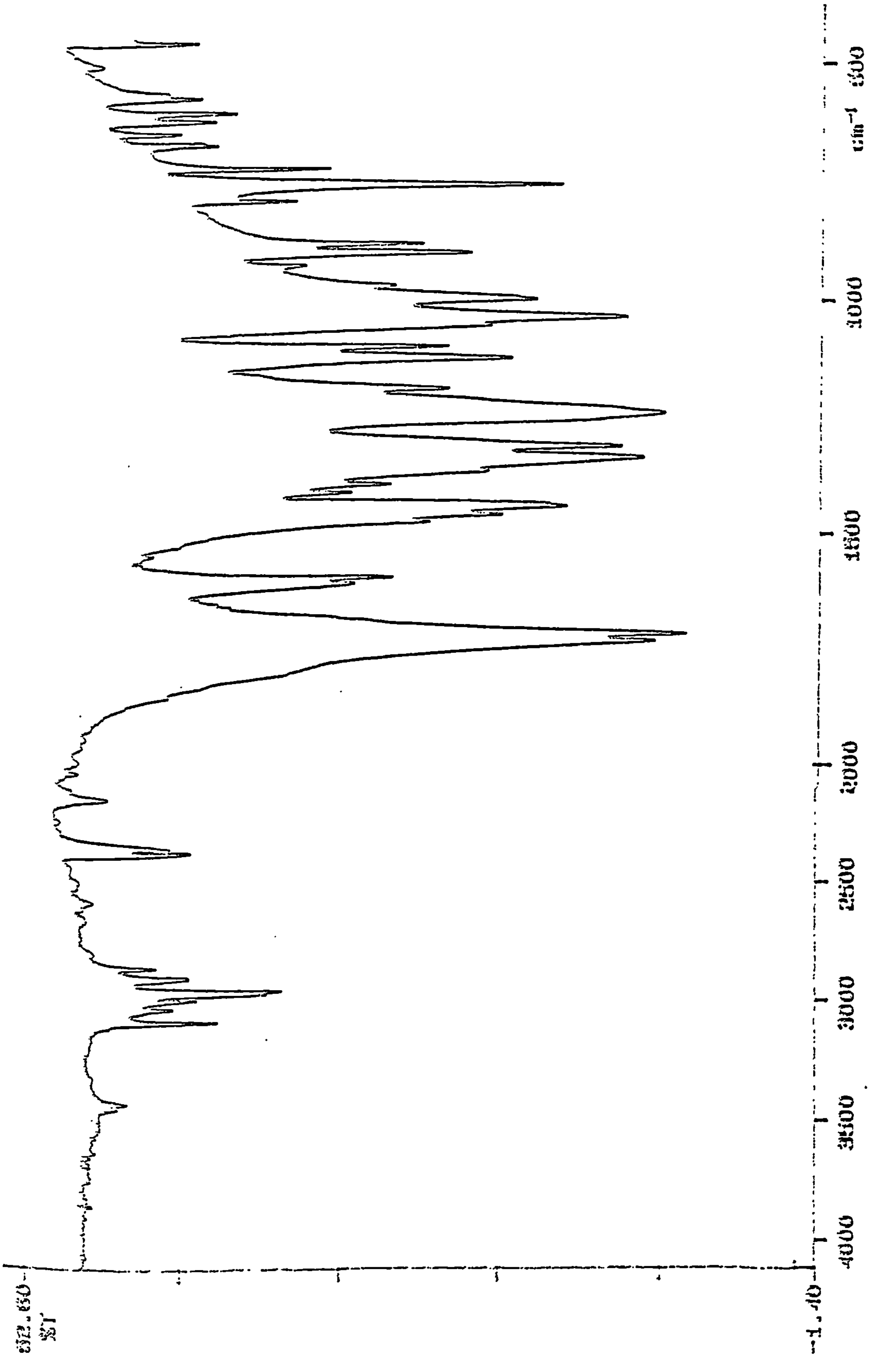
FTIR (thin film) spectrum of 3-bromopropyl acetate: acetyl chloride route



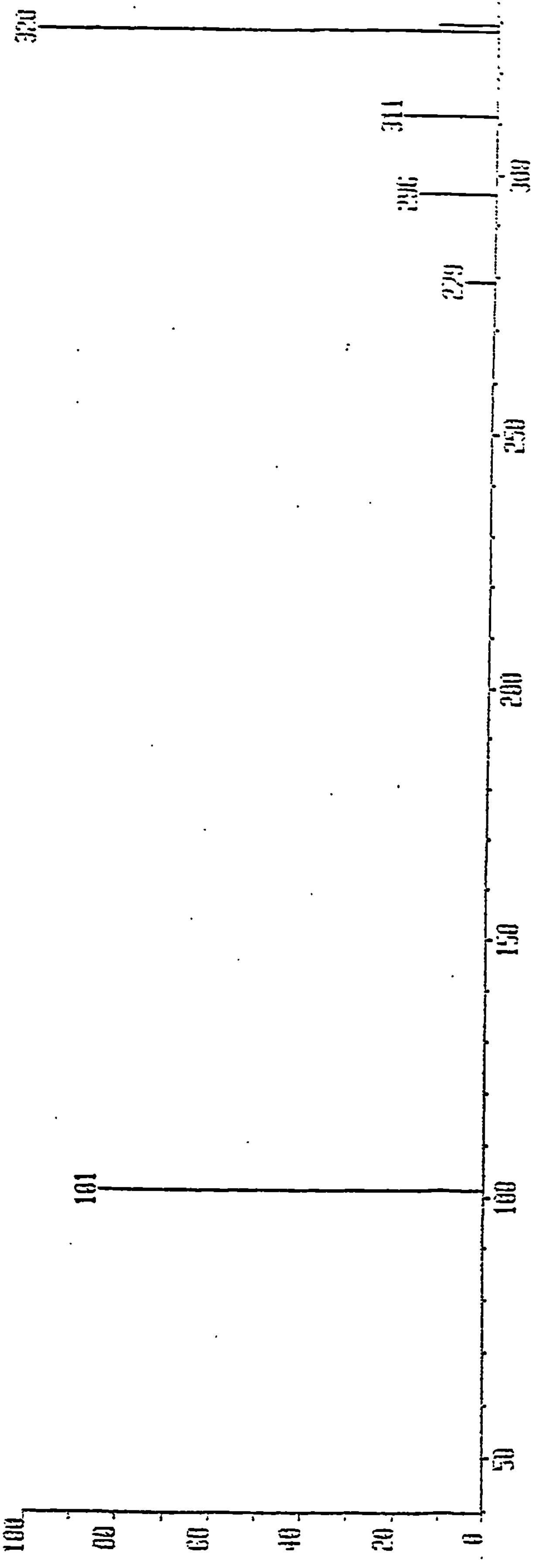
Appendix 1. 8: ^{1}H nmr spectrum (400 MHz) of dimethyl 5-(3-acetoxypropoxy)isophthalate



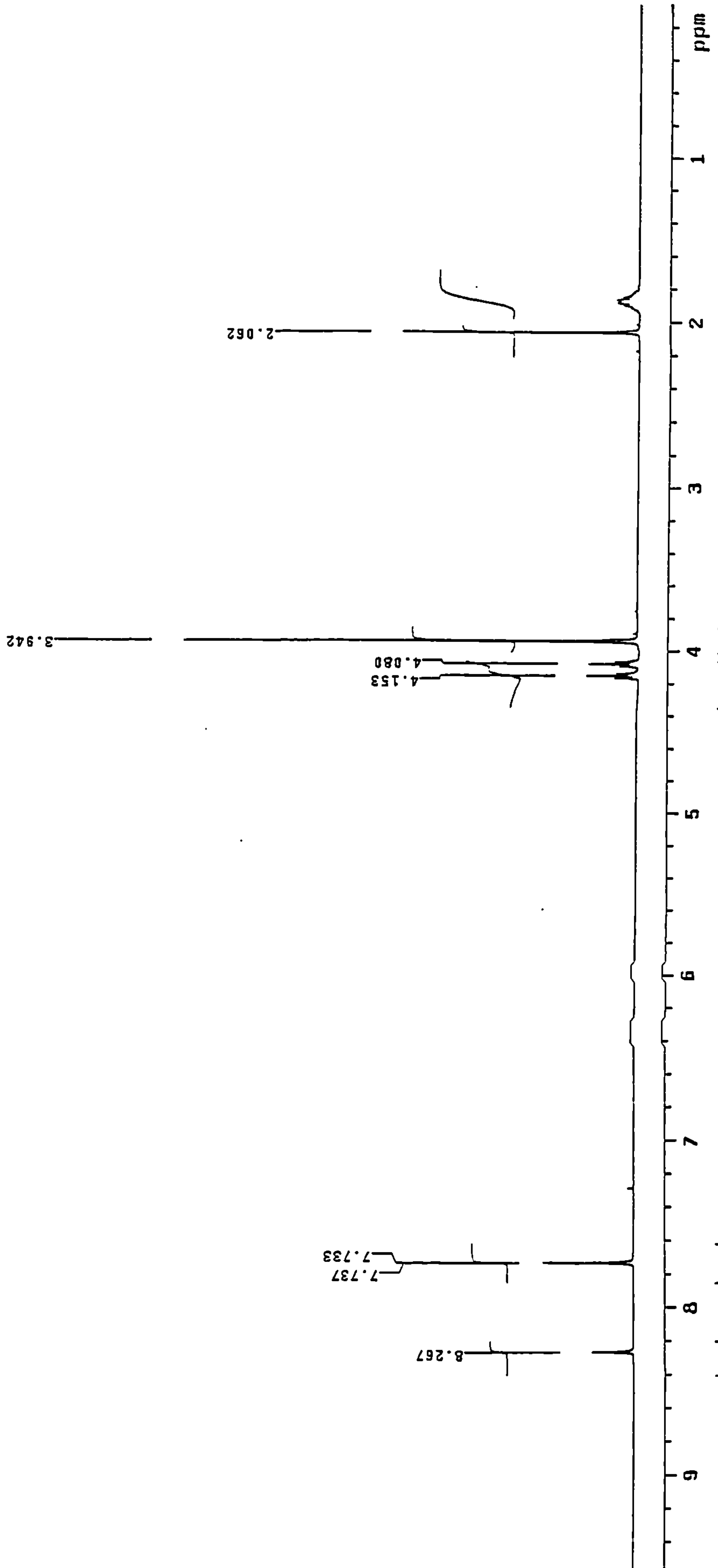
Appendix 1. 9: ^{13}C nmr spectrum (100 MHz) of dimethyl 5-(3-acetoxypropoxy)isophthalate



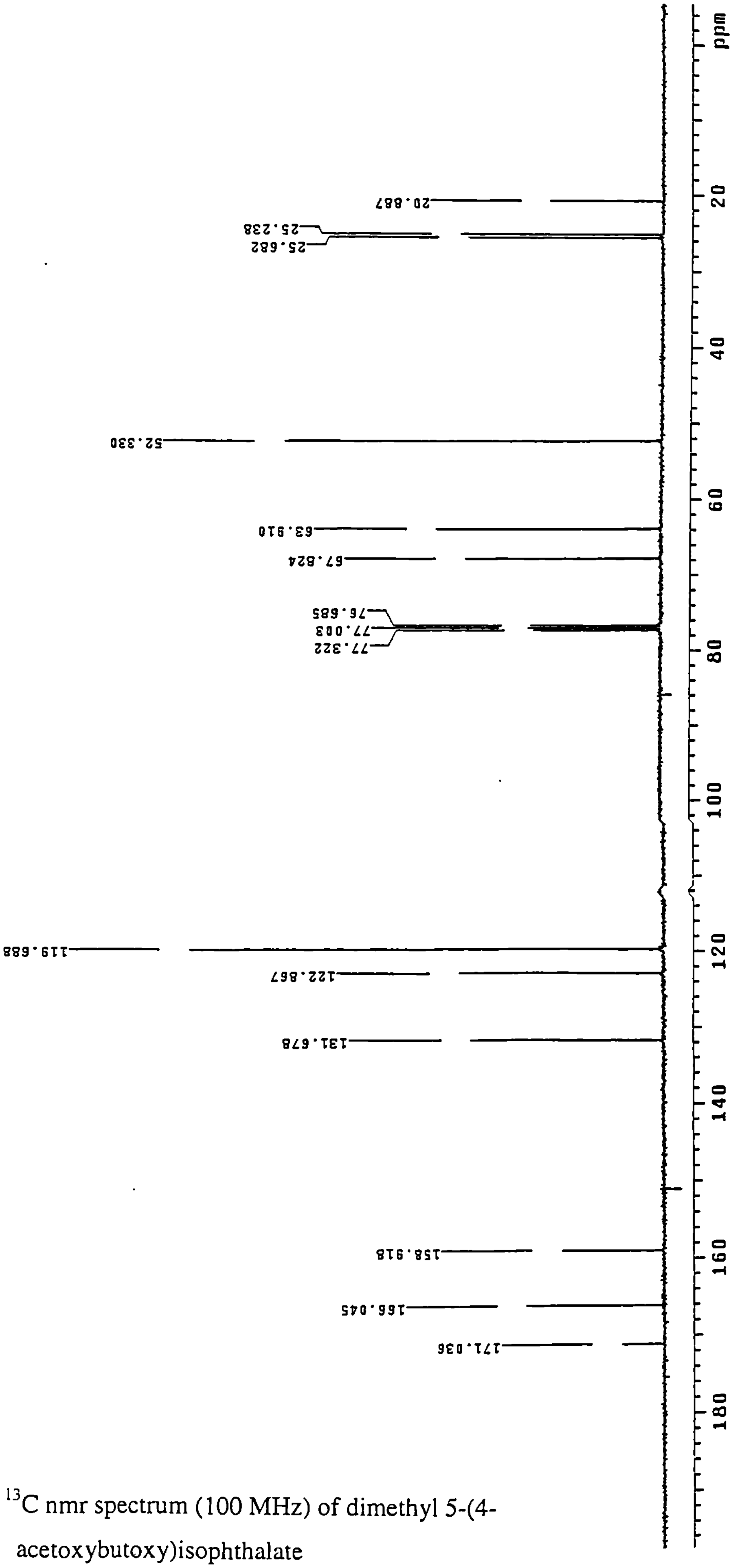
Appendix 1. 10: FTIR (KBr disc) spectrum of dimethyl 5-(3-acetoxypropoxy)isophthalate



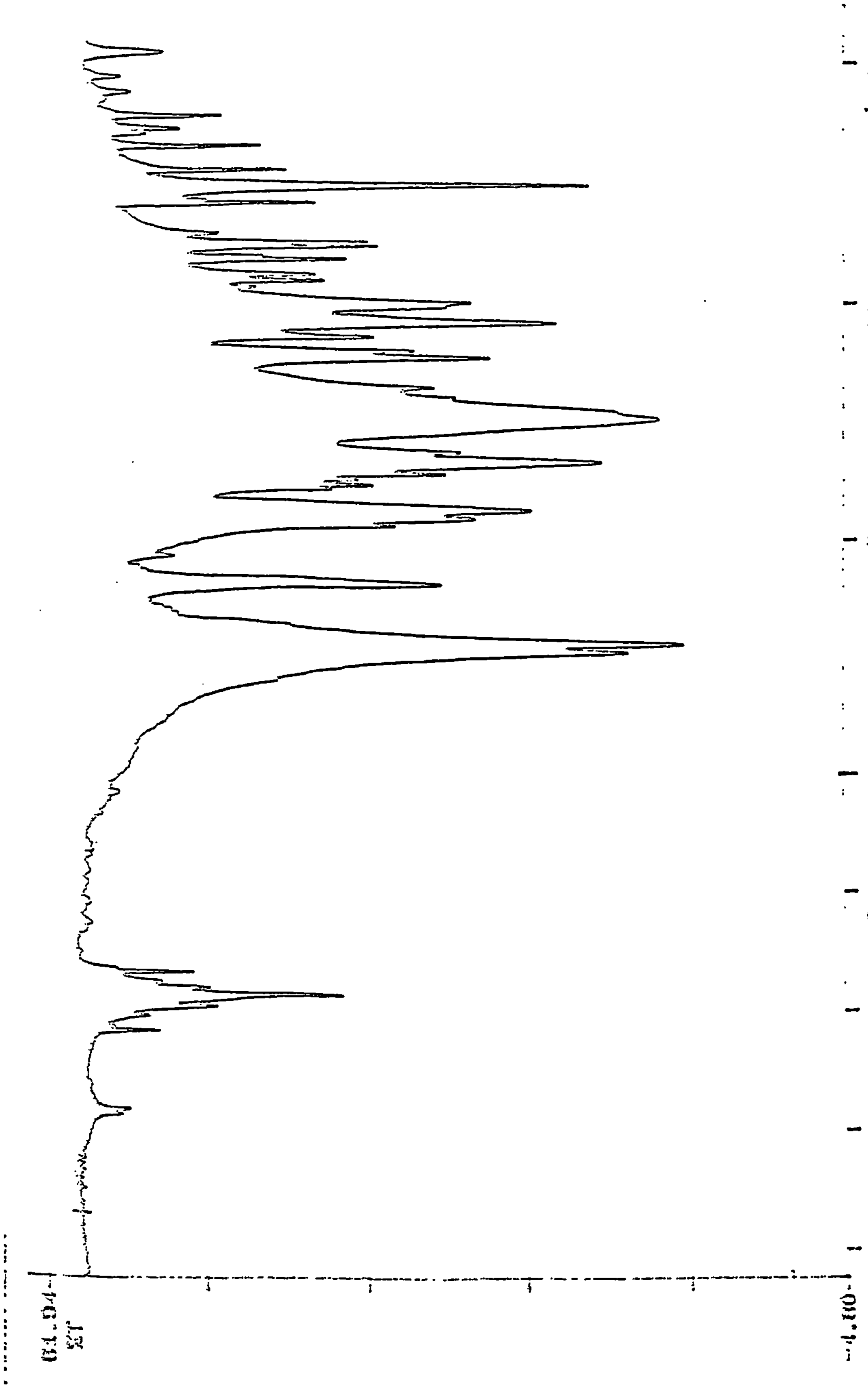
Appendix 1. 11: MS(CI+) spectrum of dimethyl 5-(3-acetoxypropoxy)isophthalate



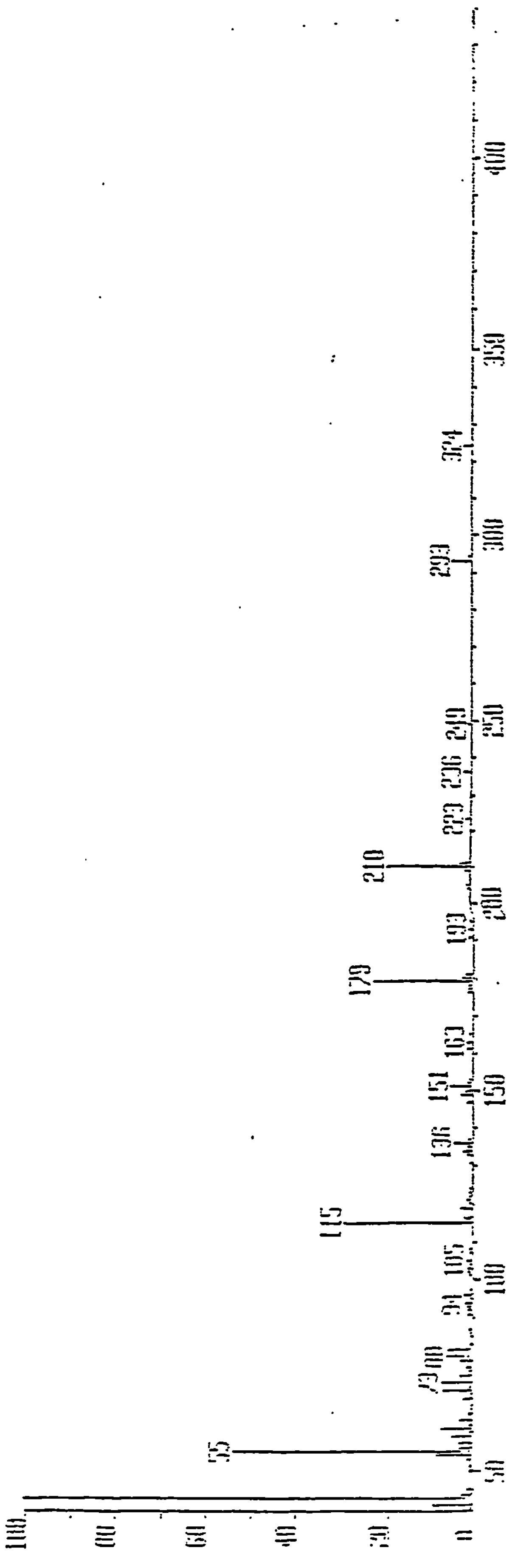
Appendix 1. 12: ^{1}H nmr spectrum (400 MHz) of dimethyl 5-(4-acetoxybutoxy)isophthalate



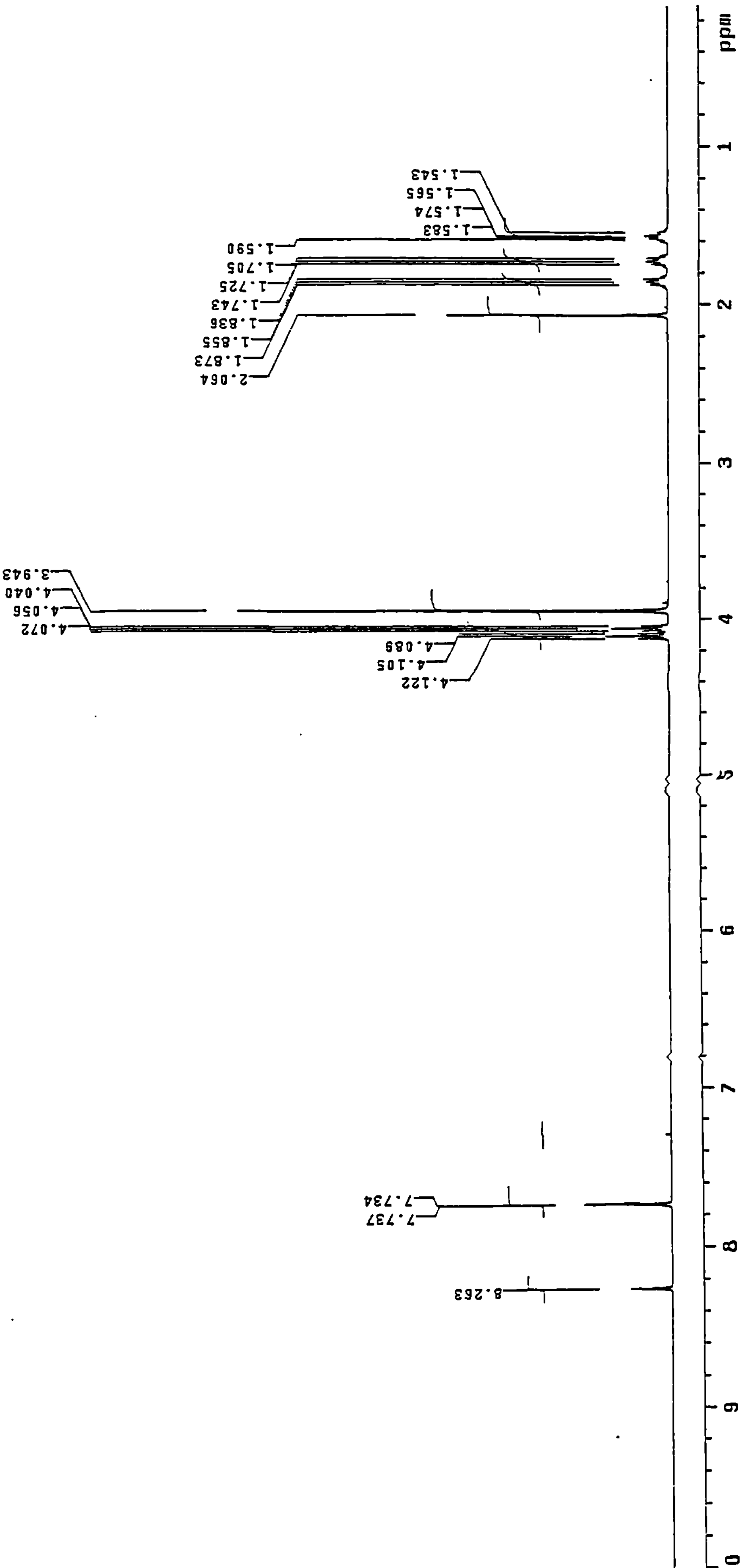
Appendix 1. 13: ^{13}C nmr spectrum (100 MHz) of dimethyl 5-(4-acetoxybutoxy)isophthalate



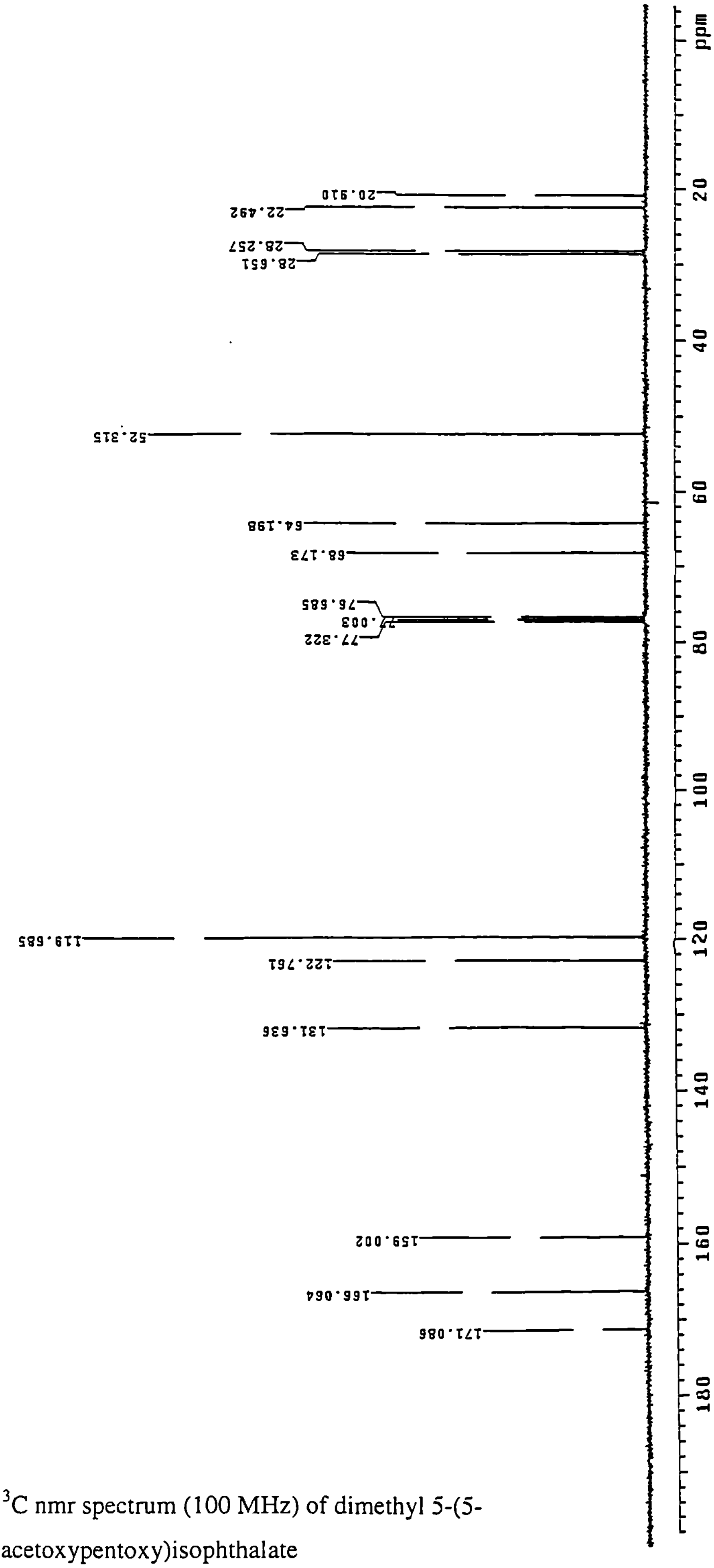
Appendix 1. 14: FTIR (KBr disc) spectrum of dimethyl 5-(4-acetoxybutoxy)isophthalate



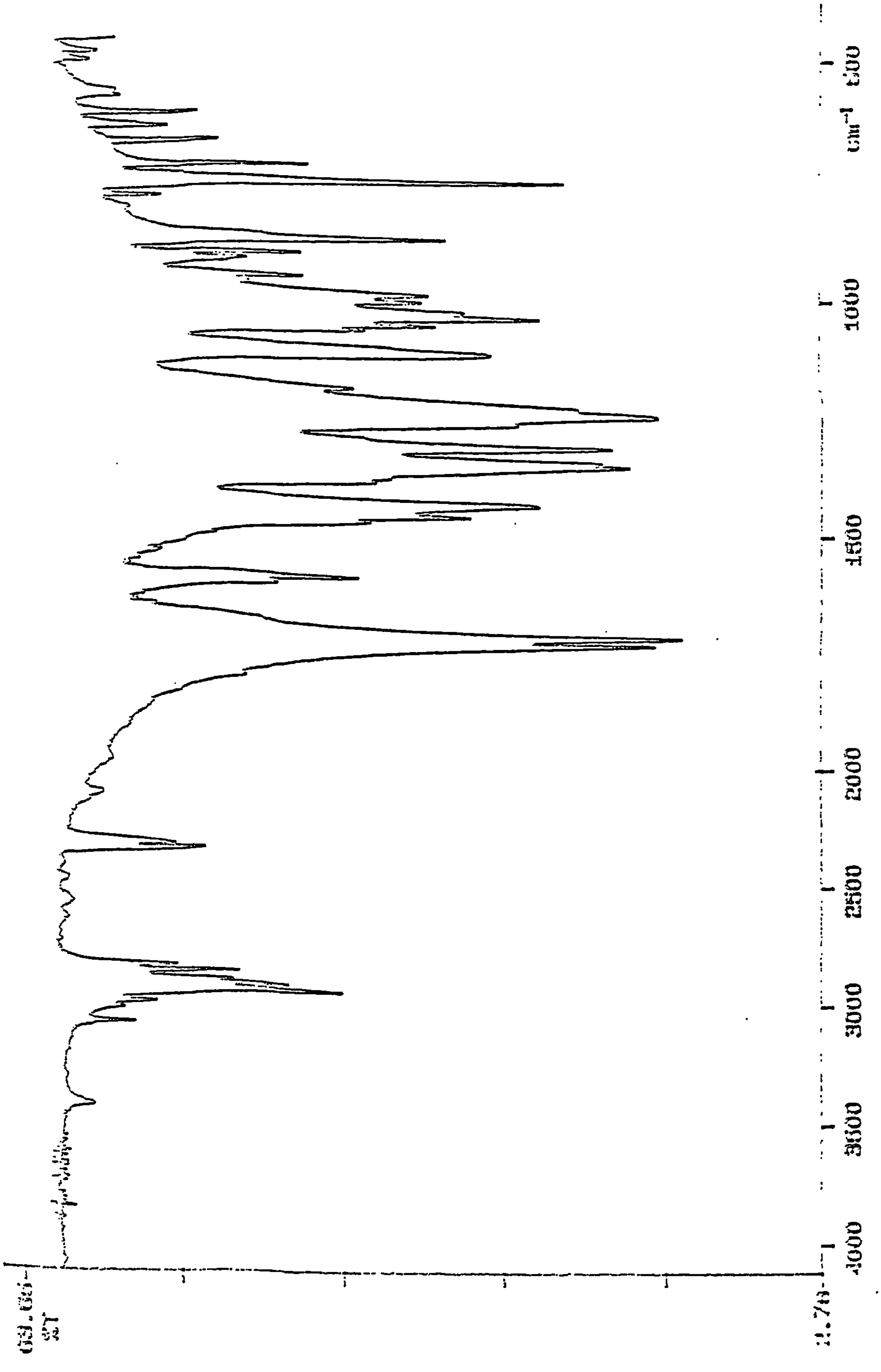
Appendix 1. 15: MS(EI+) spectrum of dimethyl 5-(4-acetoxybutoxy)isophthalate



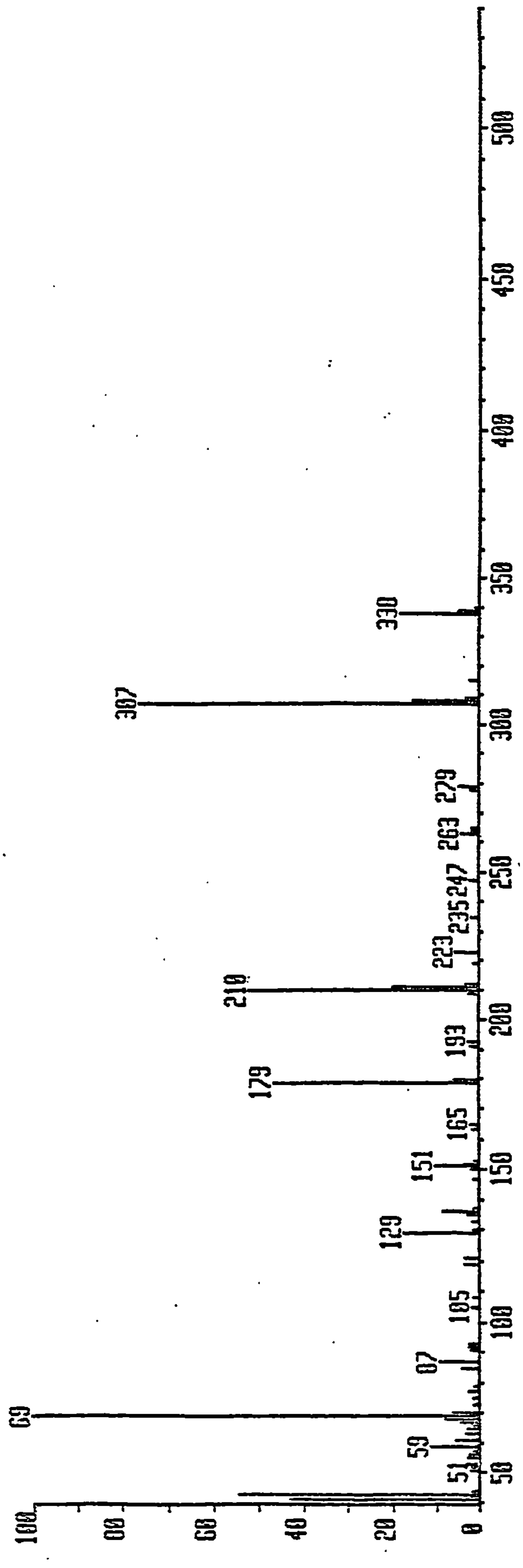
Appendix 1. 16: ^{1}H nmr spectrum (400 MHz) of dimethyl 5-(5-acetoxypentoxy)isophthalate



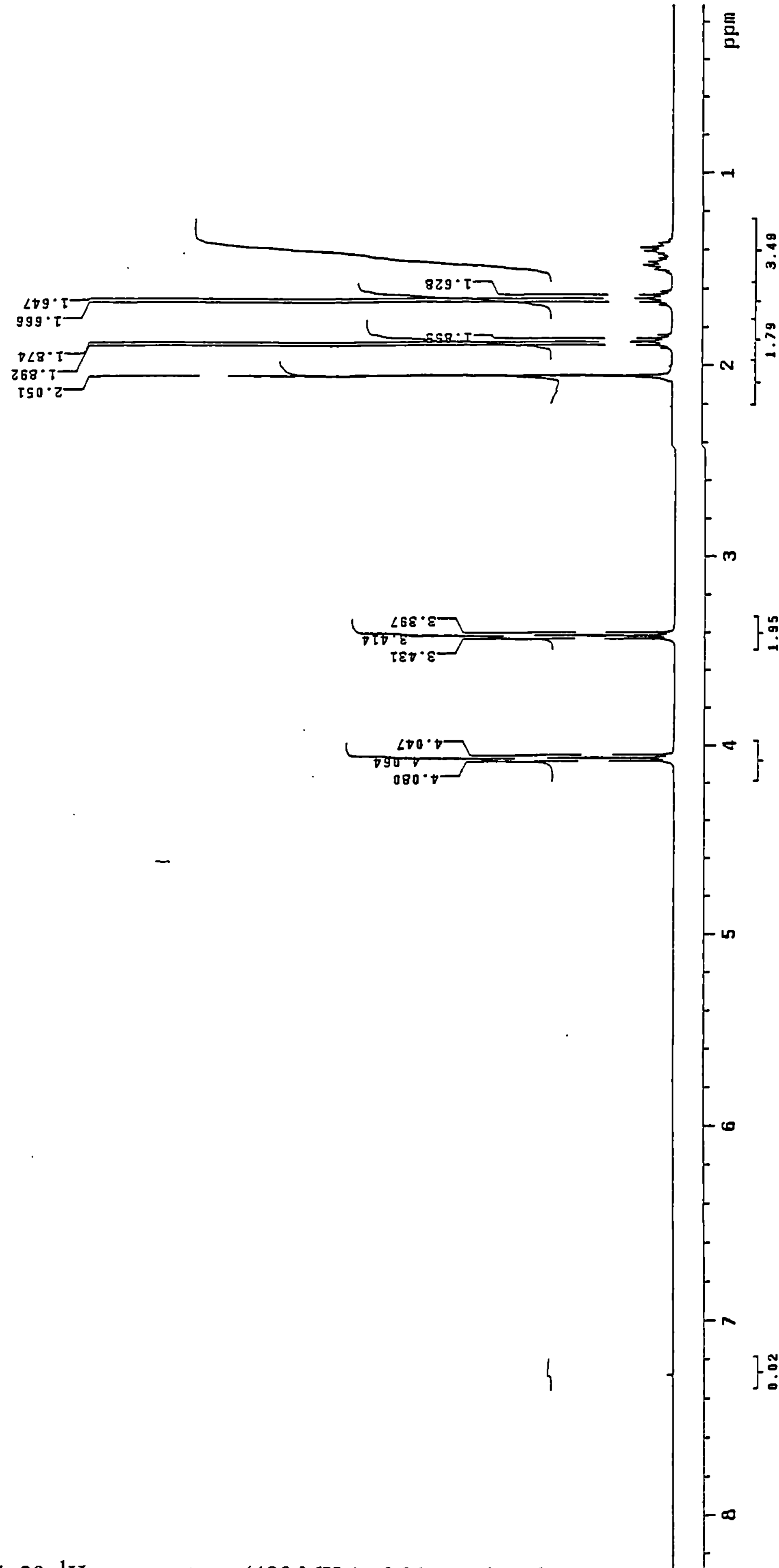
Appendix 1. 17: ^{13}C nmr spectrum (100 MHz) of dimethyl 5-(5-acetoxypentoxy)isophthalate



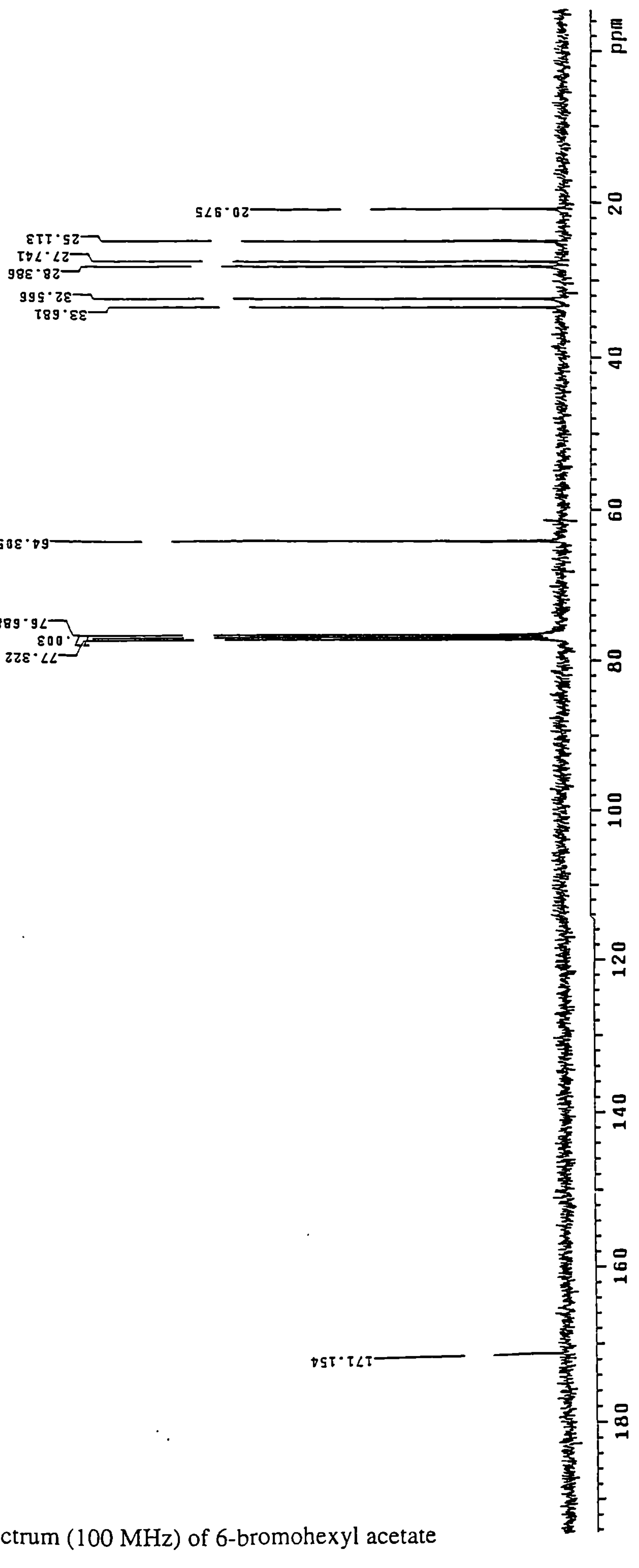
Appendix 1. 18: FTIR (KBr disc) spectrum of dimethyl 5-(5-acetoxypentoxy)isophthalate



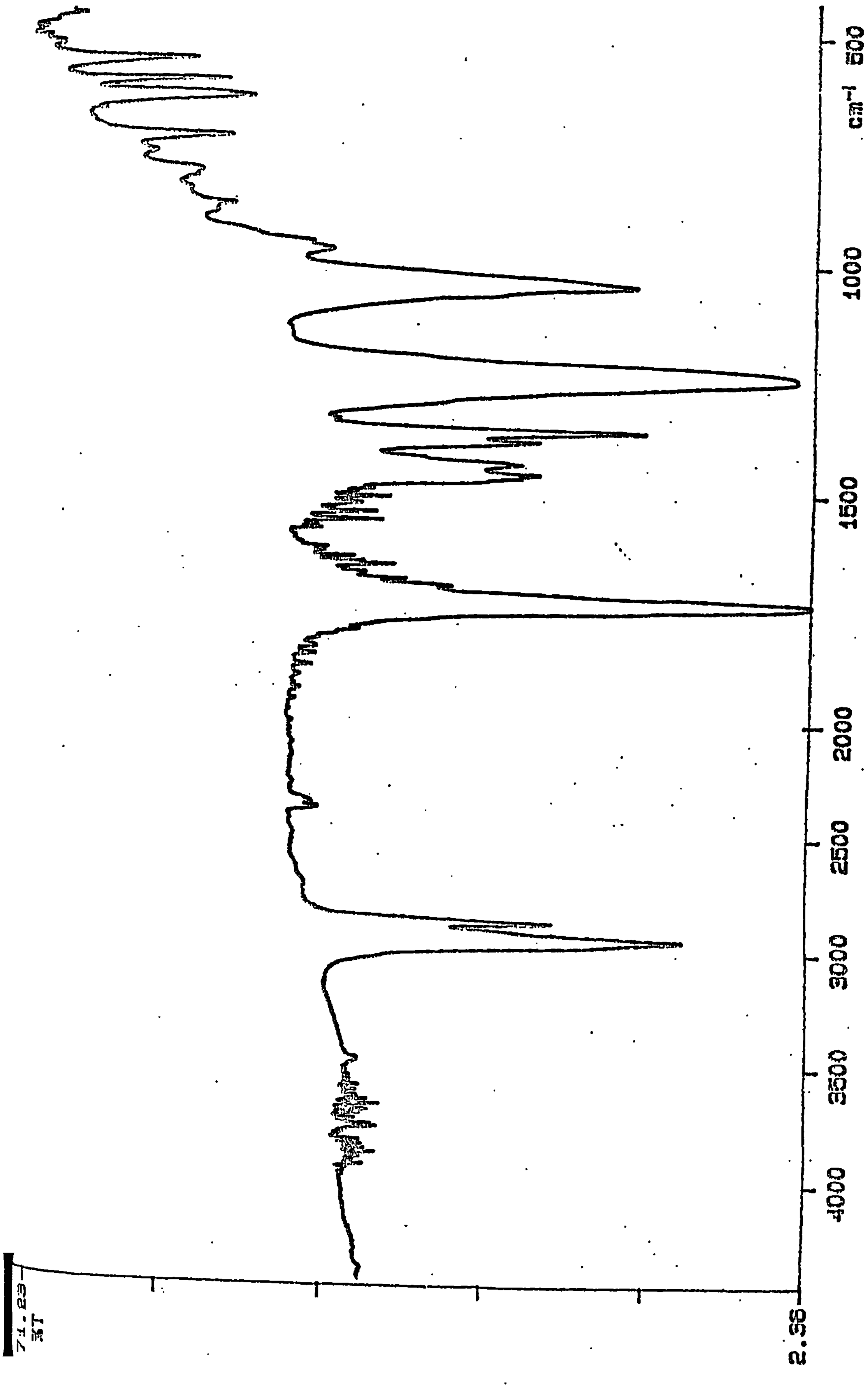
ppendix 1. 19: MS(EI+) spectrum of dimethyl 5-(5-acetoxypentoxy)isophthalate



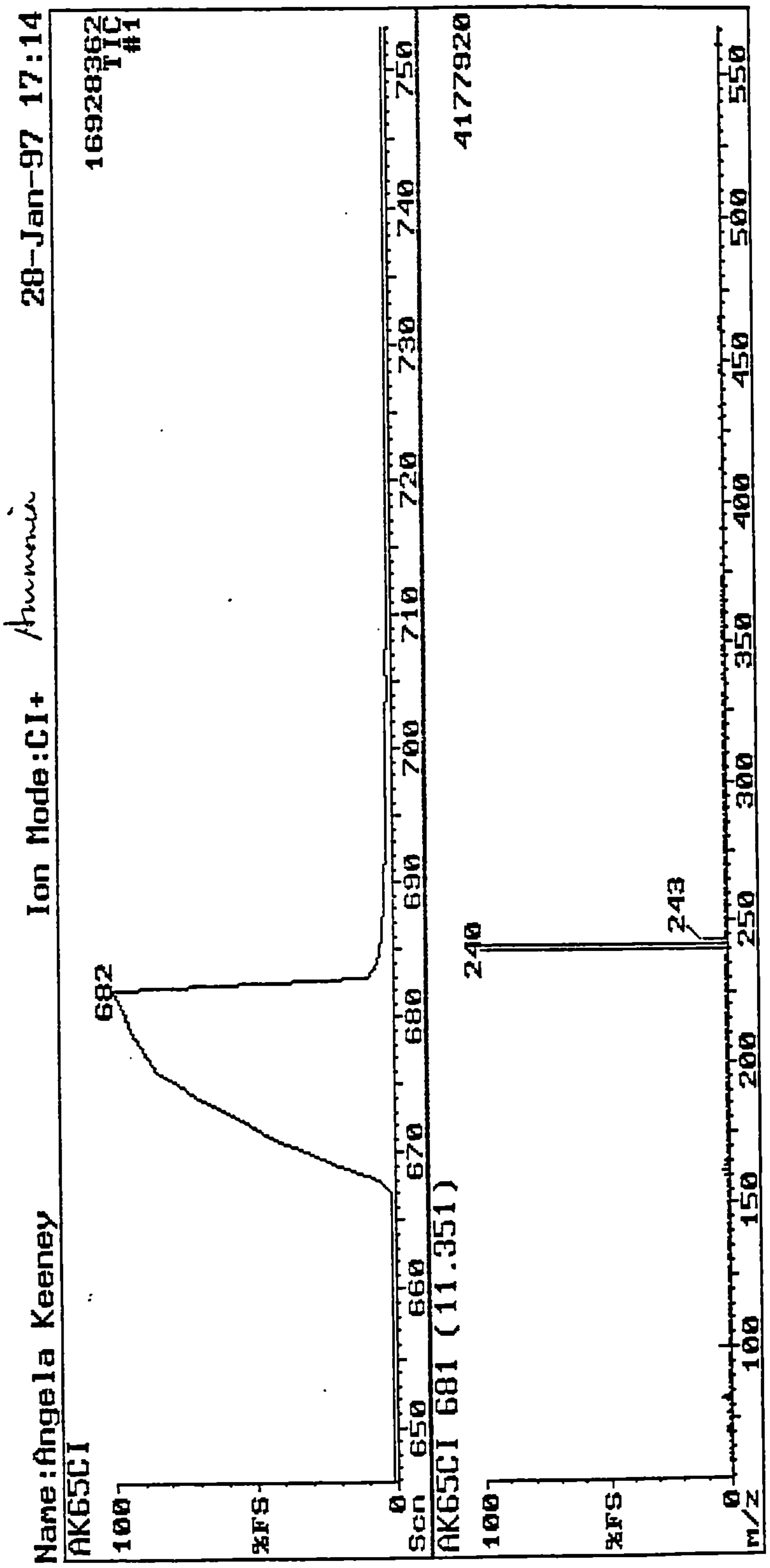
Appendix 1. 20: ^{1}H nmr spectrum (400 MHz) of 6-bromohexyl acetate



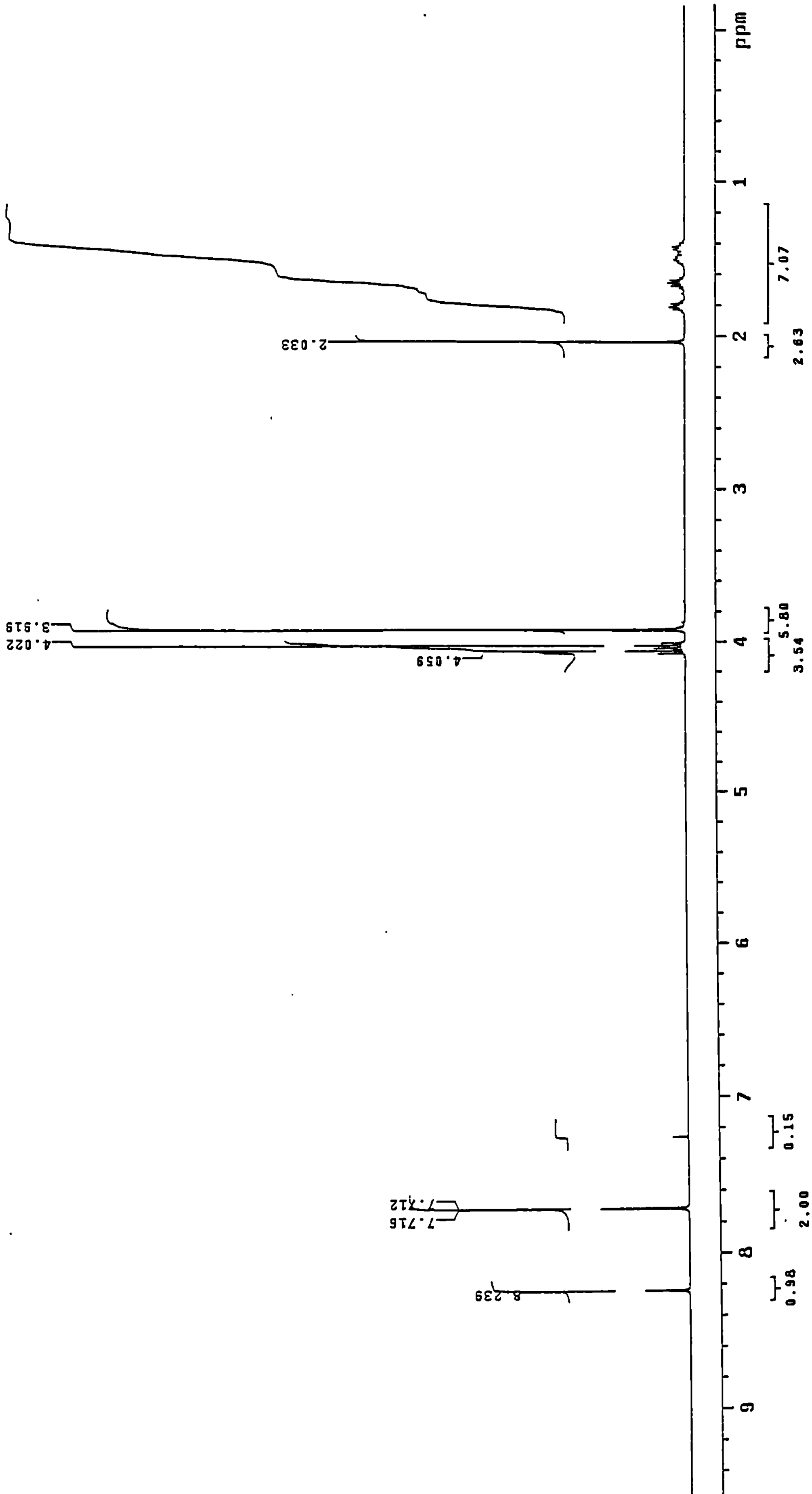
Appendix 1. 21: ^{13}C nmr spectrum (100 MHz) of 6-bromohexyl acetate



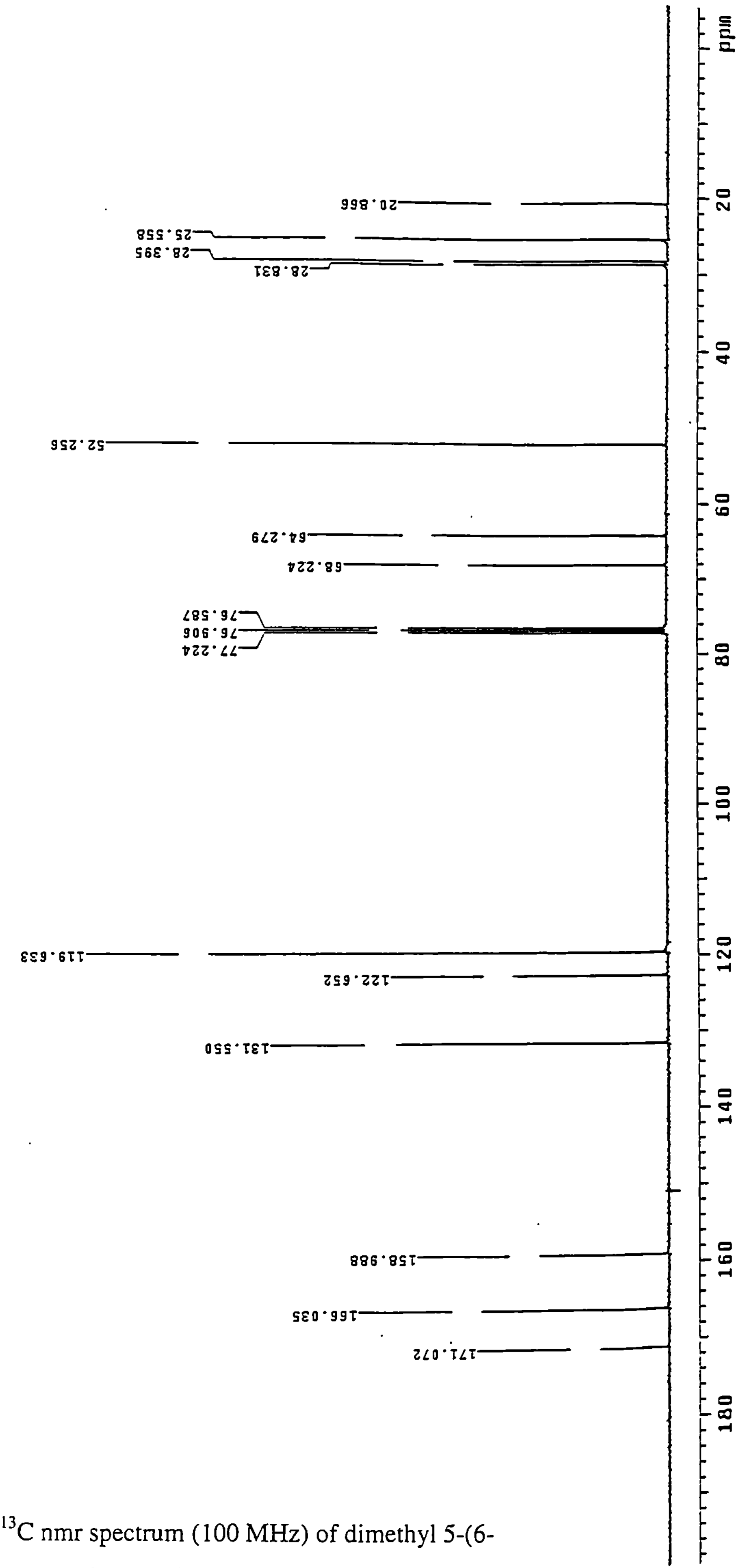
Appendix 1. 22: FTIR (thin film) spectrum of 6-bromohexyl acetate



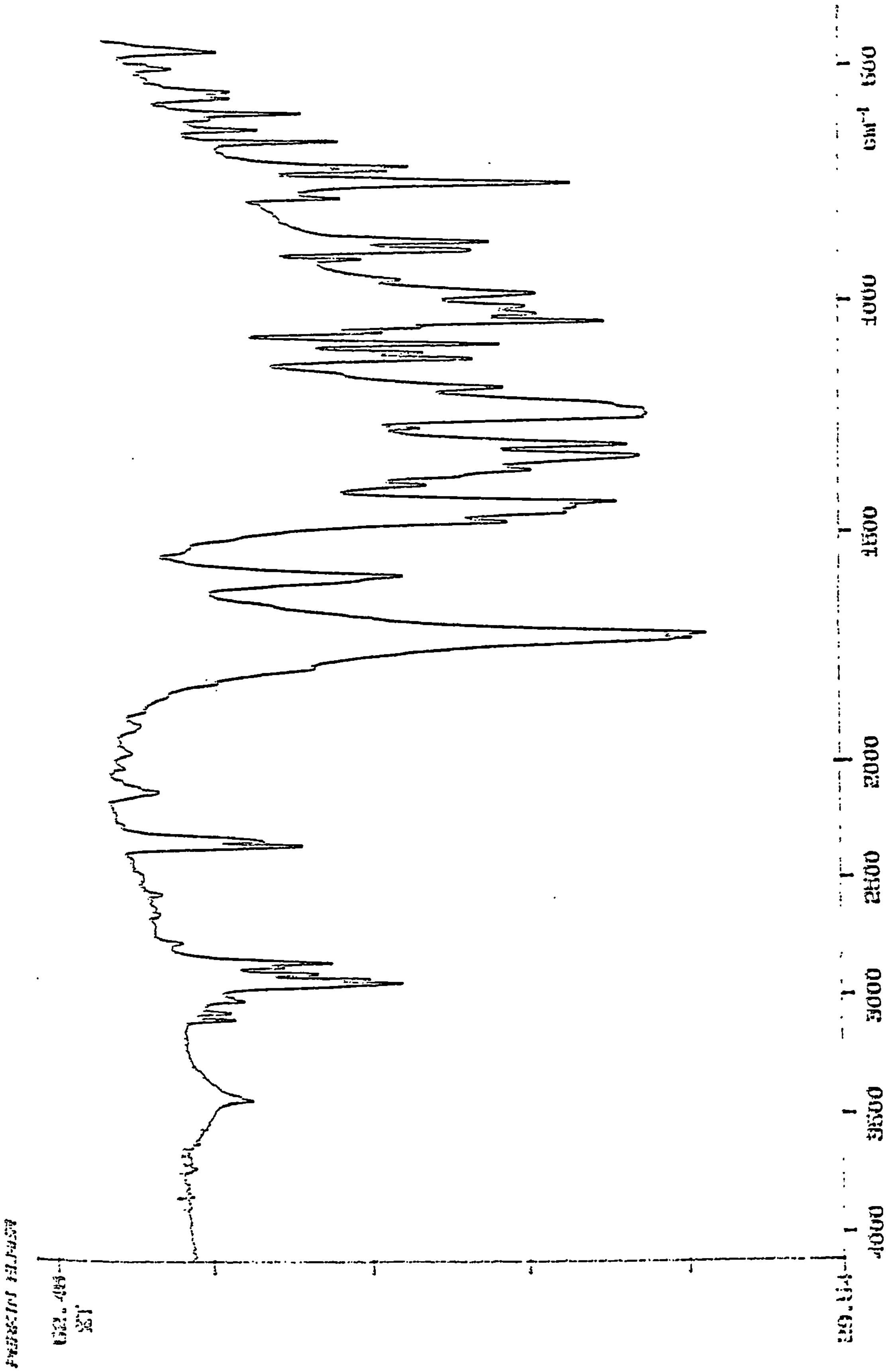
Appendix 1. 23: MS(CI+) spectrum of 6-bromohexyl acetate



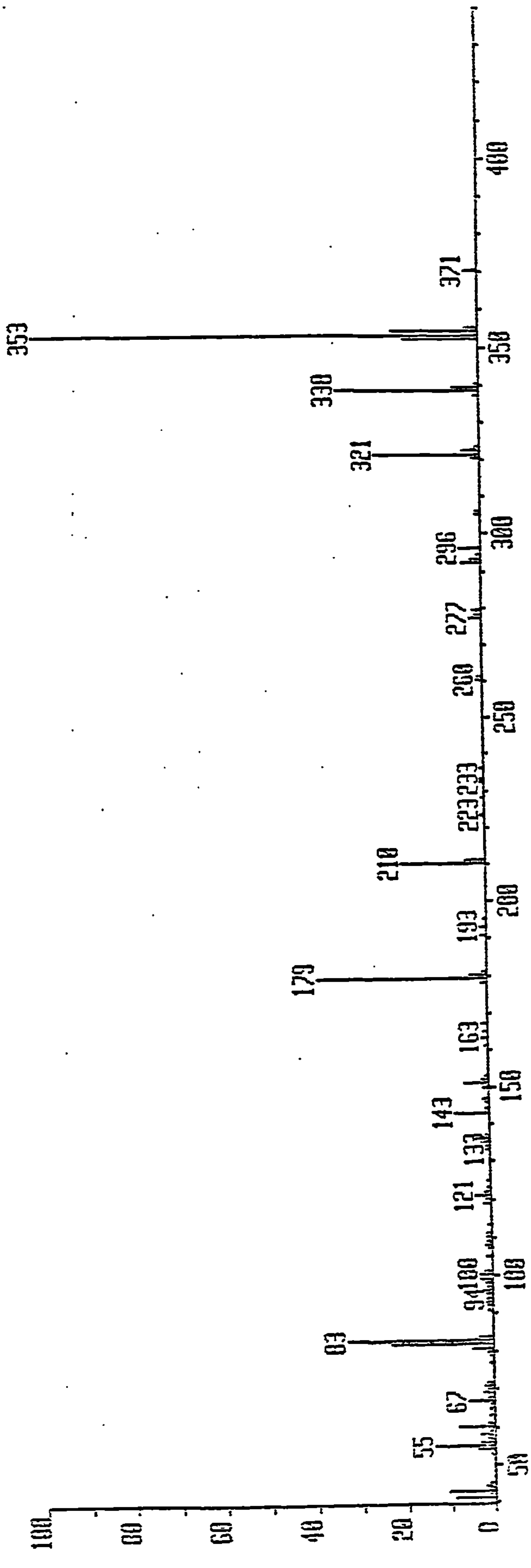
Appendix 1. 24: ^{1}H nmr spectrum (400 MHz) of dimethyl 5-(6-acetoxyhexoxy)isophthalate



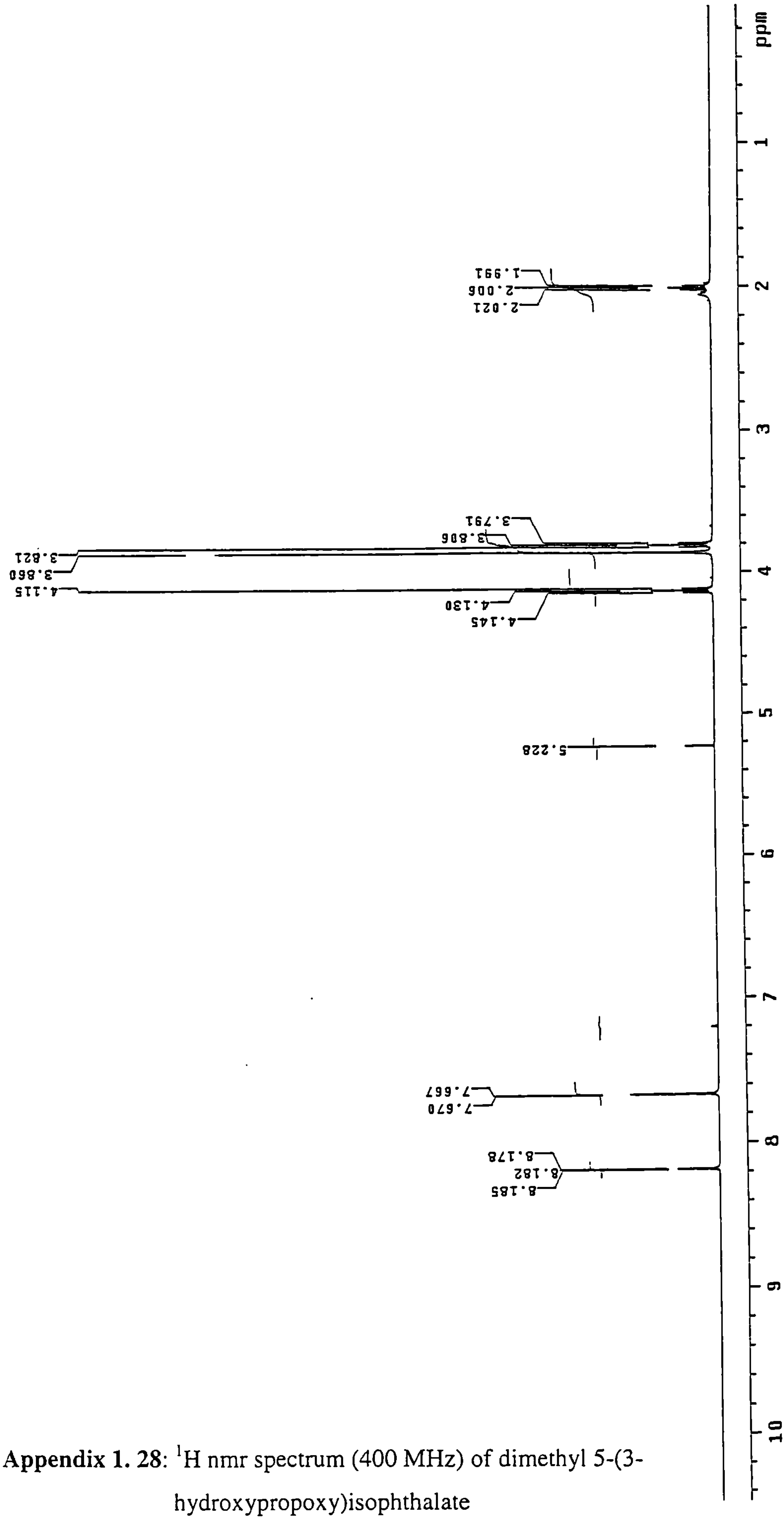
Appendix 1. 25: ^{13}C nmr spectrum (100 MHz) of dimethyl 5-(6-acetoxyhexoxy)isophthalate



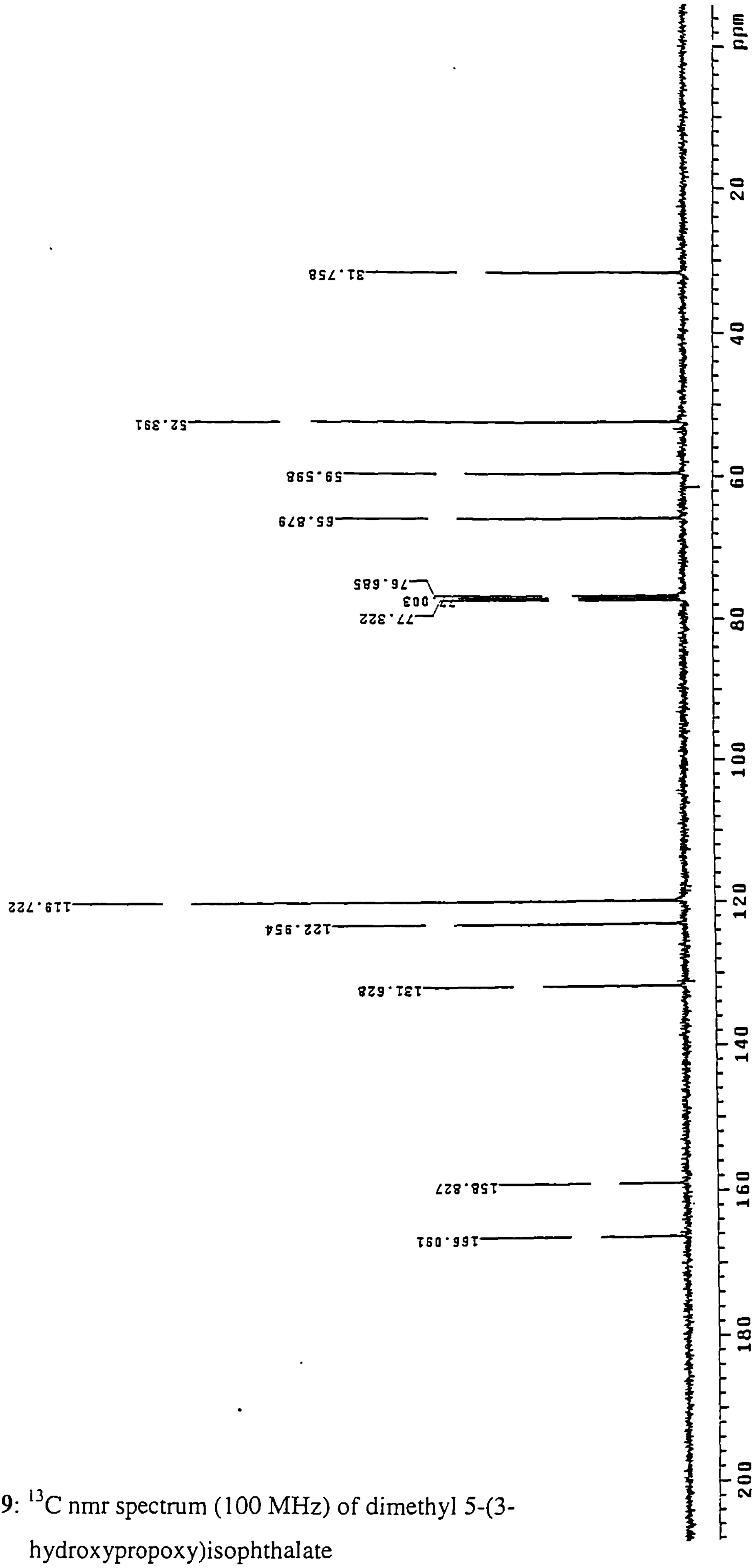
Appendix 1. 26: FTIR (KBr disc) spectrum of dimethyl 5-(6-acetoxyhexoxy)isophthalate



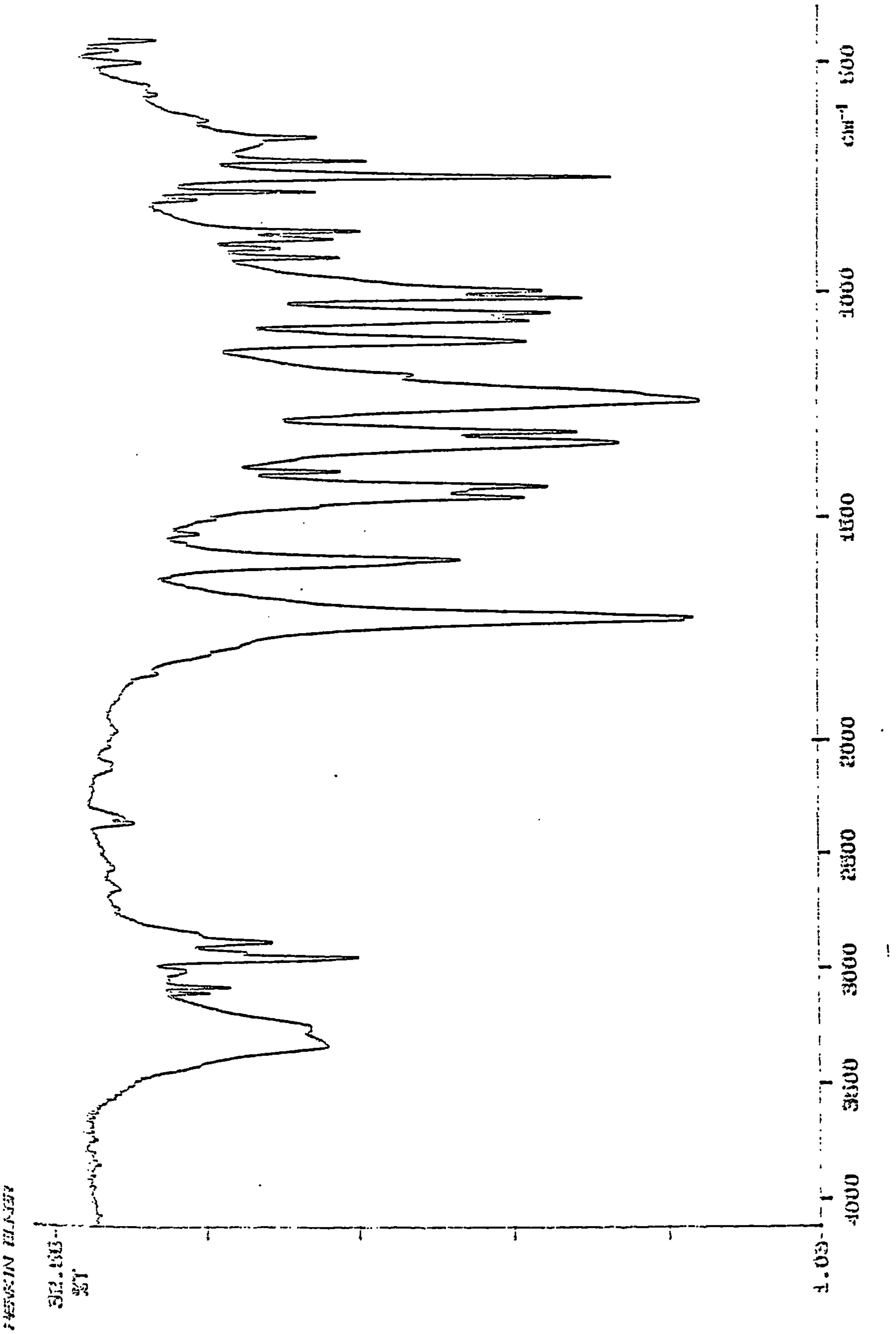
Appendix 1. 27: MS(CI+) spectrum of dimethyl 5-(6-acetoxyhexoxy)isophthalate



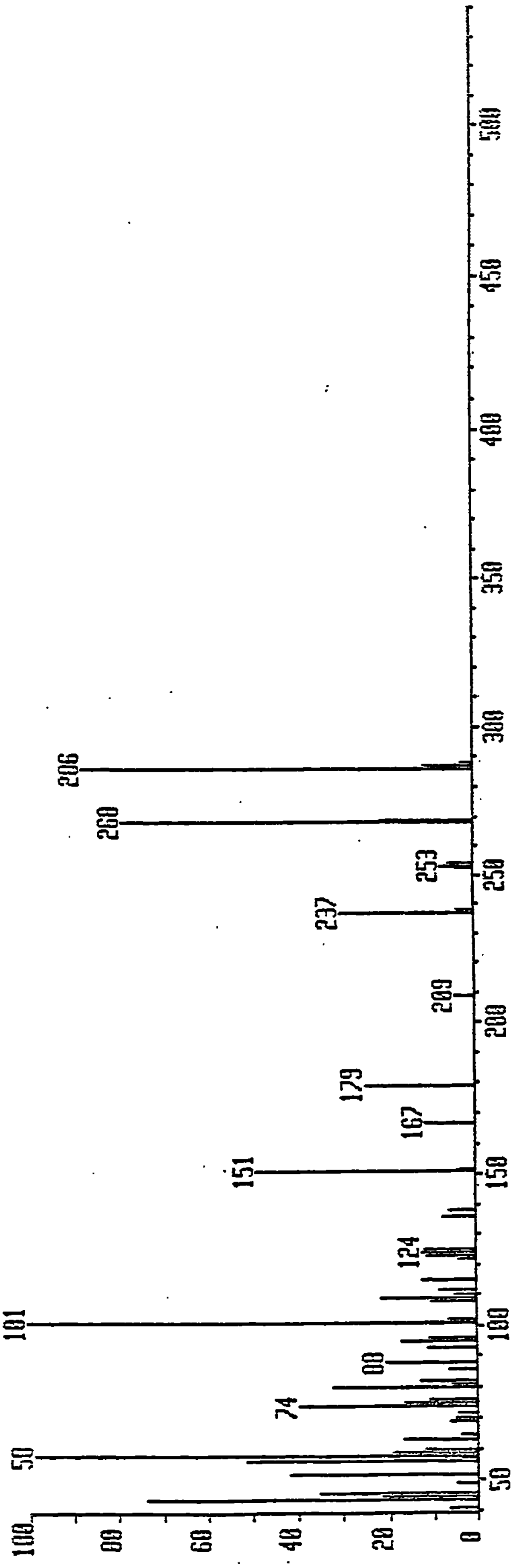
Appendix 1. 28: ^{1}H nmr spectrum (400 MHz) of dimethyl 5-(3-hydroxypropoxy)isophthalate



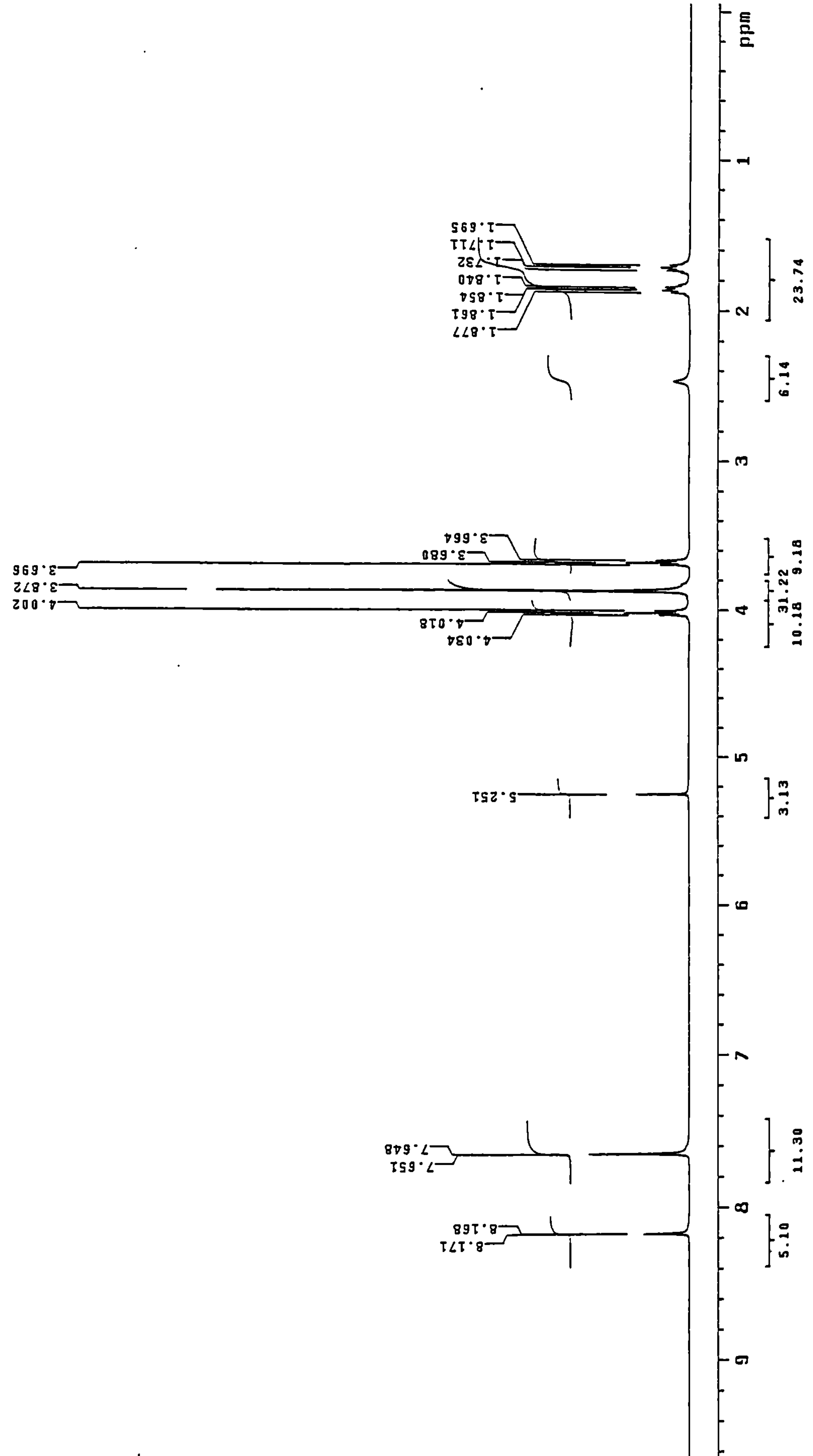
Appendix 1. 29: ^{13}C nmr spectrum (100 MHz) of dimethyl 5-(3-hydroxypropoxy)isophthalate



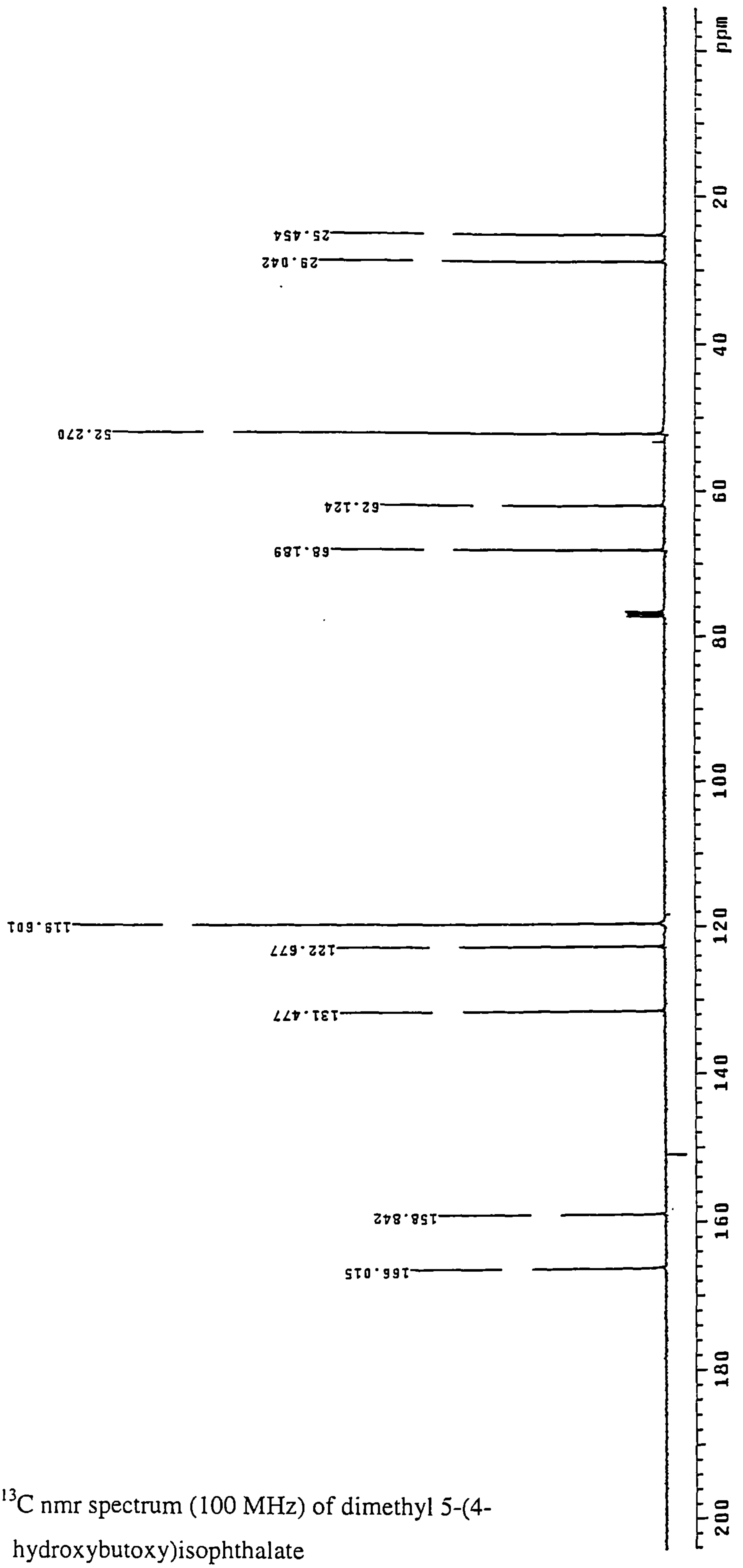
Appendix 1. 30: FTIR (KBr disc) spectrum of dimethyl 5-(3-hydroxypropoxy)isophthalate



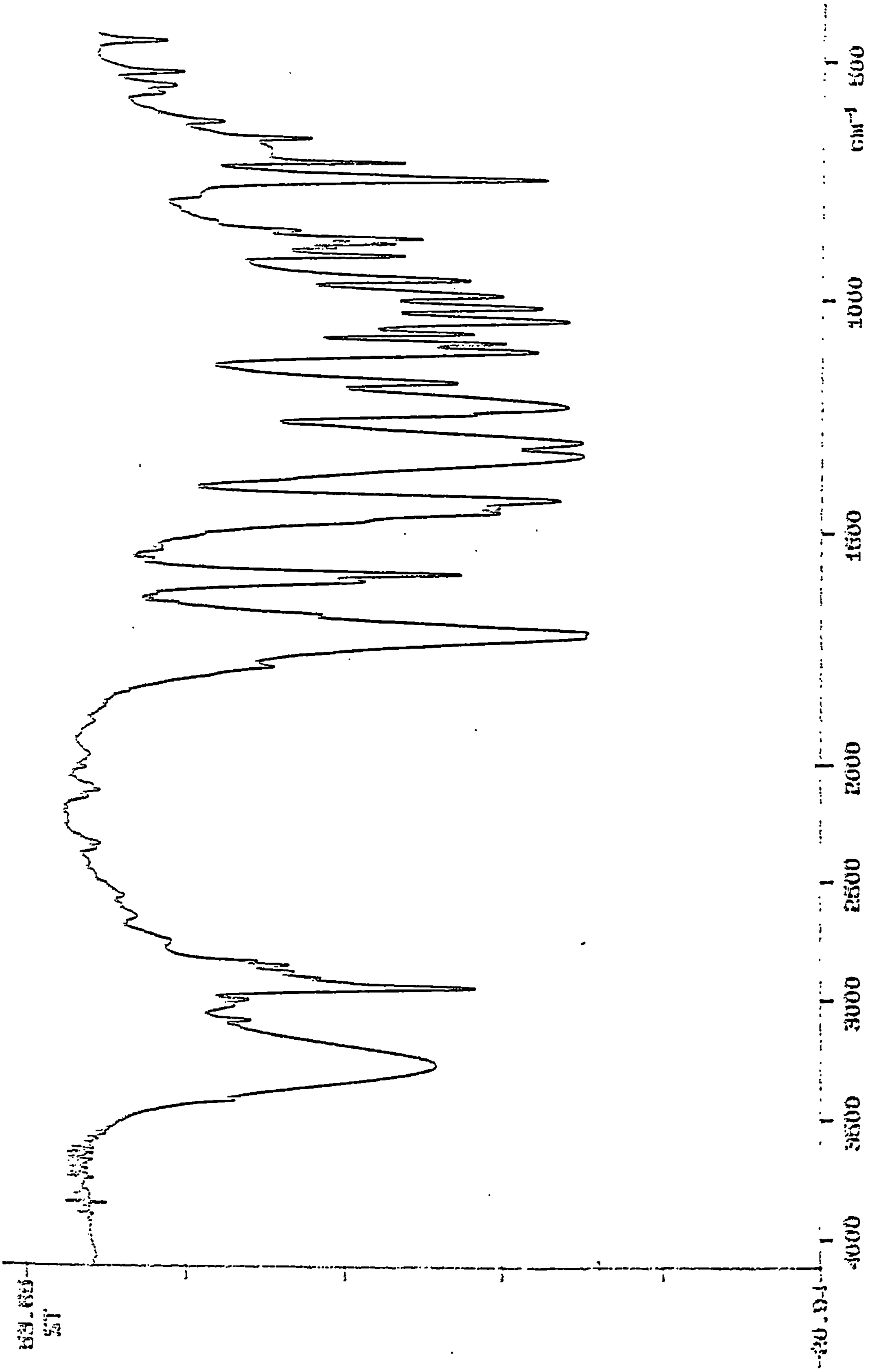
Appendix 1. 31: MS(CI+) spectrum of dimethyl 5-(3-hydroxypropoxy)isophthalate



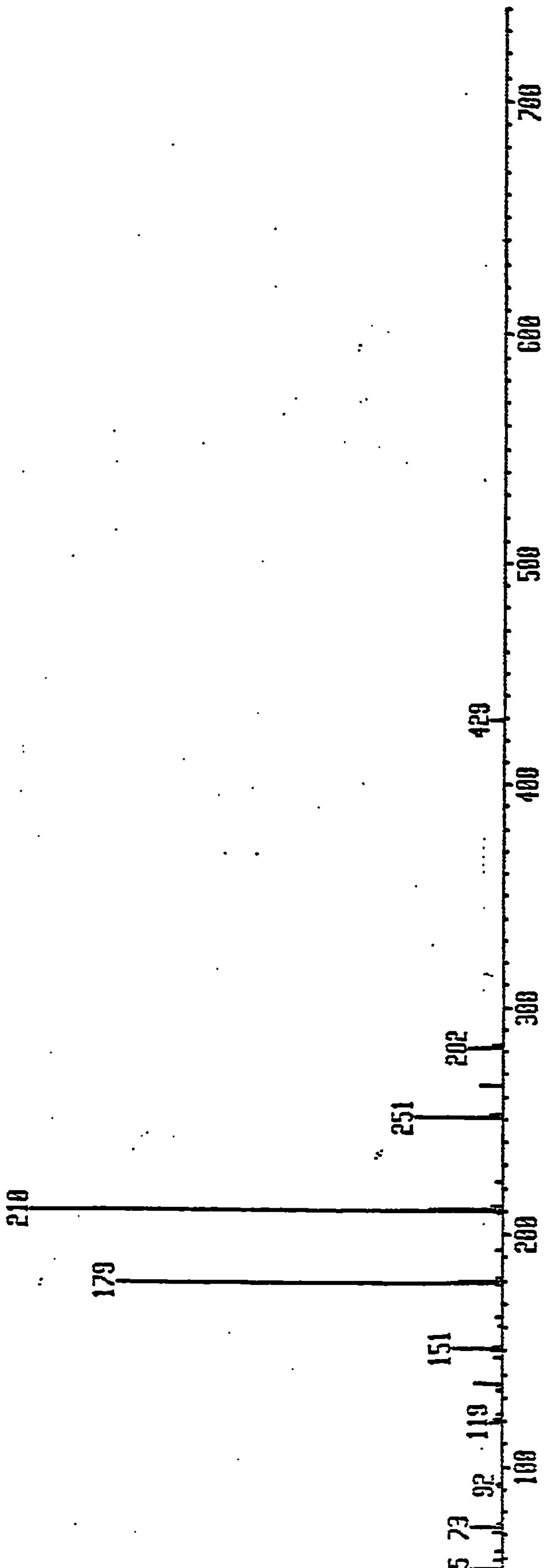
Appendix 1. 32: ^{1}H nmr spectrum (400 MHz) of dimethyl 5-(4-hydroxybutoxy)isophthalate



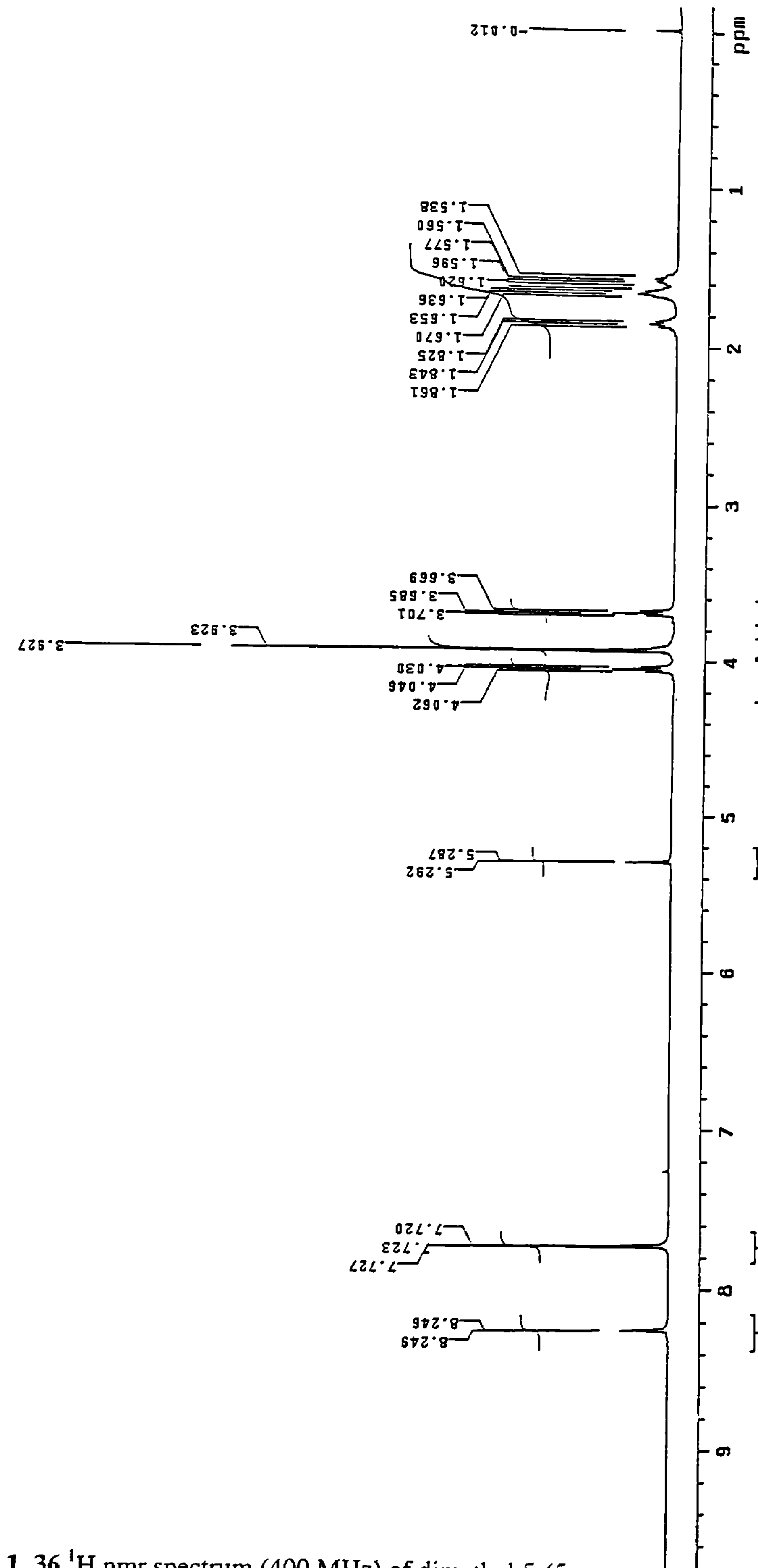
Appendix 1. 33 ^{13}C nmr spectrum (100 MHz) of dimethyl 5-(4-hydroxybutoxy)isophthalate



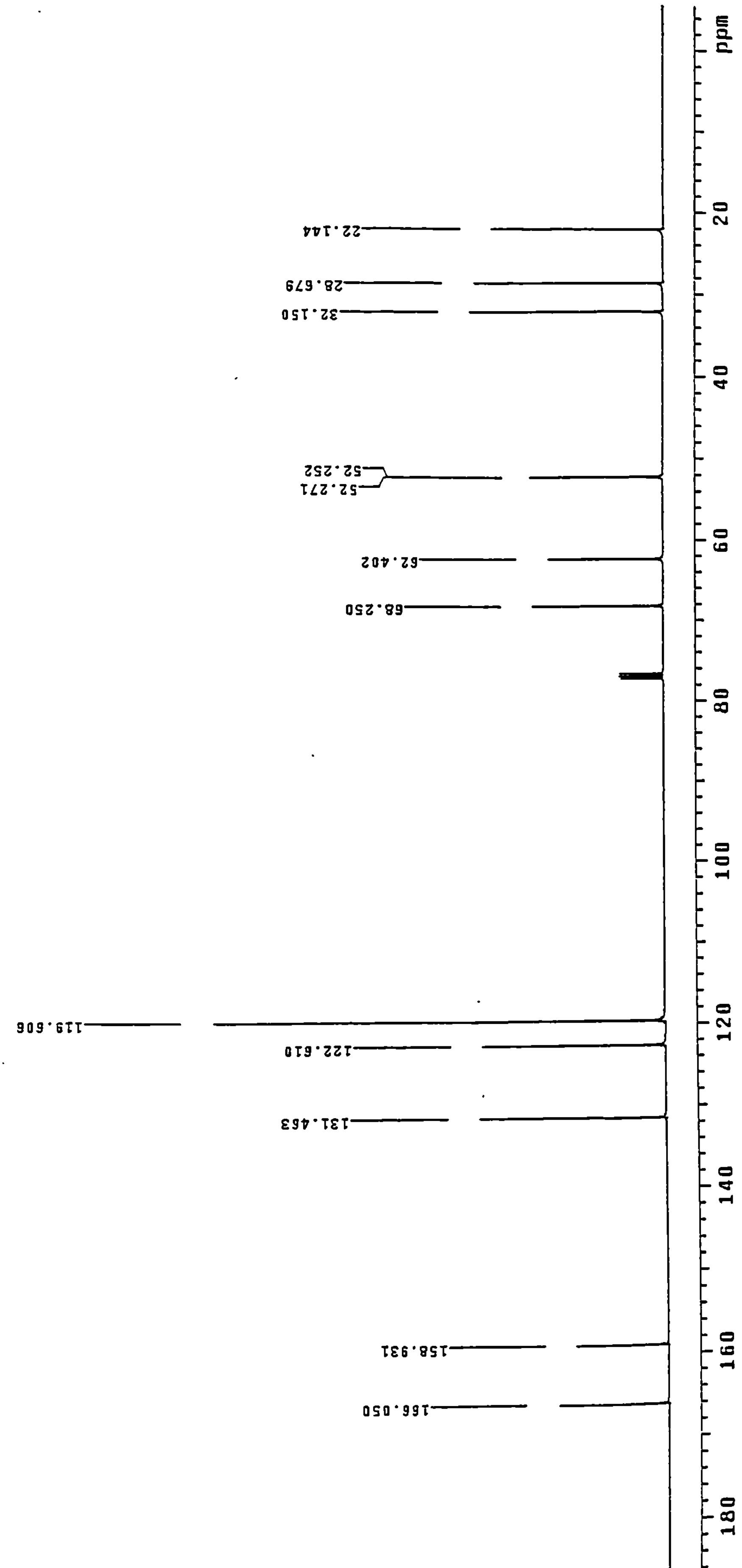
Appendix 1. 34 FTIR (KBr disc) spectrum of dimethyl 5-(4-hydroxybutoxy)isophthalate



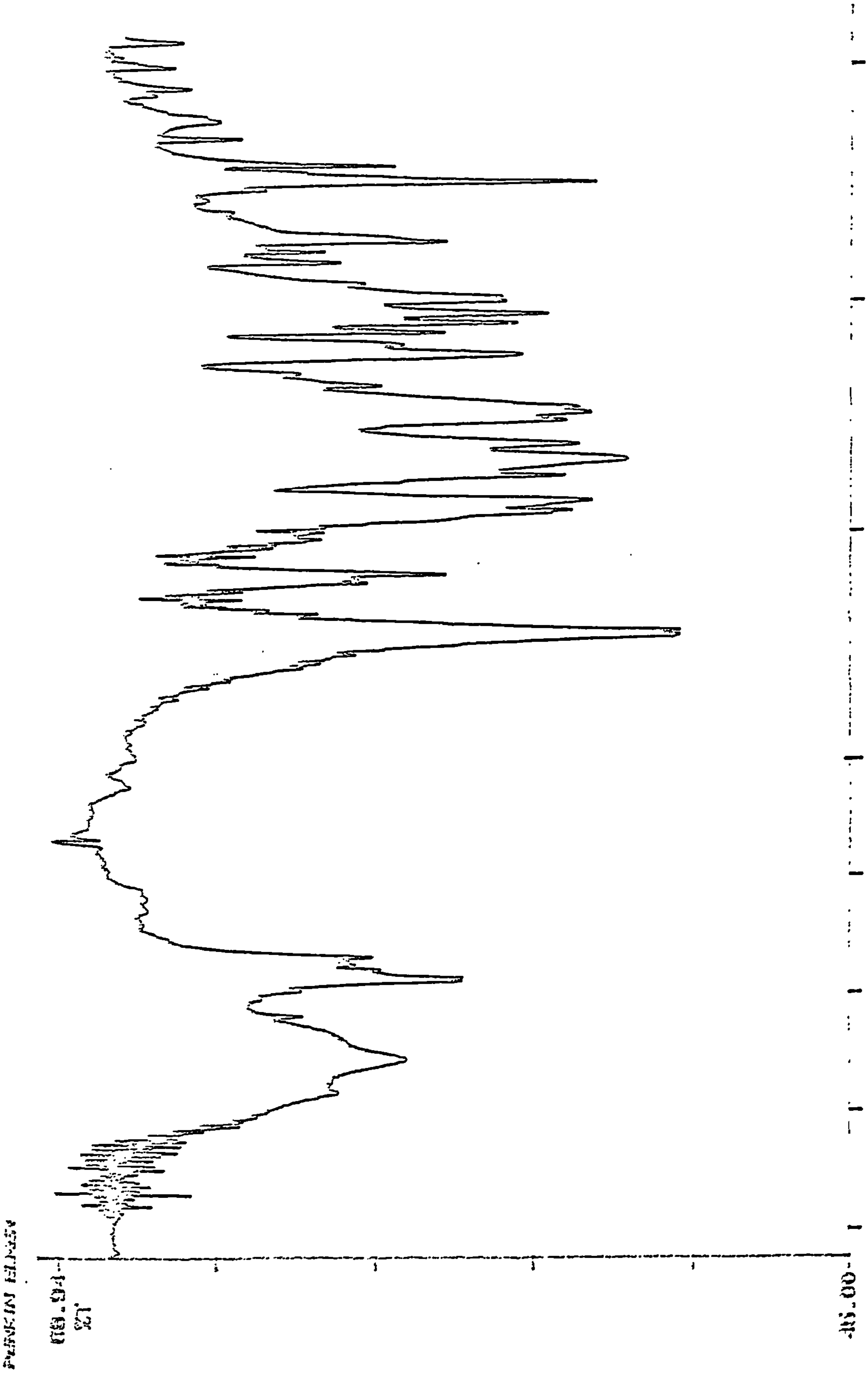
Appendix 1. 35 MS(EI+) spectrum of dimethyl 5-(4-hydroxybutoxy)isophthalate



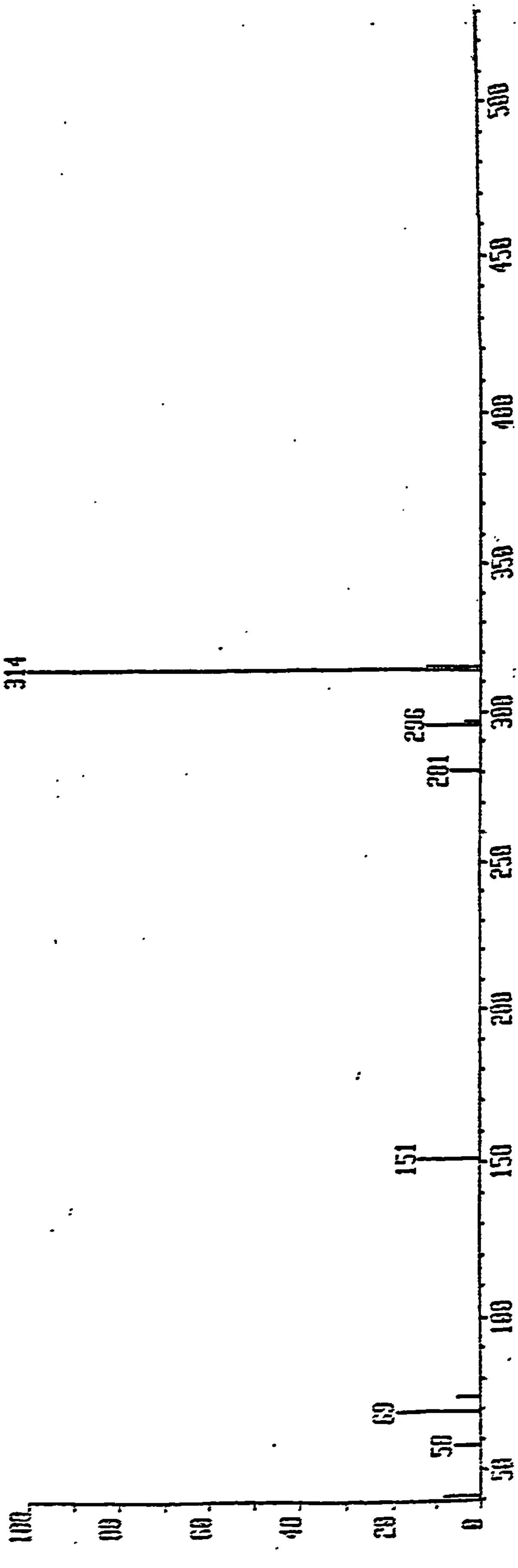
Appendix 1. 36 ^{1}H nmr spectrum (400 MHz) of dimethyl 5-(5-hydroxypentoxy)isophthalate



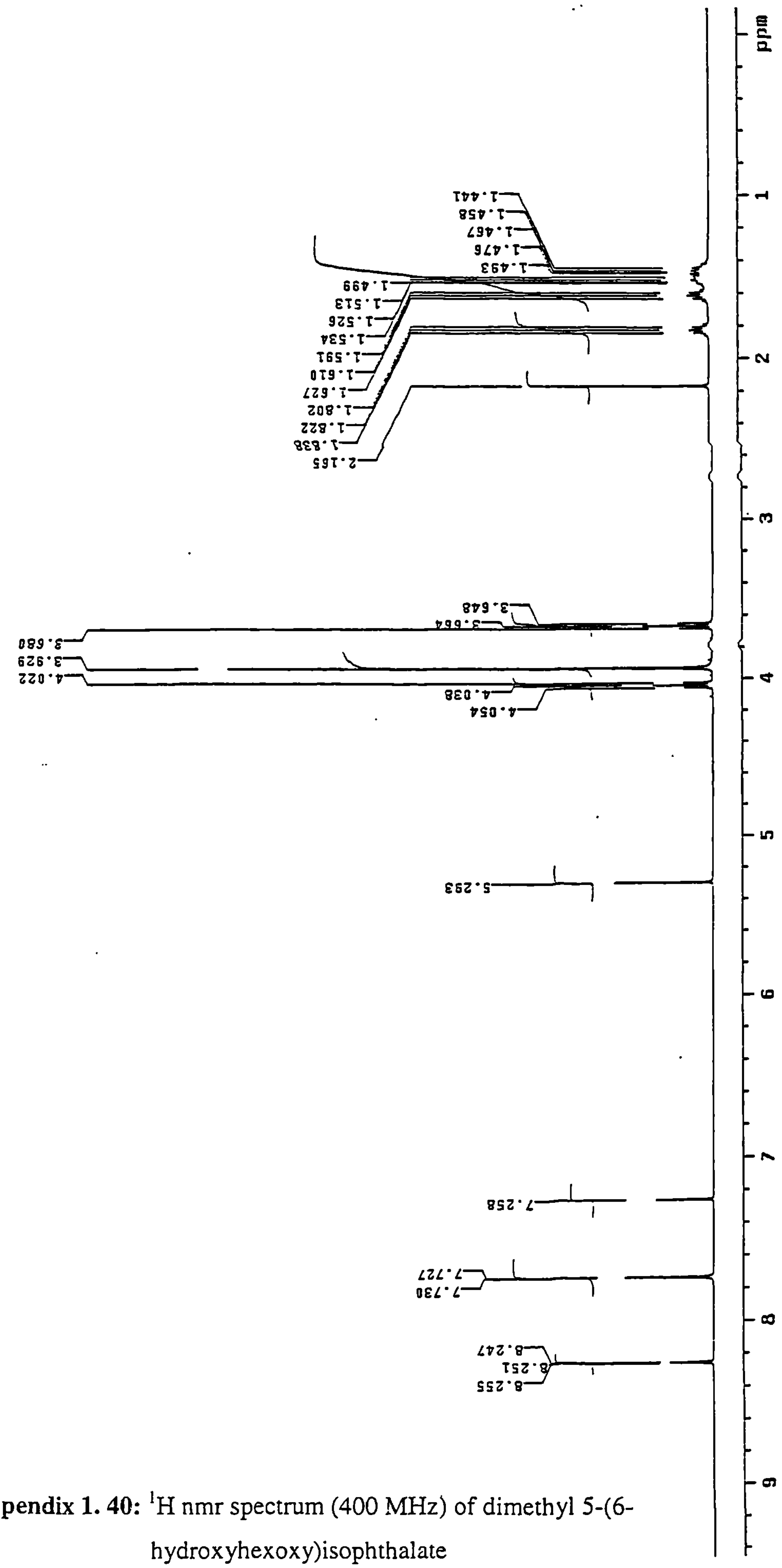
Appendix 1. 37 ^{13}C nmr spectrum (100 MHz) of dimethyl 5-(5-hydroxypentoxy)isophthalate



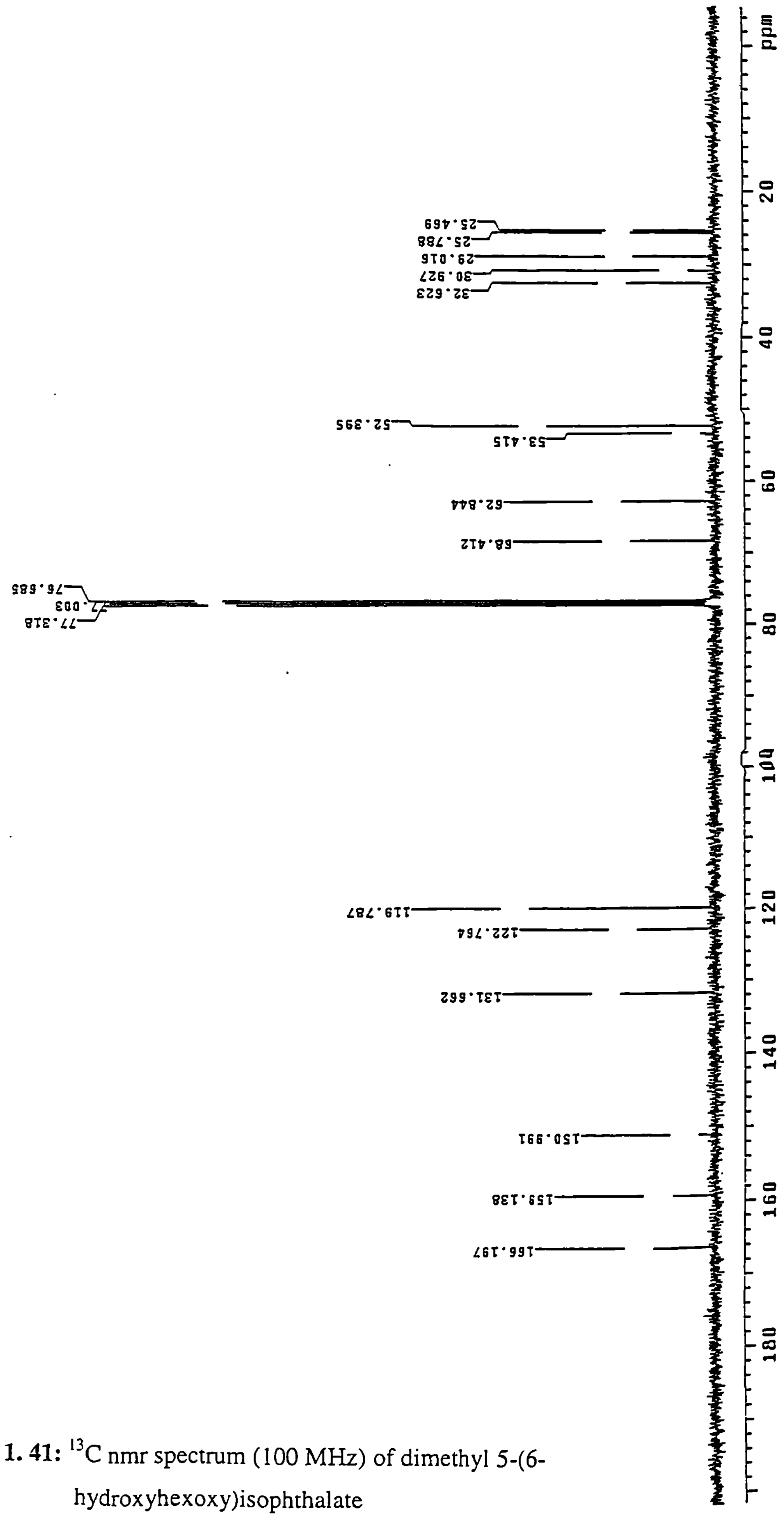
Appendix 1. 38: FTIR (KBr disc) spectrum of dimethyl 5-(5-hydroxypentoxy)isophthalate



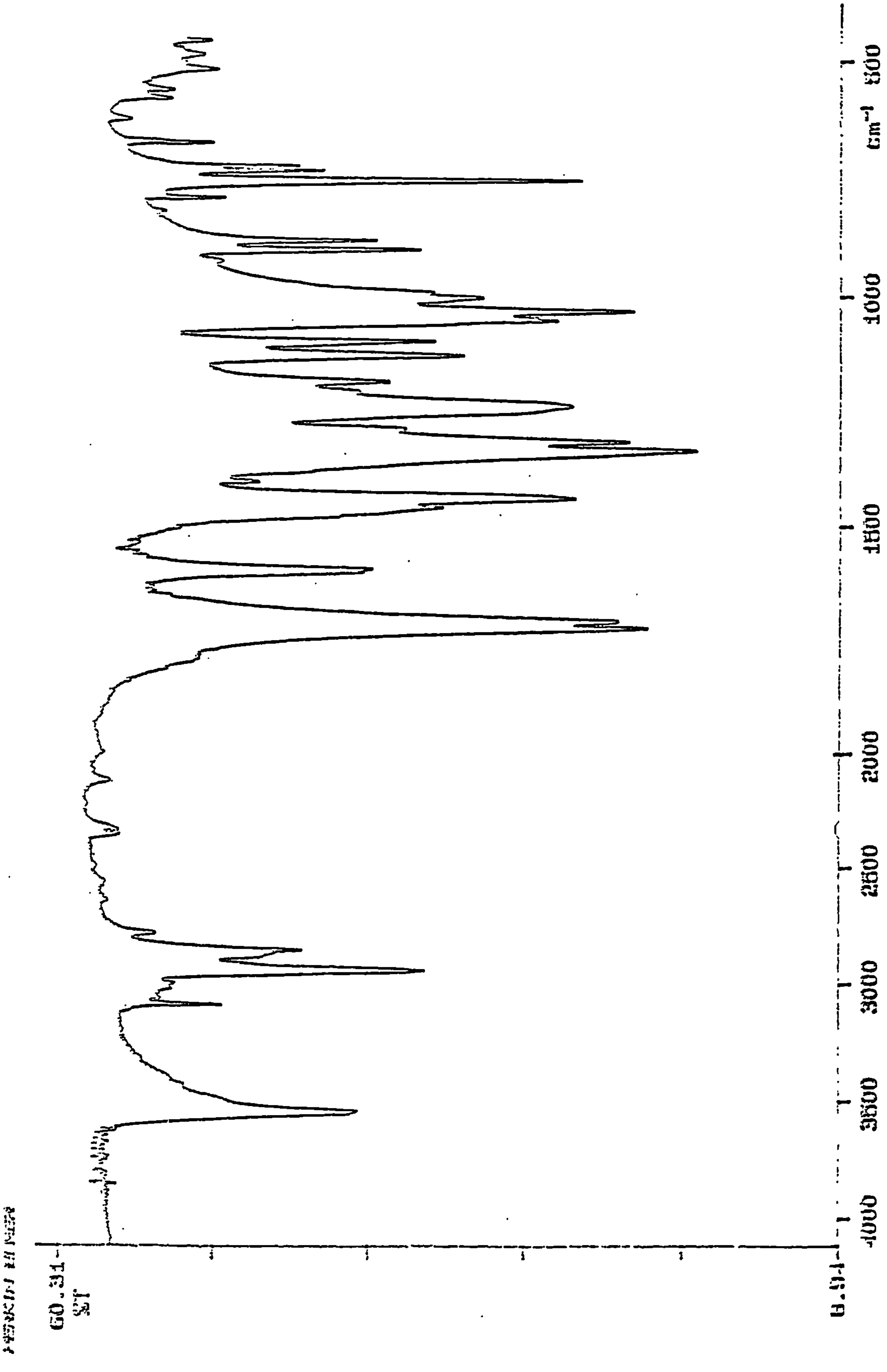
Appendix 1. 39: MS(CI+) spectrum of dimethyl 5-(5-hydroxypentoxy)isophthalate



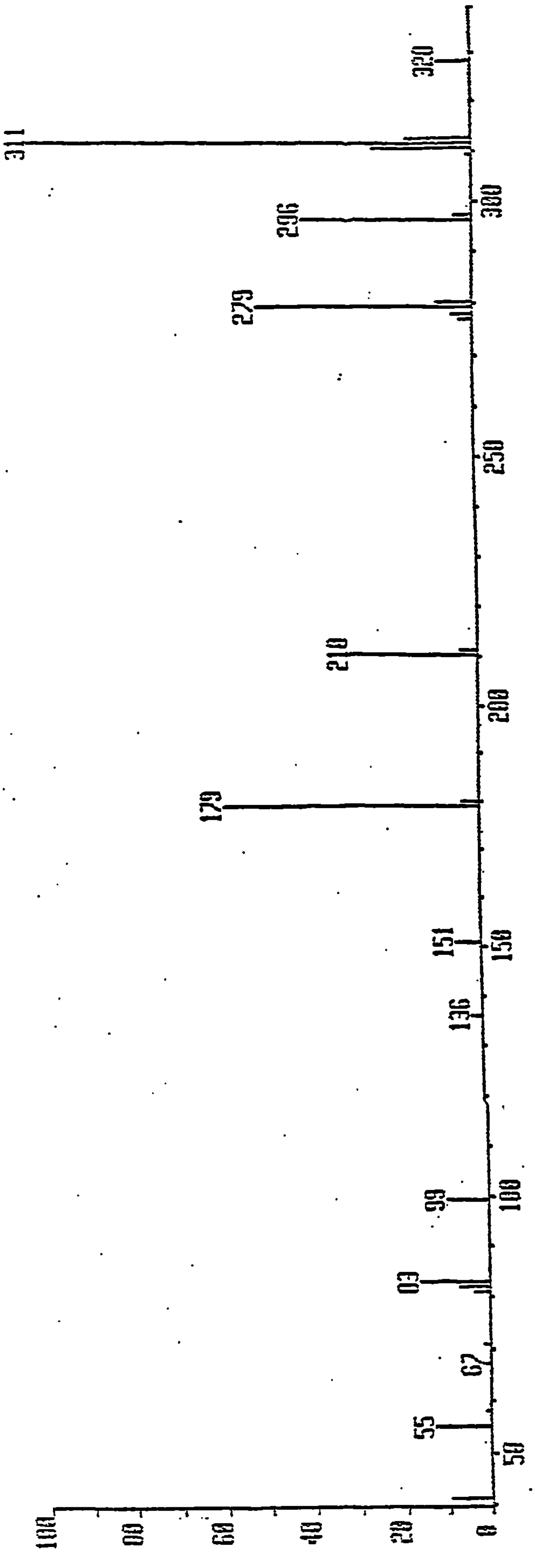
Appendix 1. 40: ^{1}H nmr spectrum (400 MHz) of dimethyl 5-(6-hydroxyhexoxy)isophthalate



Appendix 1. 41: ^{13}C nmr spectrum (100 MHz) of dimethyl 5-(6-hydroxyhexoxy)isophthalate



Appendix 1. 42: FTIR (KBr disc) spectrum of dimethyl 5-(6-hydroxyhexoxy)isophthalate



Appendix 1. 43: MS(CI+) spectrum of dimethyl 5-(6-hydroxyhexoxy)isophthalate

APPENDIX TWO

EXPERIMENTAL FOR CHAPTER 3

Experimental

Size exclusion chromatography (SEC):

Chloroform SEC was carried out at room temperature using a HPLC pump (PL: LC 110) with a solvent flow rate of 1cm^{3}min^{-1}. Polymer solutions (4-10mg/ml) were filtered through a Whatman 0.2μm filter to remove particles before injection. A guard column (5 x 0.75cm, mixed bed PL gel) was used to remove any remaining particles or aggregates. Three GPC columns (3 x 0.75cm) composed of PL gel (mixed styrene-divinyl benzene beads with diameters ranging between 3 and 100μm, pore sizes 100Å, 10^{3}Å and 10^{5}Å) were used in a series to separate the mixture on the basis of hydrodynamic volume. The columns were calibrated using Polymer Laboratories polystyrene standards (162-1040 000 amu). A differential refractometer (ERC-7515A) and a data caption unit (PL-DCU) were used in conjunction with PL GPC software (version 5.2) to obtain SEC measurements.

Tetrahydrofuran SEC was carried out using a HPLC pump (PL: LC 1120) with a solvent flow rate of 1cm^{3}min^{-1}, maintained at 30°C using a Knauer oven and control unit. Polymer solutions (1mg/ml) were filtered through a Whatman 0.2μm filter to remove particles before injection. A guard column (5 x 0.75cm, mixed bed PL gel) was used to remove any remaining particles or aggregates. Three GPC columns (3 x 0.75cm) composed of PL gel (mixed styrene-divinyl benzene beads, mixed pore sizes) were used to separate the mixture. The columns were calibrated using Polymer Laboratories polystyrene standards (162-1040 000 amu). A Viscotek differential refractometer and viscometer detector were used and the data were analysed using Viscotek Unical GPC-viscometry software version 4.06.

Thermal analysis:

Thermogravimetric analysis (TGA) was performed on a Stanton Redcroft TG760 thermobalance, at a heating rate of 10°Cmin^{-1} in a nitrogen atmosphere.

Differential scanning calorimetry (DSC) measurements were recorded using a Perkin Elmer DSC 7, under a nitrogen atmosphere. Each polymer was annealed at 200°C for 2 minutes, the sample was cooled at a rate of 200°Cmin^{-1} to 25°C where it was held for a further 5 minutes. A DSC trace was recorded at a heating rate of 10°Cmin^{-1} to 200°C. This procedure was repeated at least twice for each polymer sample.

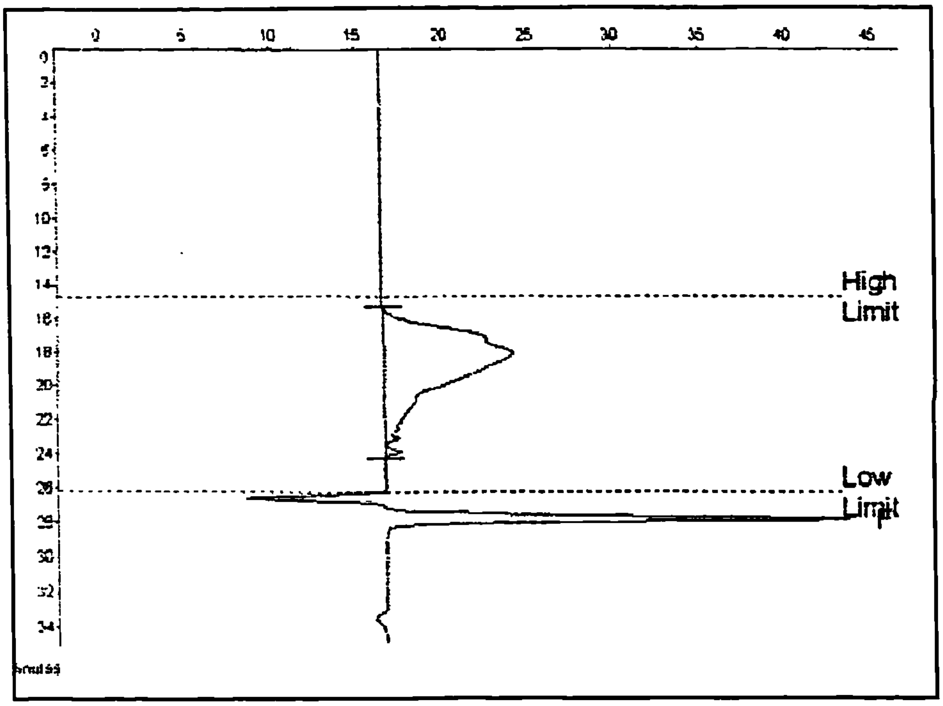
Spectroscopic analysis:

^{1}H nmr spectra were recorded using a Varian VXR 400 nmr spectrometer at 399.953 MHz (^{1}H). Deuterated chloroform was used as solvent with tetramethylsilane as an internal reference.

APPENDIX THREE

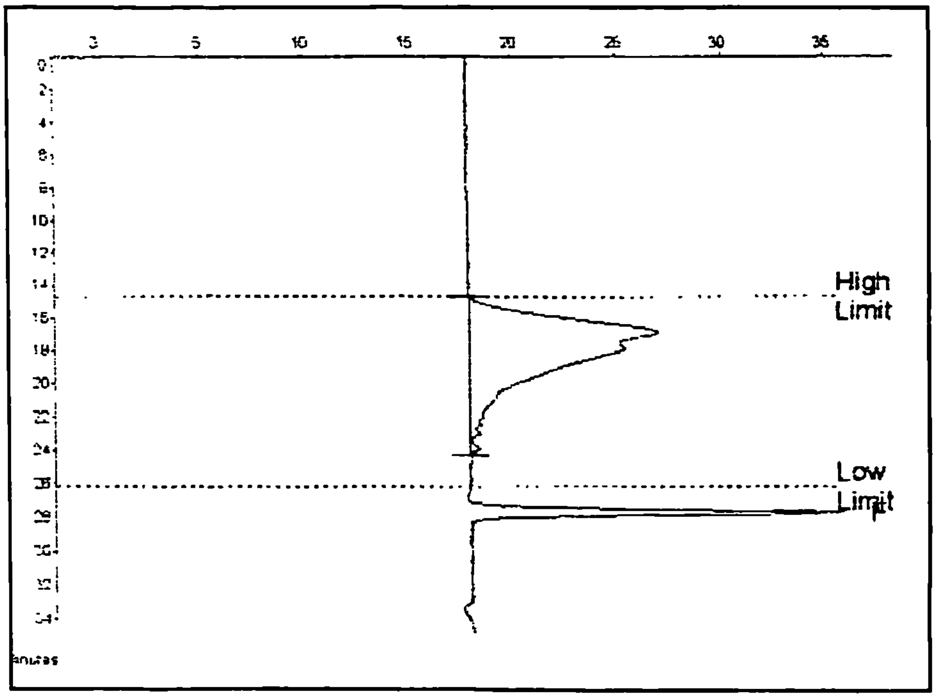
CHARACTERISATION DATA FOR CHAPTER FIVE

M_n = 8 500, M_w = 53 200, polydispersity = 6.3



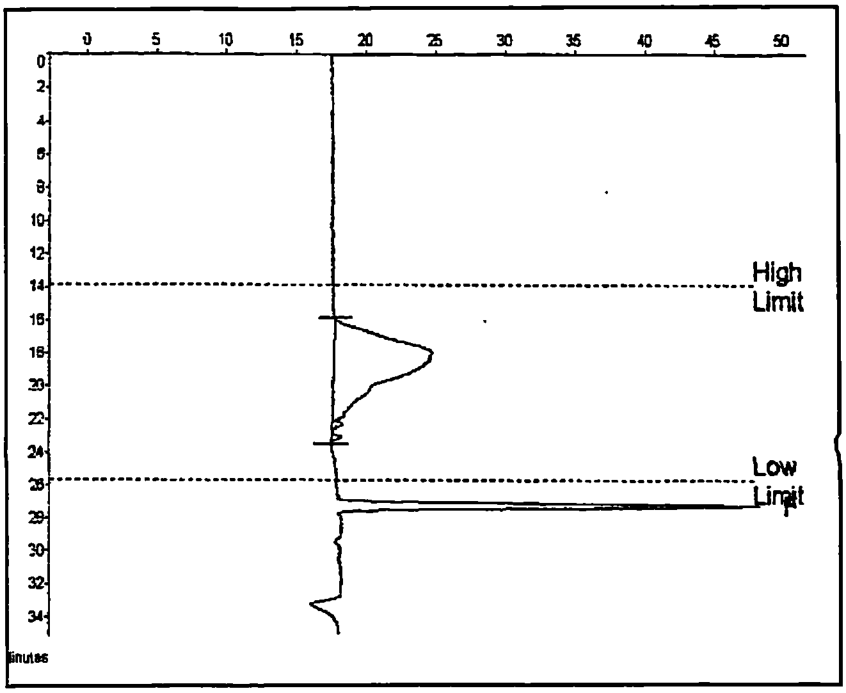
Appendix 3. 1: $CHCl_3$ SEC trace of hyperbranched poly(dimethyl 5-(3-hydroxypropoxy)isophthalate), **12**

M_n = 13 800, M_w = 101 100, polydispersity = 7.3



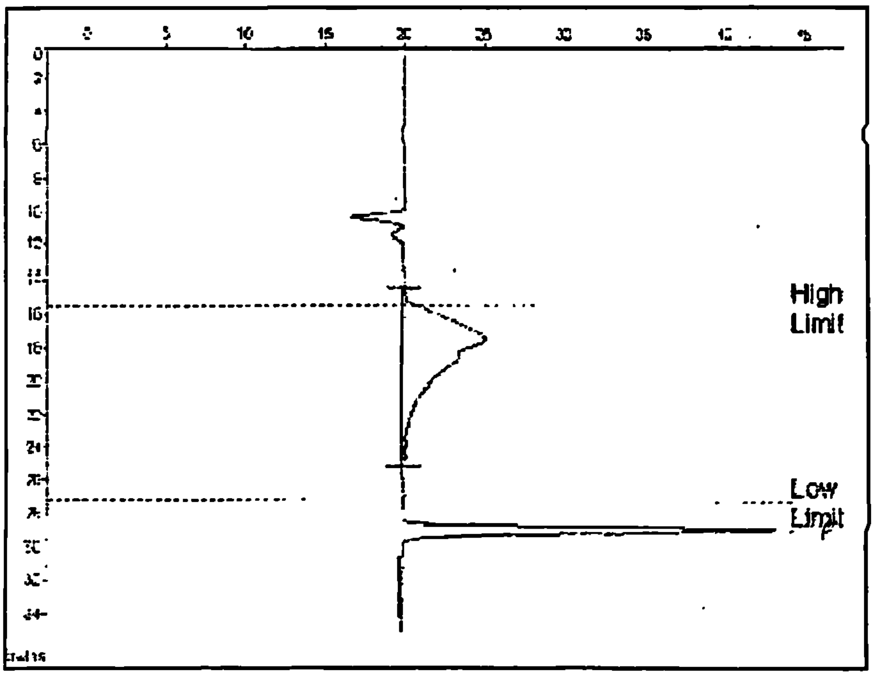
Appendix 3. 2: $CHCl_3$ SEC trace of hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophthalate), **13**

$M_n = 8\ 300$, $M_w = 30\ 700$, polydispersity = 3.7

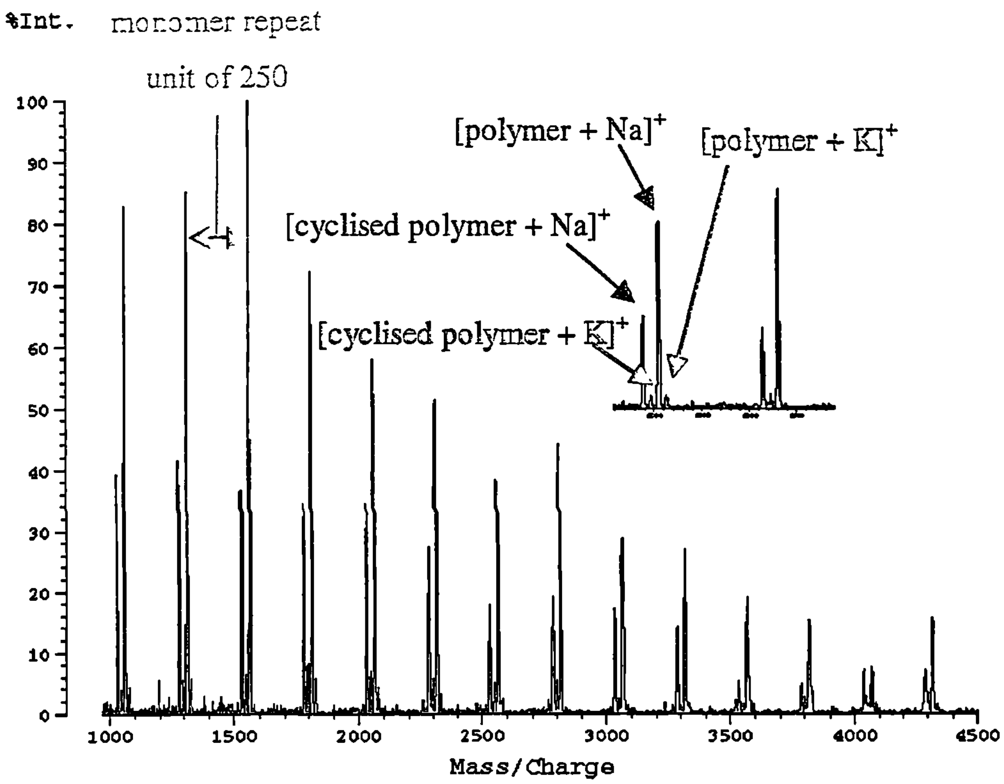


Appendix 3. 3: $CHCl_3$ SEC trace of hyperbranched poly(dimethyl 5-(5-hydroxypentoxy)isophthalate), **14**

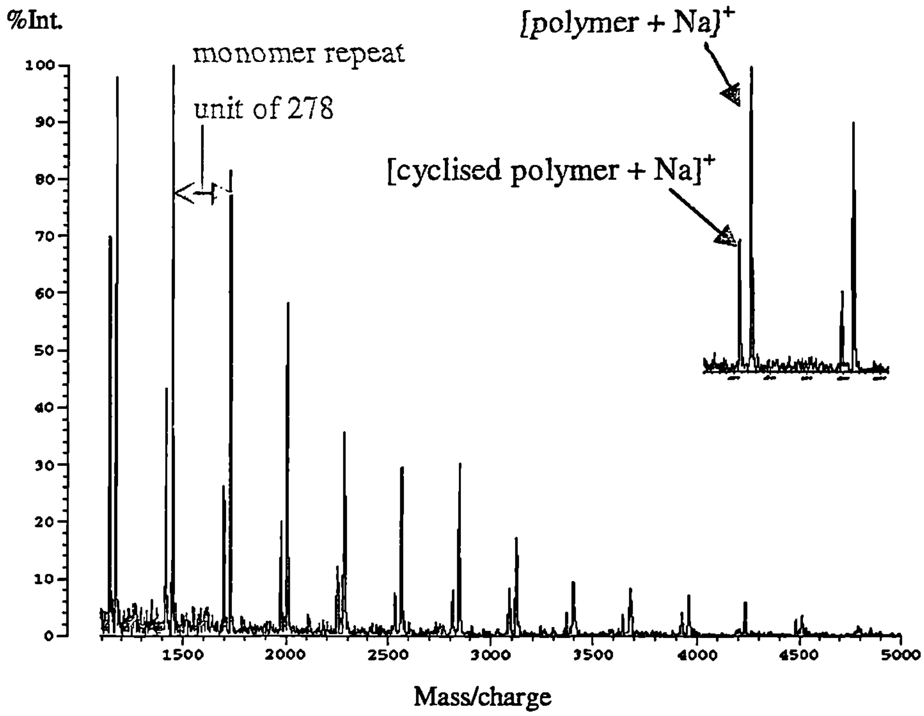
$M_n = 17\ 900$, $M_w = 141\ 700$, polydispersity = 8.0



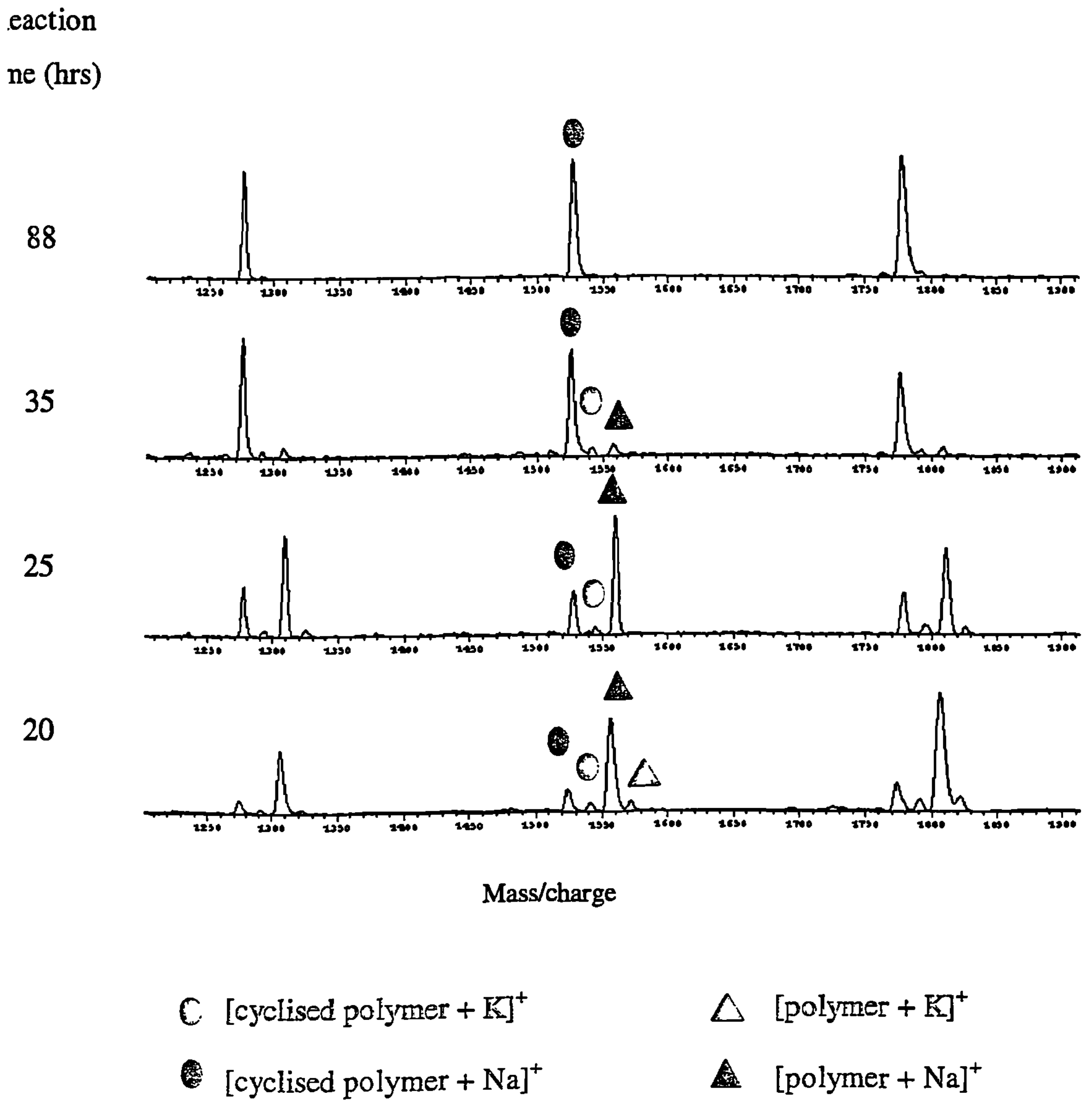
Appendix 3. 4: $CHCl_3$ SEC trace of hyperbranched poly(dimethyl 5-(6-hydroxyhexoxy)isophthalate), **15**



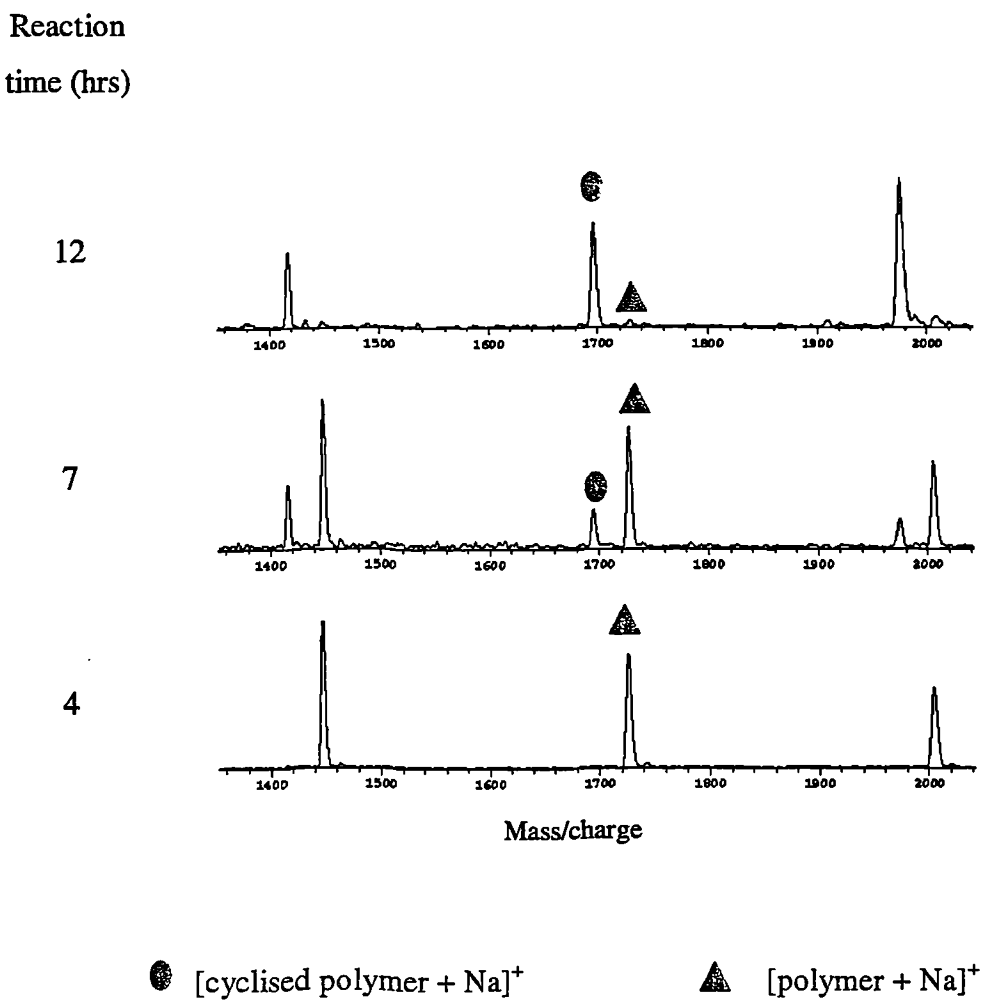
Appendix 3. 5: MALDI-TOF mass spectrum of hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophthalate), **13**



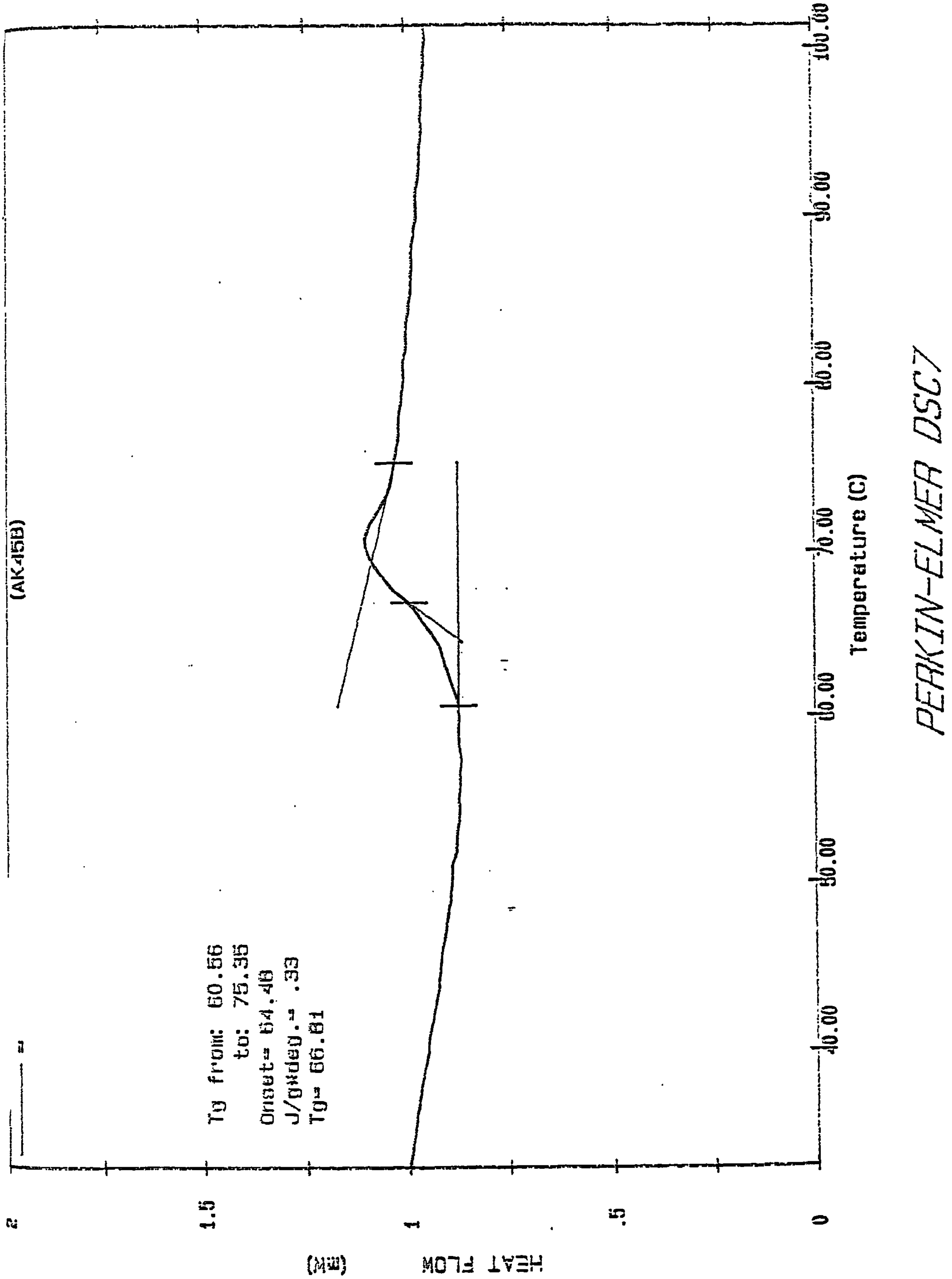
Appendix 3. 6: MALDI-TOF mass spectrum of hyperbranched poly(dimethyl 5-(6-hydroxyhexoxy)isophthalate), **15**



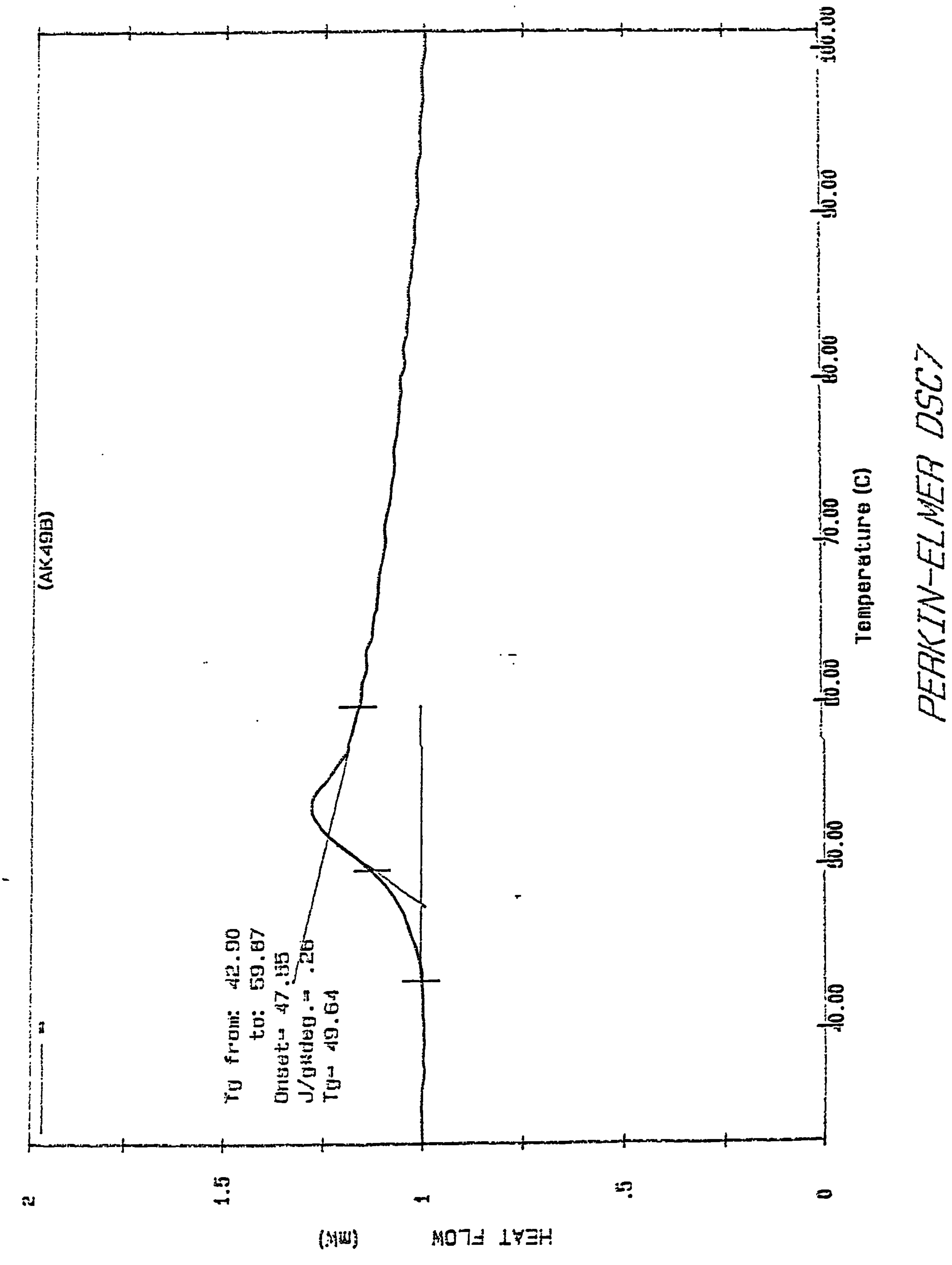
Appendix 3. 7: Change in MALDI-TOF mass spectra with reaction time for hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophthalate), **13**, prepared with no catalyst



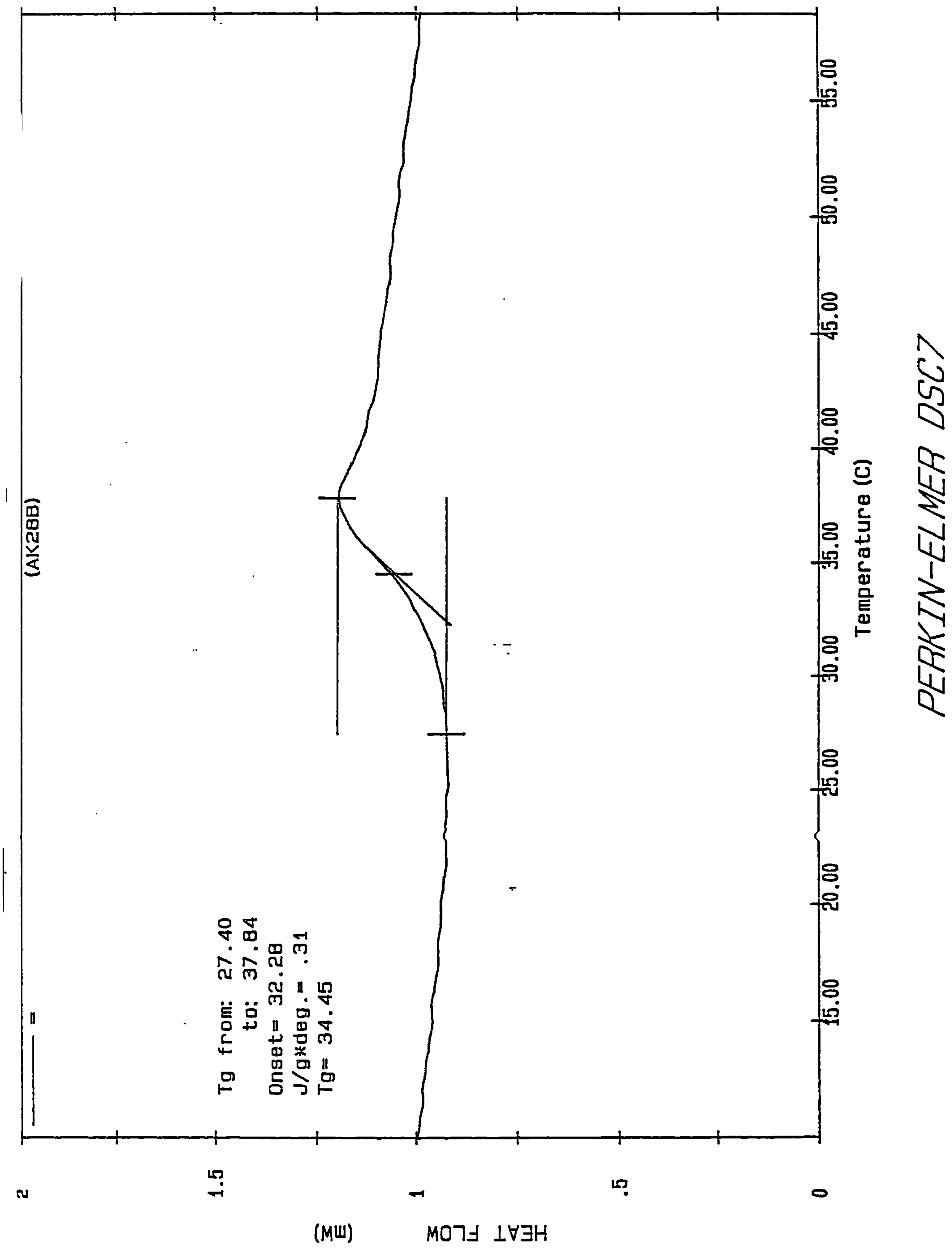
Appendix 3. 8: Change in MALDI-TOF mass spectra with reaction time for hyperbranched poly(dimethyl 5-(6-hydroxyhexoxy)isophthalate), **15**, prepared with antimony trioxide and manganese acetate catalyst system



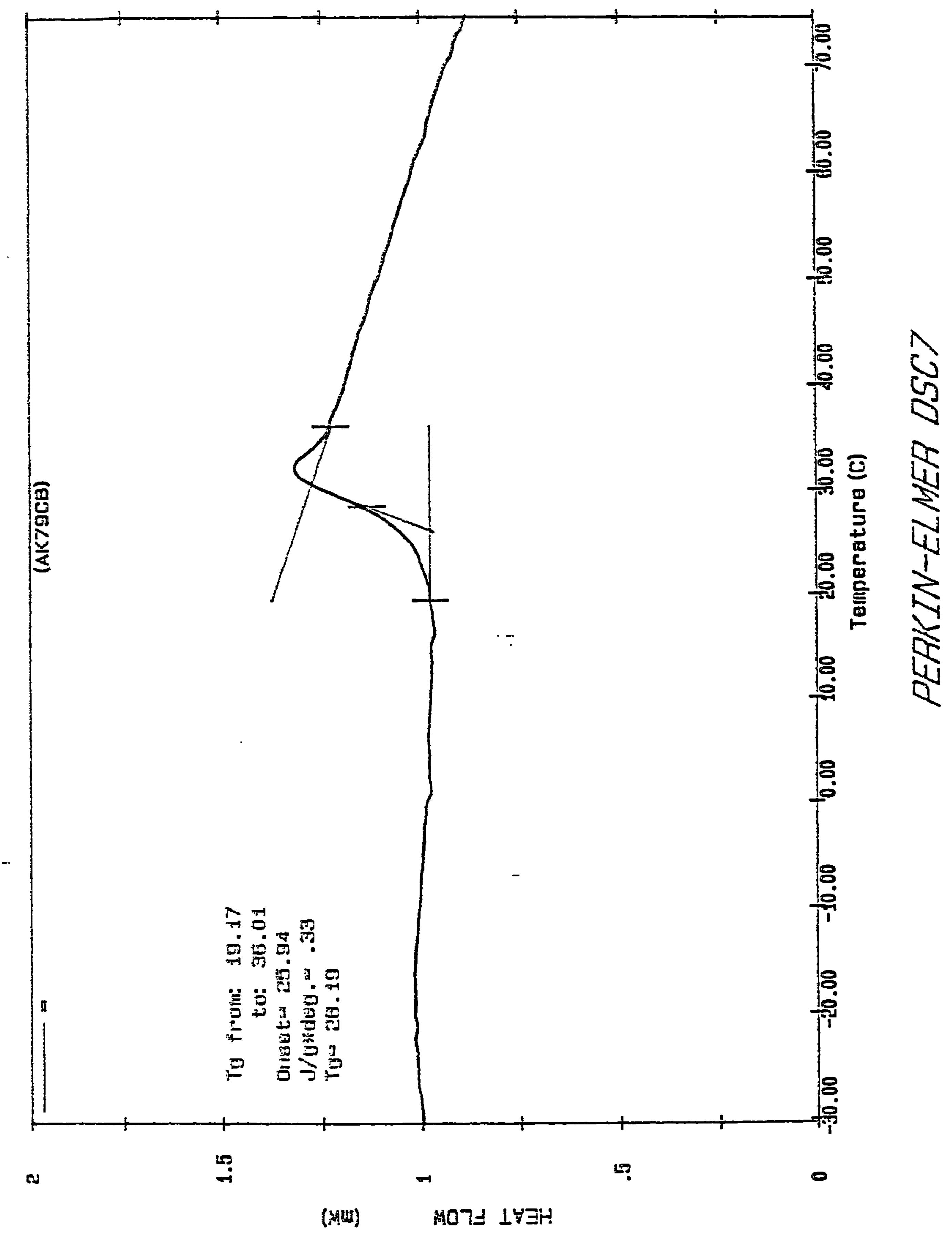
Appendix 3. 9: DSC trace of hyperbranched poly(dimethyl 5-(3-hydroxypropoxy)isophthalate), 12



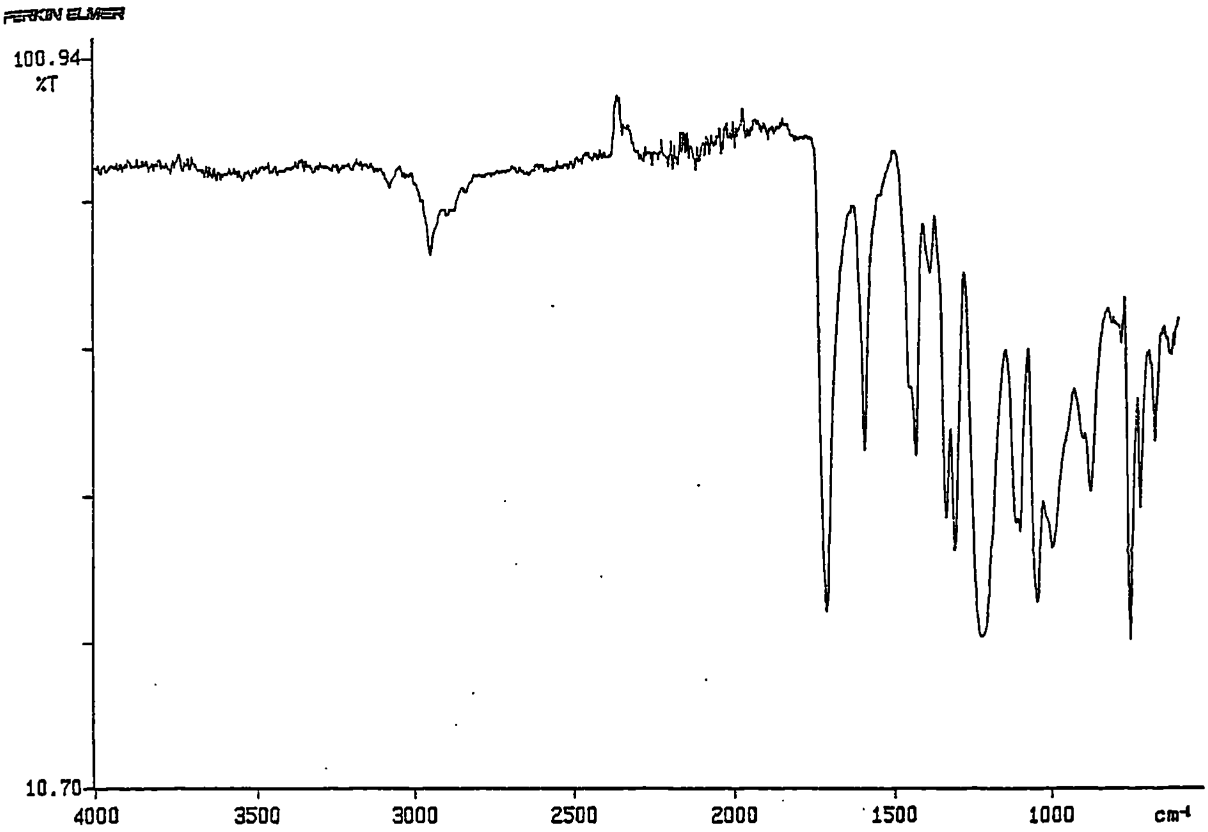
Appendix 3. 10: DSC trace of hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophthalate), **13**



Appendix 3. 11: DSC trace of hyperbranched poly(dimethyl 5-(5-hydroxypentoxy)isophthalate), **14**



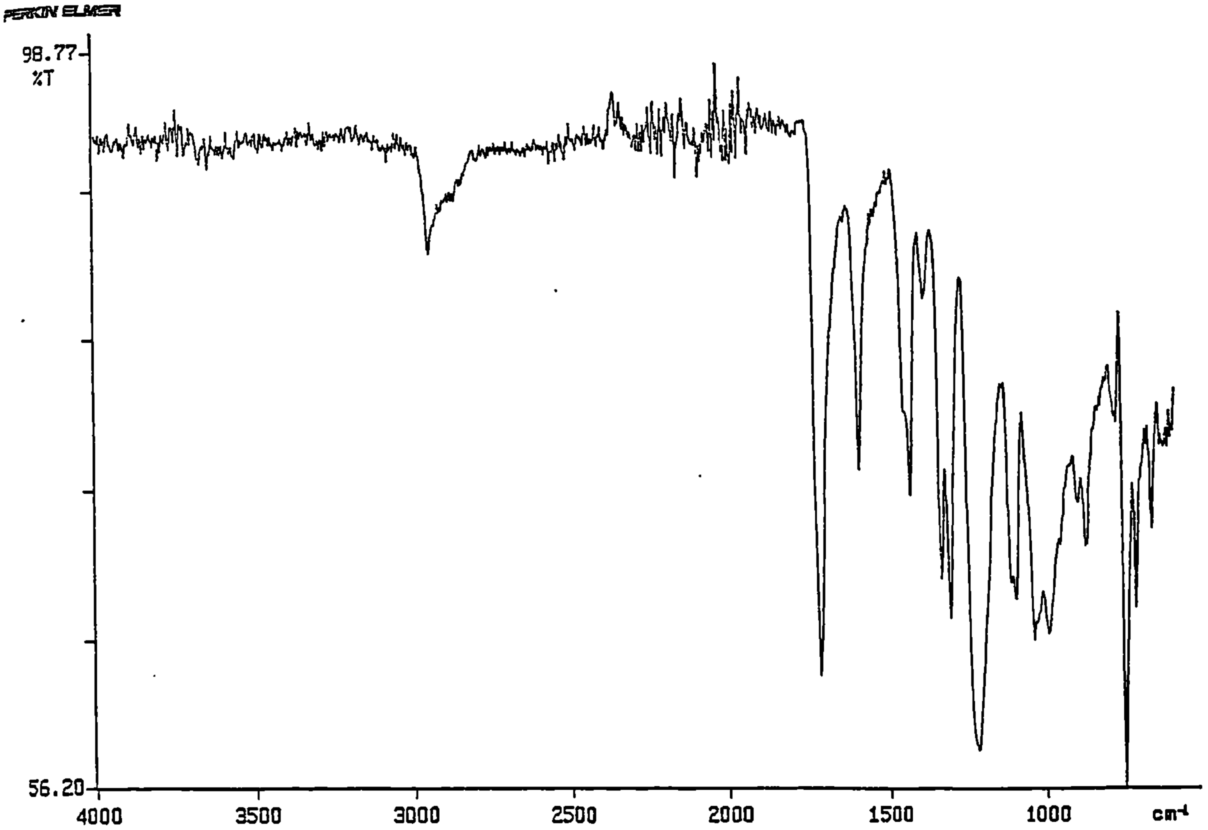
Appendix 3. 12: DSC trace of hyperbranched poly(dimethyl 5-(6-hydroxyhexoxy)isophthalate), **15**



Assignment of infrared spectrum for the hyperbranched poly(dimethyl 5-(3-hydroxypropoxy)isophthalate), **12**.

Shift cm^{-1}	Assignment
3080.2	w, aryl-H C-H stretch
2951.3	w, saturated C-H stretch
1715.4	s, aromatic C=O stretch
1593.2	m, aryl-H C-H vibration
1432.2	m, saturated C-H bend
1220.0	s, aryl C-O stretch
753.1	s, aryl H out of plane vibration

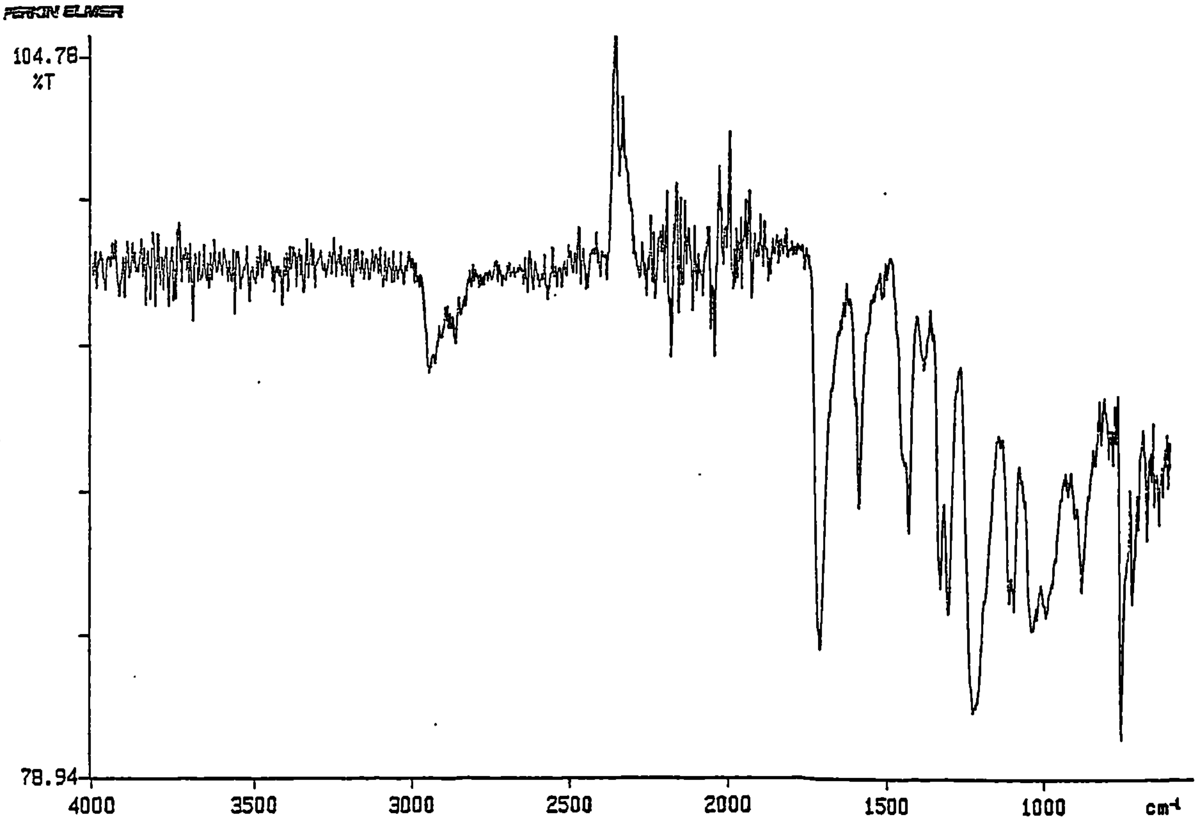
Appendix 3. 13: Infrared spectrum (solid) of the hyperbranched poly(dimethyl 5-(3-hydroxypropoxy)isophthalate), **12**.



Assignment of infrared spectrum for the hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophthalate), **13**.

Shift cm^{-1}	Assignment
3080.5	w, aryl-H C-H stretch
2951.6	w, saturated C-H stretch
1715.2	s, aromatic C=O stretch
1593.2	m, aryl-H C-H vibration
1432.3	m, saturated C-H bend
1218.1	s, aryl C-O stretch
752.8	s, aryl H out of plane vibration

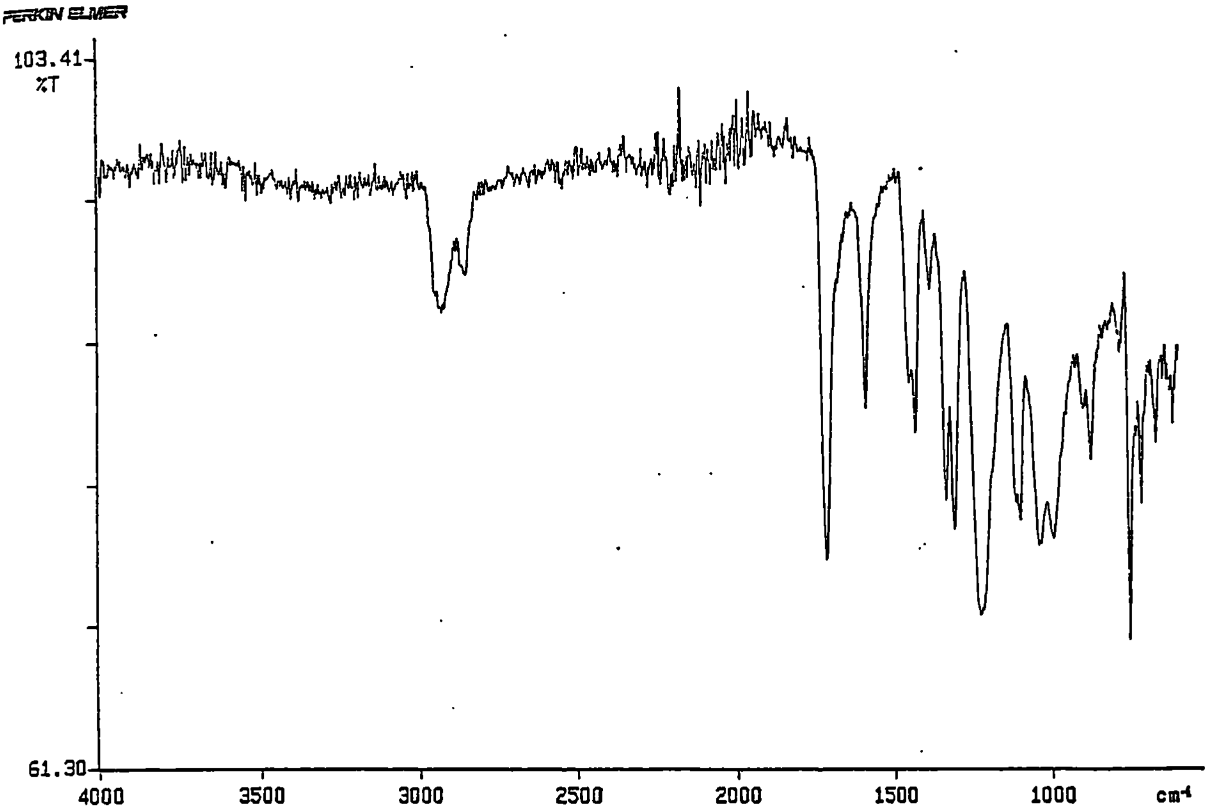
Appendix 3. 14: Infrared spectrum (solid) of the hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophthalate), **13**.



Assignment of infrared spectrum for the hyperbranched poly(dimethyl 5-(5-hydroxypentoxy)isophthalate), **14**.

Shift cm^{-1}	Assignment
2951.3	w, saturated C-H stretch
1713.8	s, aromatic C=O stretch
1593.0	m, aryl-H C-H vibration
1432.3	m, saturated C-H bend
1227.7	s, aryl C-O stretch
752.8	s, aryl H out of plane vibration

Appendix 3. 15: Infrared spectrum (solid) of the hyperbranched poly(dimethyl 5-(5-hydroxypentoxy)isophthalate), **14**.

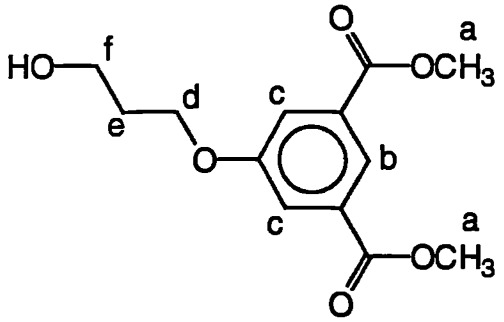


Assignment of infrared spectrum for the hyperbranched poly(dimethyl 5-(6-hydroxyhexoxy)isophthalate), **15**.

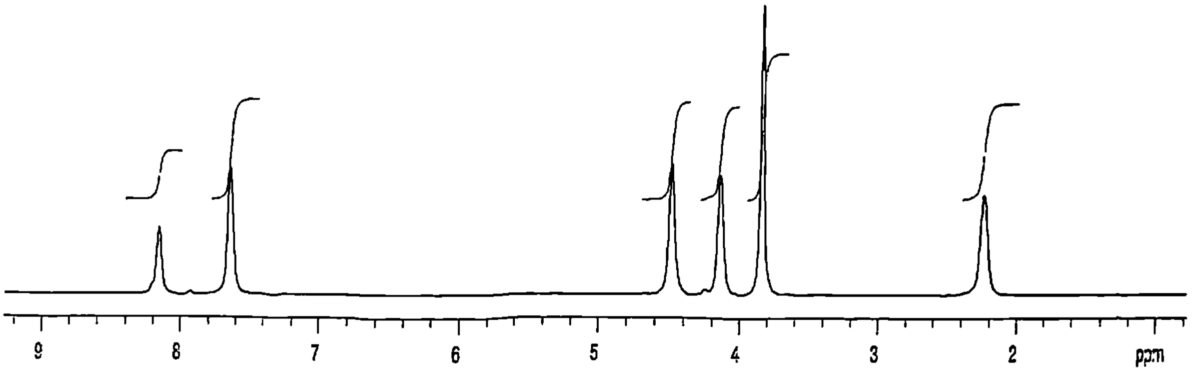
Shift cm^{-1}	Assignment
2929.5	w, saturated C-H stretch
1715.8	s, aromatic C=O stretch
1593.0	m, aryl-H C-H vibration
1432.9	m, saturated C-H bend
1225.6	s, aryl C-O stretch
752.6	s, aryl H out of plane vibration

Appendix 3. 16: Infrared spectrum (solid) of the hyperbranched poly(dimethyl 5-(6-hydroxyhexoxy)isophthalate), **15**.

Assignment of ^{1}H nmr spectrum for the hyperbranched polymer (**12**) derived from monomer **8**:

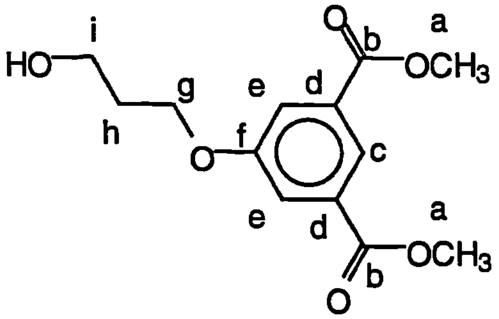


Shift δppm	Integral	Assignment
2.24	2.0	e
3.85	3.3	a
4.15	2.1	d
4.49	2.1	f
7.65	2.0	c
8.16	1.1	b

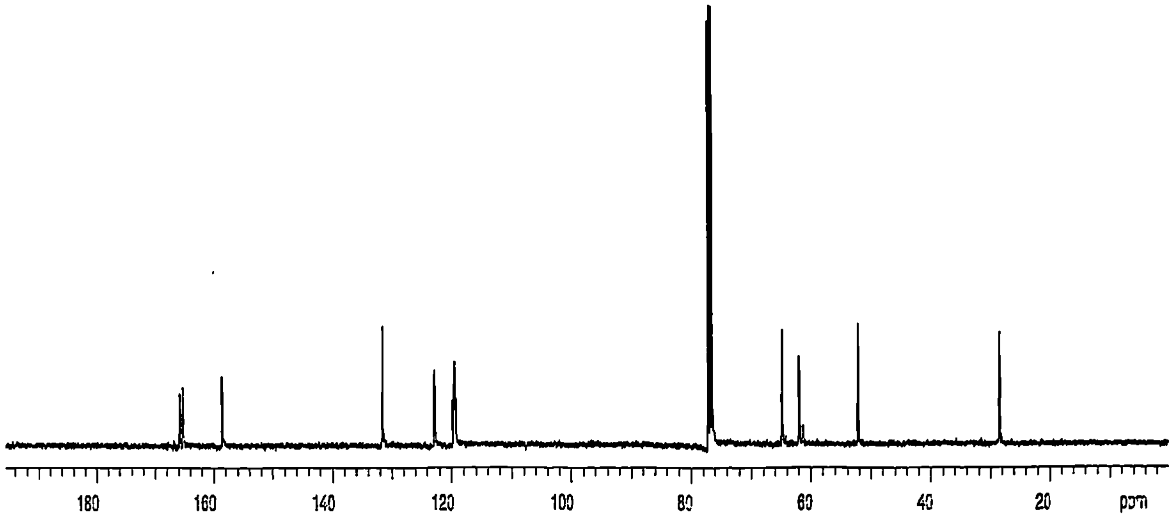


Appendix 3. 17: ^{1}H nmr spectrum (400MHz) of the hyperbranched poly(dimethyl 5-(3-hydroxypropoxy)isophthalate), **12.**

Assignment of ^{13}C nmr spectrum for the hyperbranched polymer derived (**12**) from monomer **8**:

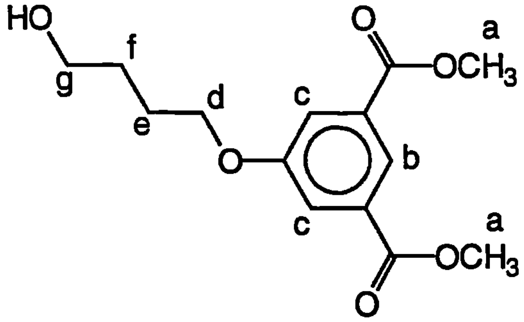


Shift δppm	Assignment
28.6	h
52.4	a
62.2	g
65.1	i
119.7, 119.9	e
123.0	c
131.8	d
158.8	f
165.4, 166.0	b

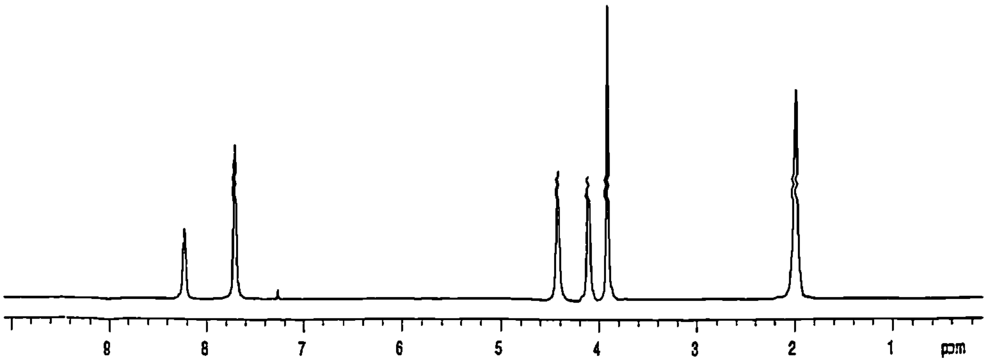


Appendix 3. 18: ^{13}C nmr spectrum (100MHz) of the hyperbranched poly(dimethyl 5-(3-hydroxypropoxy)isophthalate), **12.**

Assignment of ^1H nmr spectrum for the hyperbranched polymer (**13**) derived from monomer **9**:

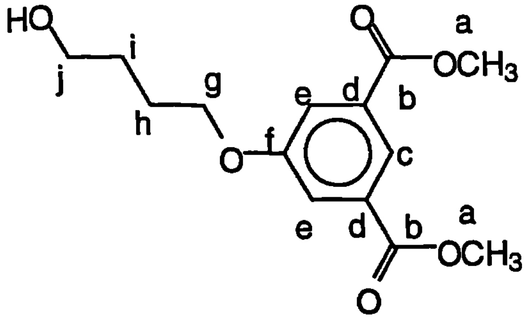


Shift δppm	Multiplicity	Assignment
1.99	4	e, f
3.92	3.2	a
4.13	2.1	d
4.43	2.1	g
7.72	2.1	c
8.23	0.99	b

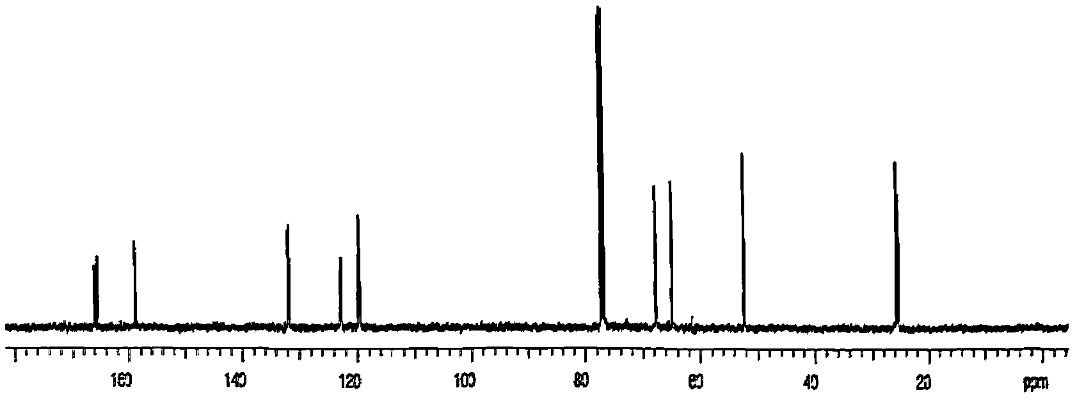


Appendix 3. 19: ^1H nmr spectrum (400MHz) of the hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophthalate), **13**.

Assignment of ^{13}C nmr spectrum for the hyperbranched polymer (13) derived from monomer 9:

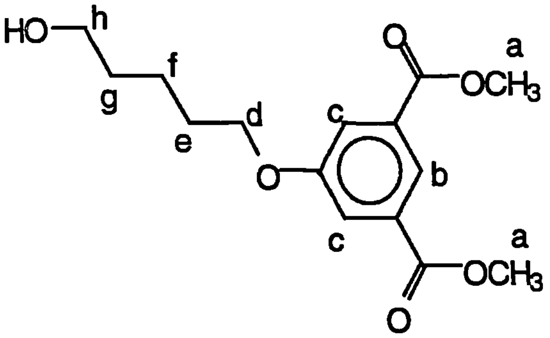


Shift δppm	Assignment
25.4	h
25.8	i
52.4	a
64.9	g
67.8	j
119.5, 119.7, 119.8	e
122.8	c
131.6, 131.8	d
158.9	f
165.6, 166.0	b

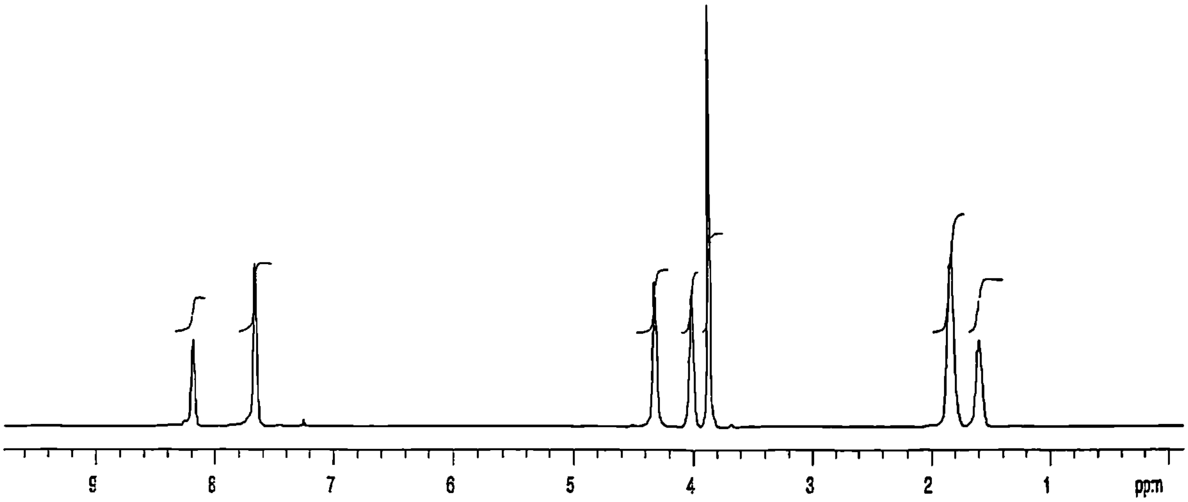


Appendix 3. 20: ^{13}C nmr spectrum (100MHz) of the hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophthalate), **13.**

Assignment of ^{1}H nmr spectrum for the hyperbranched polymer (**14**) derived from monomer **10**:

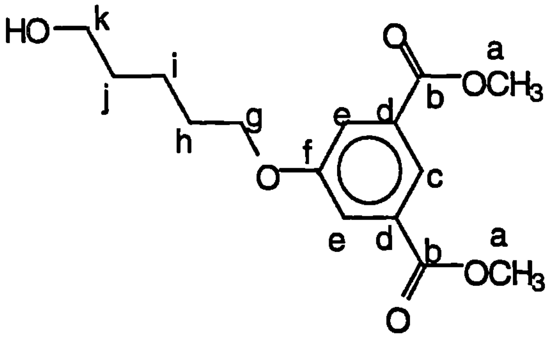


Shift δppm	Multiplicity	Assignment
1.602	1.82	f
1.84	3.6	g, e
3.74	3.4	a
4.02	1.9	d
4.32	1.9	h
7.67	2.1	c
8.19	1	b

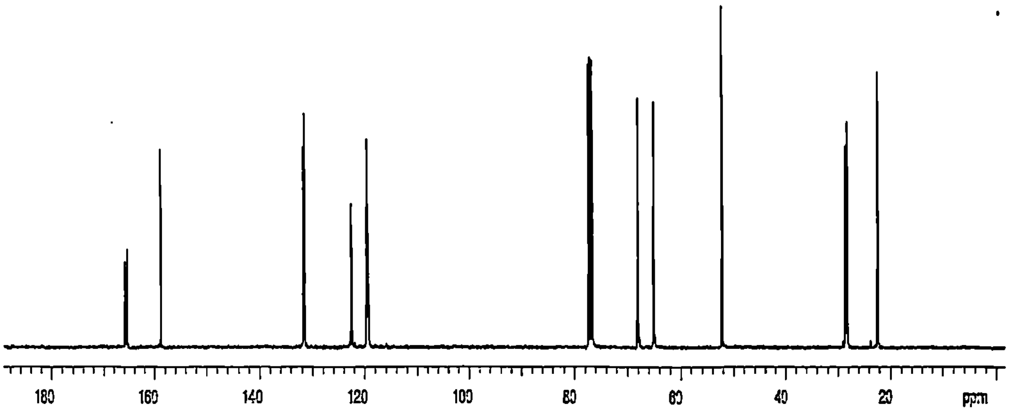


Appendix 3. 21: ^{1}H nmr spectrum (400MHz) of the hyperbranched poly(dimethyl 5-(5-hydroxypentoxy)isophthalate), **14**.

Assignment of ^{13}C nmr spectrum for the hyperbranched polymer (**14**) derived from monomer **10**:

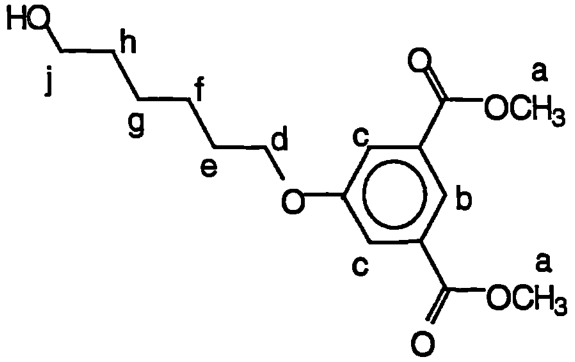


Shift δppm	Assignment	Shift δppm	Assignment
22.4	i	119.4, 119.5, 119.7	e
28.3	h	122.6	c
28.6	j	131.5, 131.8	d
52.2	a	158.9	f
65.0	g	165.5	b
68.0	k		

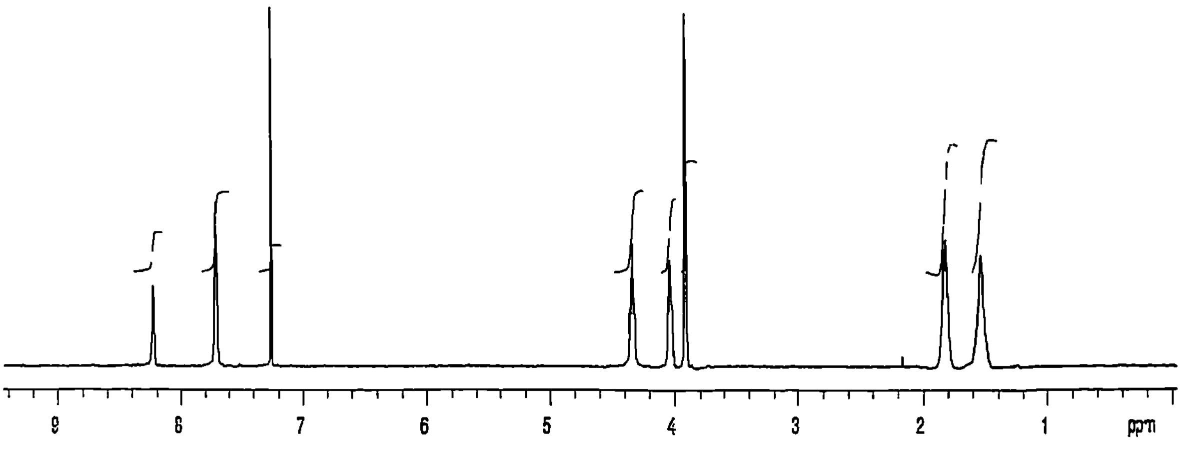


Appendix 3. 22: ^{13}C nmr spectrum (100MHz) of the hyperbranched poly(dimethyl 5-(5-hydroxypentoxy)isophthalate), **14**.

Assignment of ^{1}H nmr spectrum for the hyperbranched polymer (**15**) derived from monomer **11**:

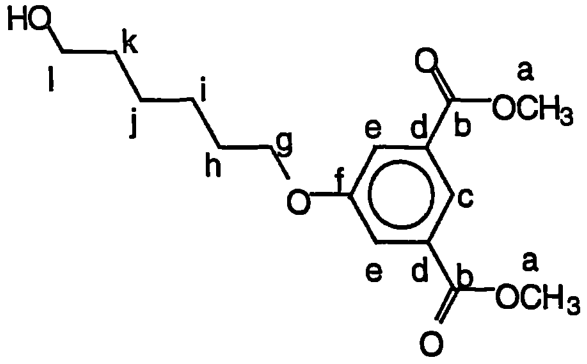


Shift δppm	Multiplicity	Assignment
1.54	4.15	g, f
1.82	3.8	h, e
3.91	3.2	a
4.04	2.2	d
4.34	2.2	h
7.71	2.1	c
8.24	1	b

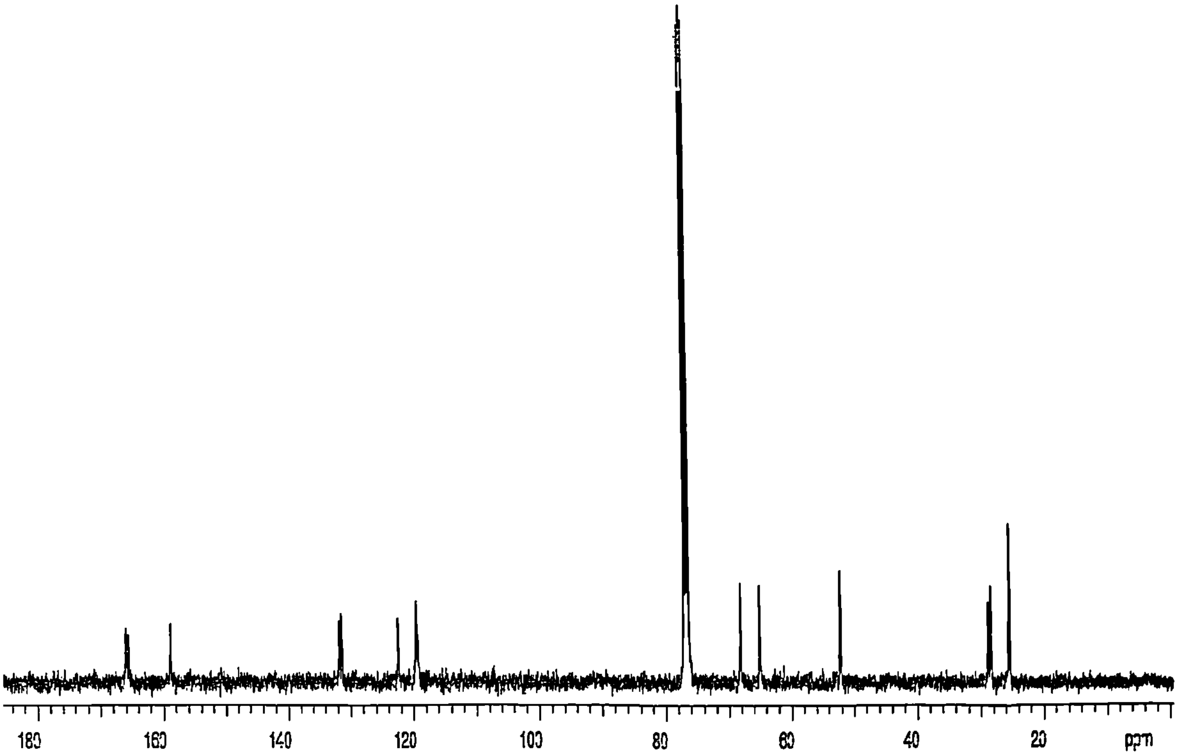


Appendix 3. 23: ^{1}H nmr spectrum (400MHz) of the hyperbranched poly(dimethyl 5-(6-hydroxyhexoxy)isophthalate), **15**.

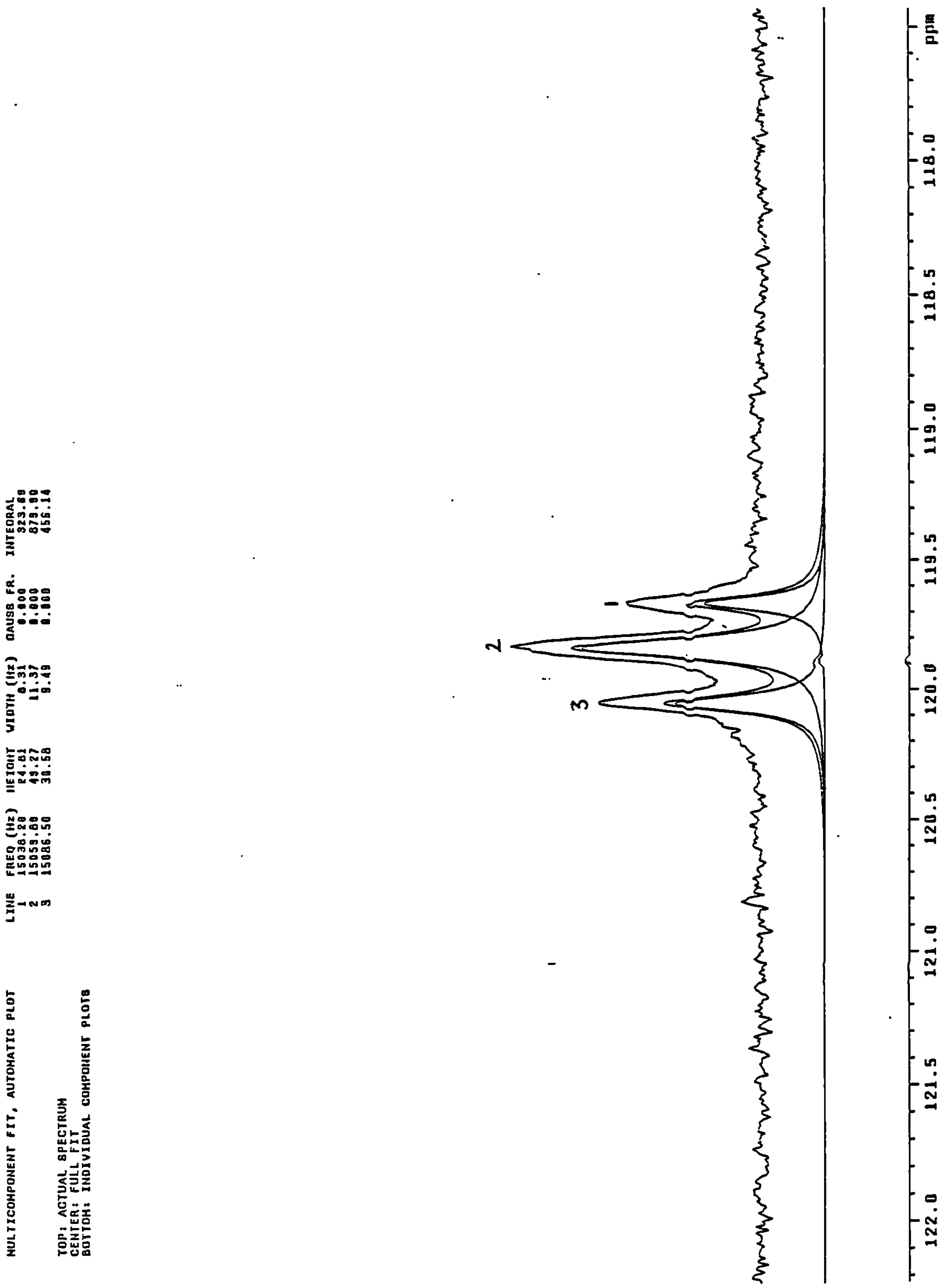
Assignment of ^{13}C nmr spectrum for the hyperbranched polymer (**15**) derived from monomer **11**:



Shift δppm	Assignment	Shift δppm	Assignment
25.7	i, j	119.7, 119.9	e
28.6	h	122.7	c
29.0	k	131.6, 132.0	d
52.3	a	159.1	f
65.3	g	165.7, 166,1	b
68.3	l		

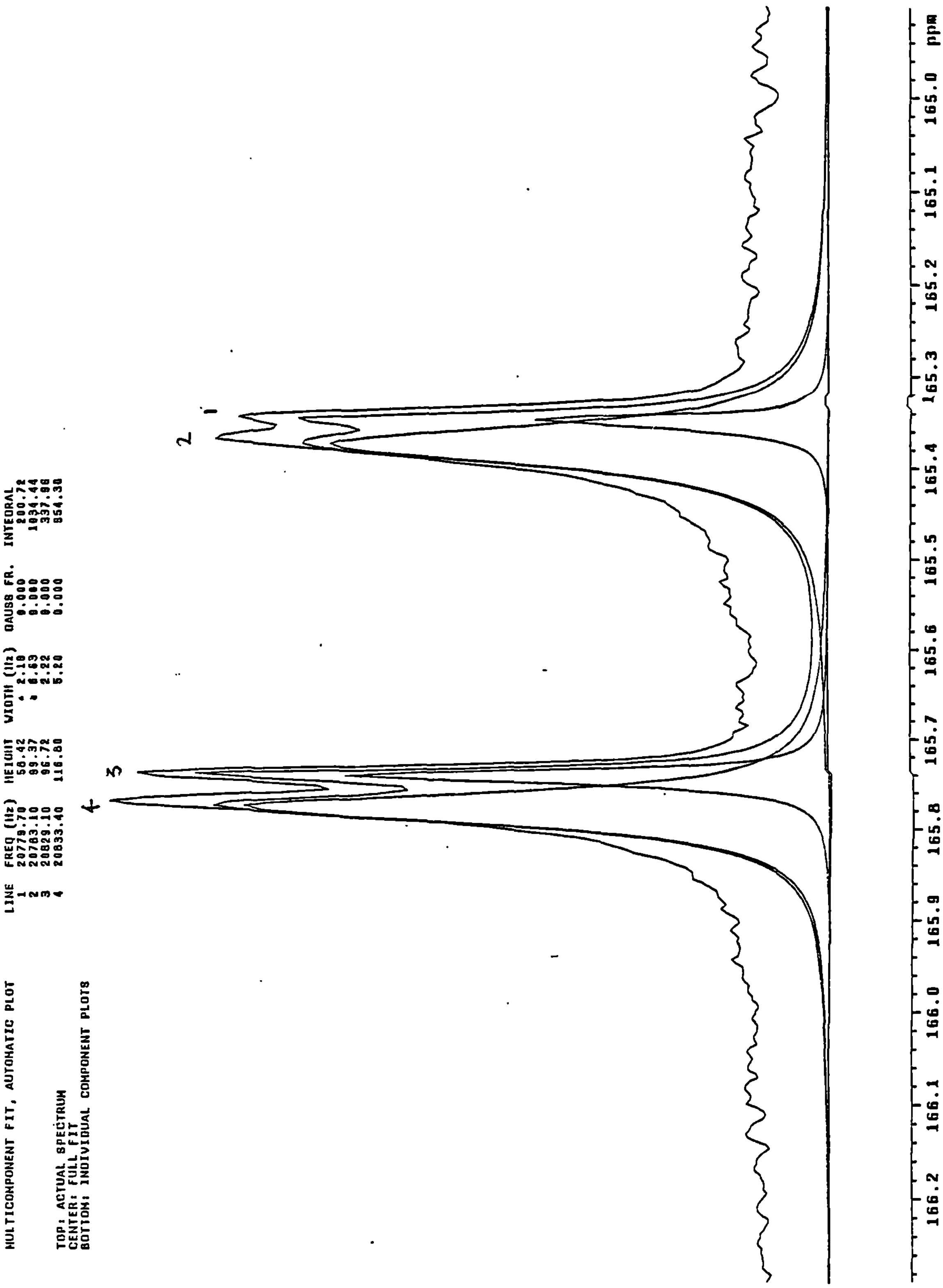


Appendix 3. 24: ^{13}C nmr spectrum (100MHz) of the hyperbranched poly(dimethyl 5-(6-hydroxyhexoxy)isophthalate), **15**.



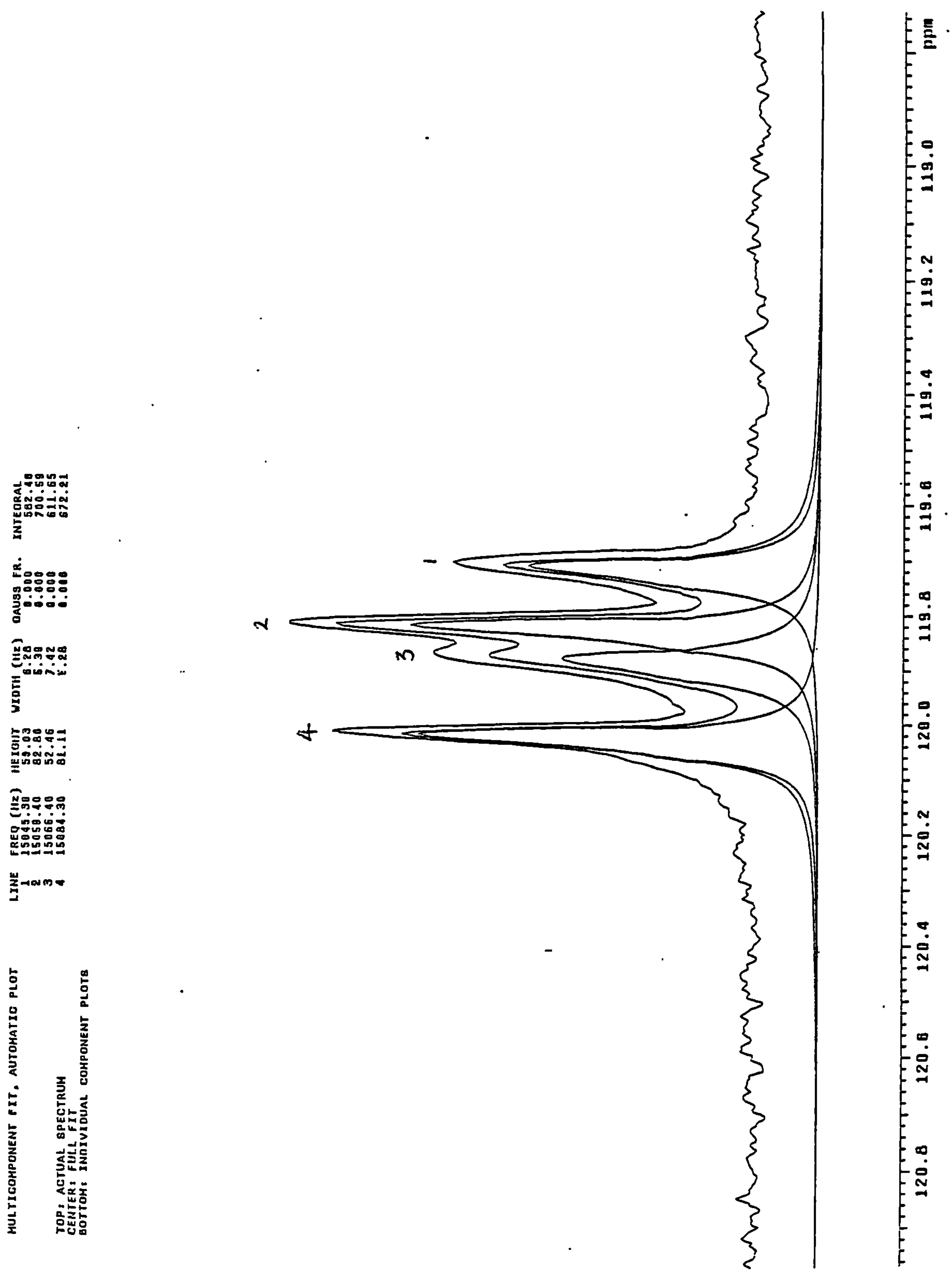
LINE	FREQ (Hz)	HEIGHT	WIDTH (Hz)	GAUSS FR.	INTEGRAL
1	15038.20	24.81	8.31	0.000	323.68
2	15059.80	49.27	11.37	0.000	879.90
3	15086.50	30.58	9.49	0.000	456.14

Appendix 3. 25: ^{13}C nmr expansion of the multiplet due to the aromatic carbon (3) in hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophthalate), **13**, and its Laurentzian deconvolution



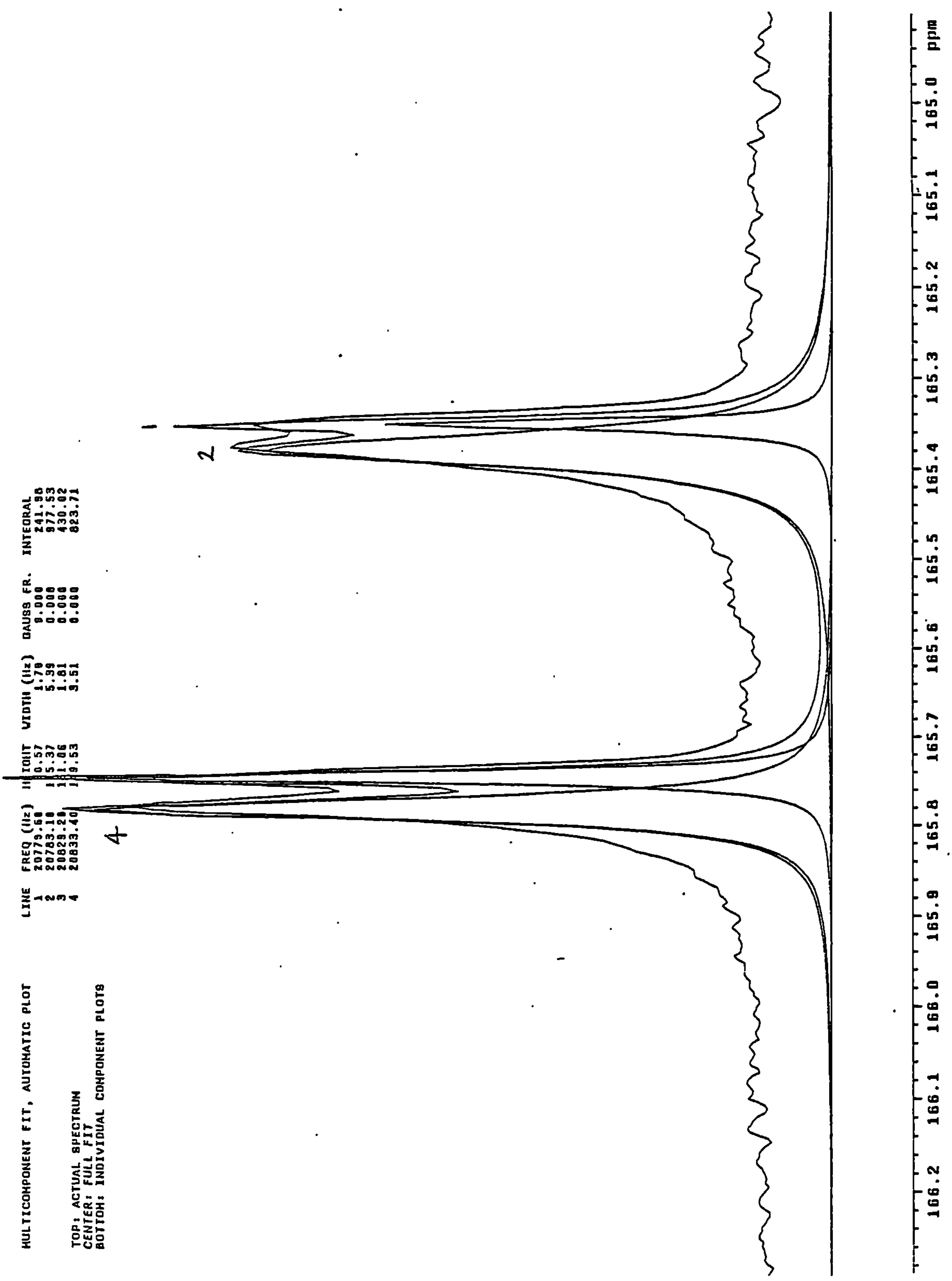
```
MULTICOMPONENT FIT, AUTOMATIC PLOT

TOP: ACTUAL SPECTRUM
CENTER: FULL FIT
BOTTOM: INDIVIDUAL COMPONENT PLOTS

LINE  FREQ (Hz)  HEIGHT  WIDTH (Hz)  GAUSS FR.  INTEGRAL
 1    20779.70    56.42   * 2.10      0.000      200.72
 2    20783.10    99.37   * 6.69      0.000     1034.44
 3    20829.10    96.72     2.22      0.000      337.96
 4    20833.40   116.80     5.20      0.000      854.30
```

Appendix 3. 26: ^{13}C nmr expansion of the multiplet due to the carbonyl carbon (5) in hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophthalate), **13**, and its Laurentzian deconvolution



LINE	FREQ (Hz)	HEIGHT	WIDTH (Hz)	GAUSS FR.	INTEGRAL
1	15045.30	59.03	6.28	0.000	582.48
2	15059.40	82.80	5.39	0.000	700.59
3	15066.40	52.46	7.42	0.000	611.65
4	15084.30	81.11	6.28	0.000	672.21

Appendix 3. 27: ^{13}C nmr expansion of the multiplet due to the aromatic carbon (3) in hyperbranched poly(dimethyl 5-(5-hydroxypentoxy)isophthalate), **14**, and its Laurentzian deconvolution

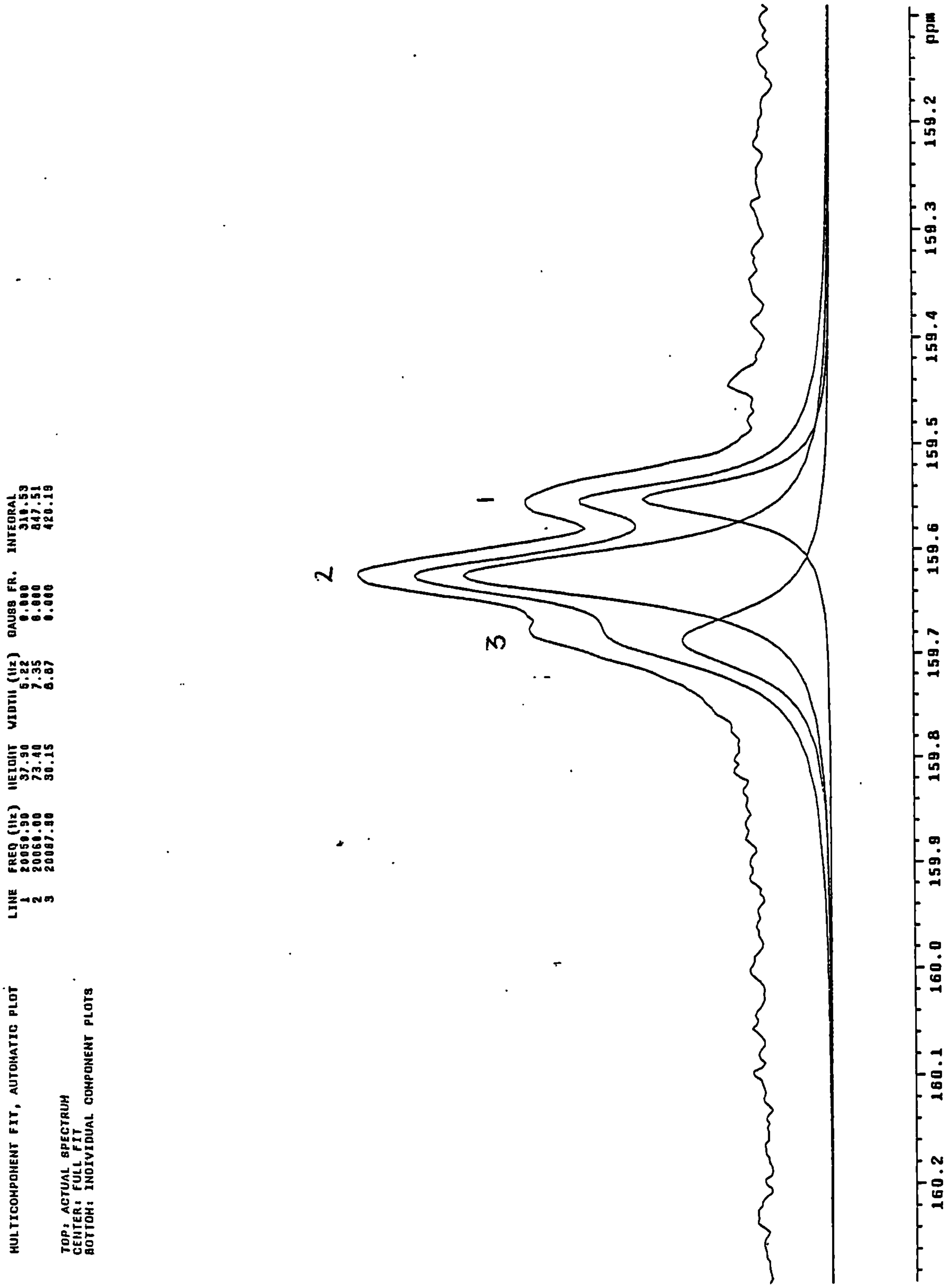


MULTICOMPONENT FIT, AUTOMATIC PLOT

TOP: ACTUAL SPECTRUM
CENTER: FULL FIT
BOTTOM: INDIVIDUAL COMPONENT PLOTS

LINE	FREQ (Hz)	HEIGHT	WIDTH (Hz)	GAUSS FR.	INTEGRAL
1	20779.60	[illegible]0.57	1.70	0.000	241.98
2	20783.10	1[illegible]5.37	5.99	0.000	977.53
3	20829.20	1[illegible]1.06	1.81	0.000	430.02
4	20833.40	1[illegible]9.53	3.51	0.000	823.71

Appendix 3. 28: ^{13}C nmr expansion of the multiplet due to the carbonyl carbon (5) in hyperbranched poly(dimethyl 5-(5-hydroxypentoxy)isophthalate), **14**, and its Laurentzian deconvolution

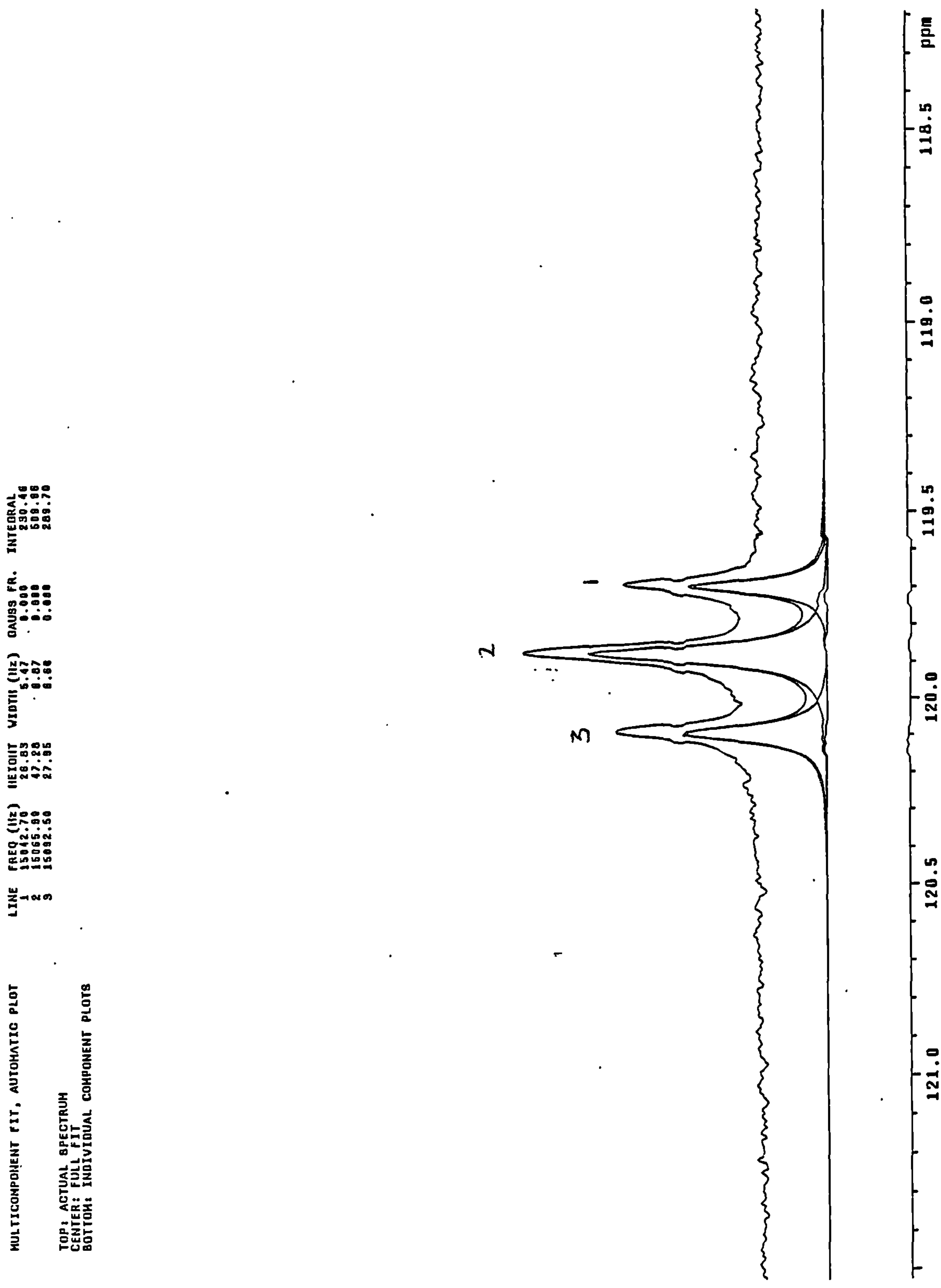


MULTICOMPONENT FIT, AUTOMATIC PLOT

LINE	FREQ (Hz)	HEIGHT	WIDTH (Hz)	GAUSS FR.	INTEGRAL
1	20050.90	37.90	5.22	0.000	310.53
2	20060.00	73.40	7.35	0.000	847.51
3	20067.80	30.15	6.87	0.000	420.19

TOP: ACTUAL SPECTRUM
CENTER: FULL FIT
BOTTOM: INDIVIDUAL COMPONENT PLOTS

Appendix 3. 29: ^{13}C nmr expansion of the multiplet due to the aromatic carbon (4) in hyperbranched poly(dimethyl 5-(5-hydroxypentoxy)isophthalate), **14**, and its Laurentzian deconvolution



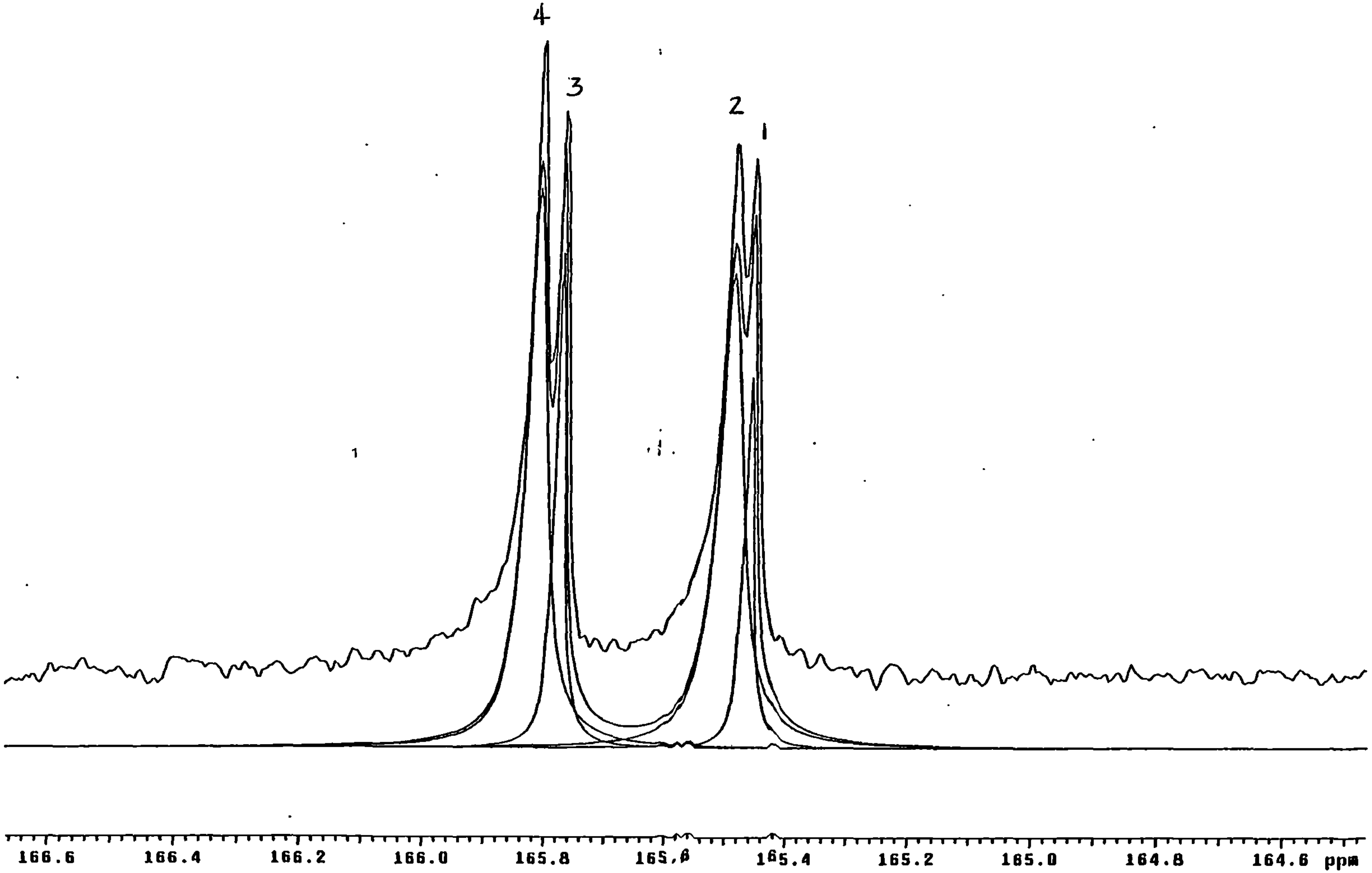
```
MULTICOMPONENT FIT, AUTOMATIC PLOT        LINE  FREQ (Hz)  HEIGHT  WIDTH (Hz)  GAUSS FR.  INTEGRAL
                                            1   15042.70    26.83     5.47       0.000     230.46
TOP: ACTUAL SPECTRUM                        2   15065.80    47.28     6.87       0.000     508.86
CENTER: FULL FIT                            3   15092.50    27.85     6.60       0.000     289.70
BOTTOM: INDIVIDUAL COMPONENT PLOTS
```

Appendix 3. 30: ^{13}C nmr expansion of the multiplet due to the aromatic carbon (3) in hyperbranched poly(dimethyl 5-(6-hydroxyhexoxy)isophthalate), 15, and its Laurentzian deconvolution

MULTICOMPONENT FIT, AUTOMATIC PLOT

TOP: ACTUAL SPECTRUM
CENTER: FULL FIT
BOTTOM: INDIVIDUAL COMPONENT PLOTS

LINE	FREQ (Hz)	HEIGHT	WIDTH (Hz)	GAUSS FR.	INTEGRAL
1	20793.70	68.84	2.29	0.000	247.33
2	20797.80	88.53	5.78	0.000	803.67
3	20833.00	92.27	2.26	0.000	327.85
4	20838.20	104.45	4.74	0.000	777.86



Appendix 3. 31: ^{13}C nmr expansion of the multiplet due to the carbonyl carbon (5) in hyperbranched poly(dimethyl 5-(6-hydroxyhexoxy)isophthalate), **15**, and its Laurentzian deconvolution

APPENDIX FOUR

EXPERIMENTAL AND CHARACTERISATION DATA FOR CHAPTER SIX

EXPERIMENTAL

All instrumentation and experimental details for SEC, MALDI-TOF MS, TGA and ^{1}H and ^{13}C nmr spectroscopy reported in Chapter 6 was the same as that described in Chapter 5. Experimental details for DSC results given in Chapter 6 are described below.

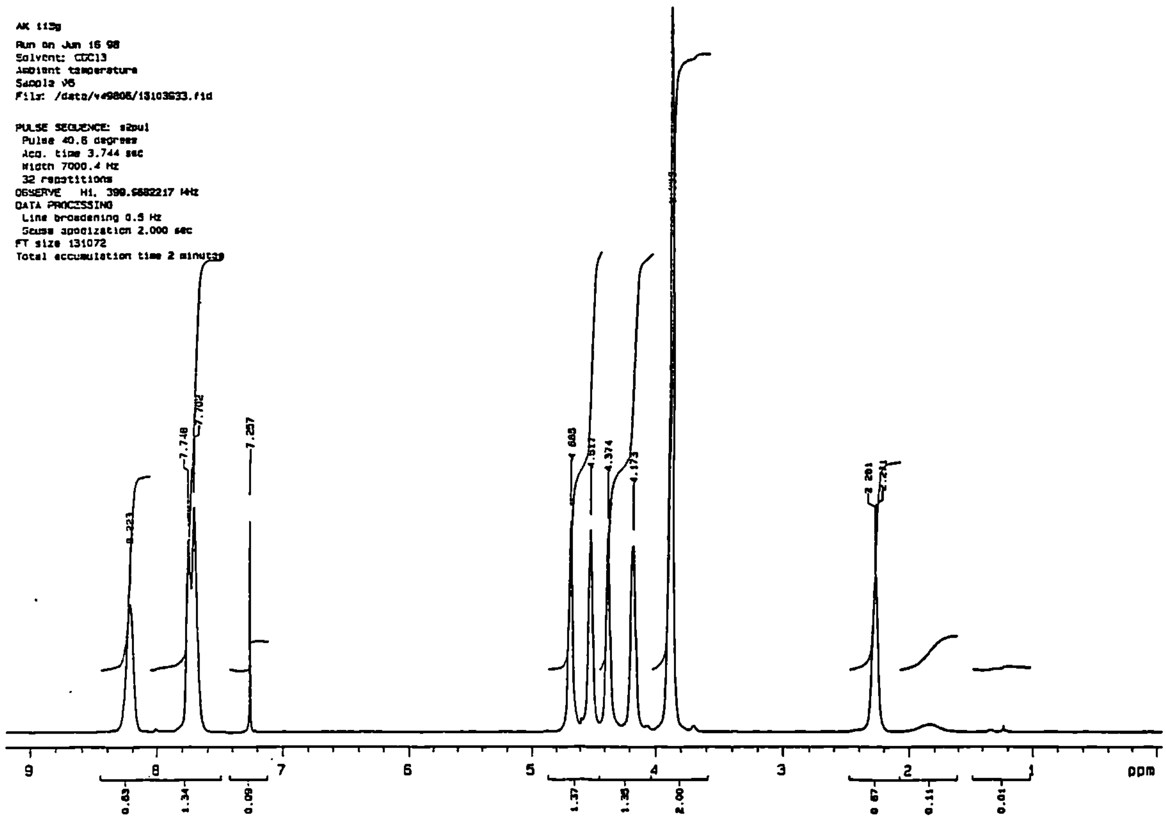
DSC

DSC measurements were recorded using a Perkin Elmer Pyris 1 DSC, under a helium atmosphere. Typically each polymer was annealed at 200°C for 1 minute, the sample was cooled at a rate of 200°Cmin^{-1} to 0°C where it was held for a further 5 minutes. A DSC trace was recorded from 0°C to 100°C at a heating rate of 10°Cmin^{-1}. This procedure was repeated at least twice for each polymer sample. The data were analysed using Pyris Manager Software 2.04. For each polymer sample individual methods describing specific temperatures and heating/cooling rates are given on the DSC traces (Appendices 4.29 – 4.42).

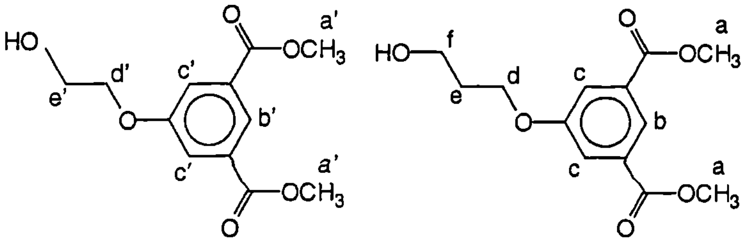
APPENDICES CONTENTS

^{1}H nmr spectra	Appendices 4.1 – 4.14
^{13}C nmr spectra*	Appendices 4.15 – 4.28
DSC traces	Appendices 4.29 – 4.42
MALDI-TOF mass spectra	Appendices 4.43 – 4.50

*Unless otherwise indicated all peaks are singlets in the assignment of ^{13}C nmr spectra.

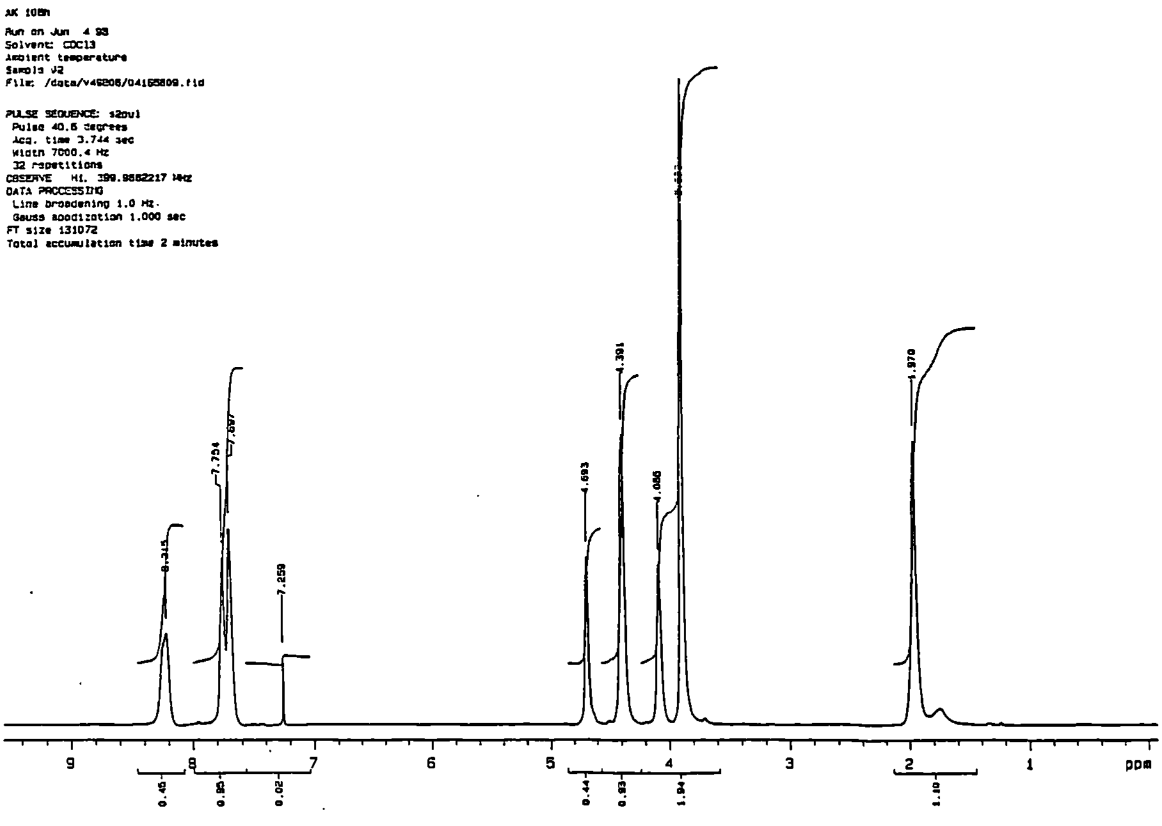


Assignment of ^{1}H nmr spectrum for the hyperbranched copolymer (**CP16**) prepared from monomers dimethyl 5-(2-hydroxyethoxy)isophthalate and dimethyl 5-(3-hydroxypropoxy)isophthalate, **8**:



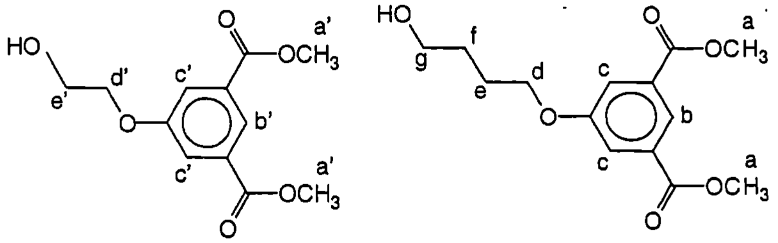
Shift δppm	Integral	Assignment
2.28	1	e
3.85	3	a, a'
4.17	1	d
4.37, 4.52	1	f, d'
4.69	1	e'
7.78	2	c, c'
8.22	1	b, b'

Appendix 4. 1: ^{1}H nmr spectrum (400MHz) of the hyperbranched copolymer **CP16**



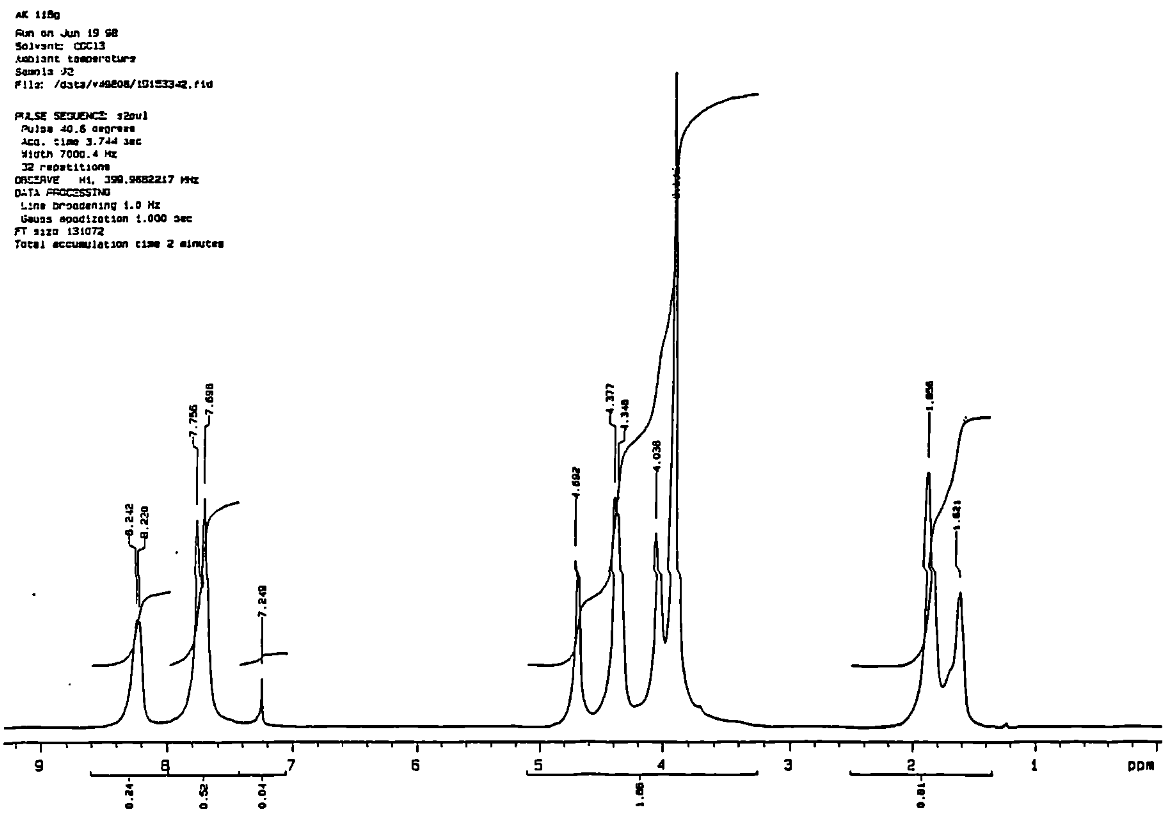
```
AK 108h
Run on Jun  4 93
Solvent: CDCl3
Ambient temperature
Sample V2
File: /data/v46206/04165809.fid

PULSE SEQUENCE: s2pul
 Pulse 40.6 degrees
 Acq. time 3.744 sec
 Width 7000.4 Hz
 32 repetitions
OBSERVE   H1, 399.9662217 MHz
DATA PROCESSING
 Line broadening 1.0 Hz.
 Gauss apodization 1.000 sec
FT size 131072
Total accumulation time 2 minutes
```

Assignment of ^{1}H nmr spectrum for the hyperbranched copolymer (**CP17**) prepared from monomers dimethyl 5-(2-hydroxyethoxy)isophthalate and dimethyl 5-(4-hydroxybutoxy)isophthalate, **9**:

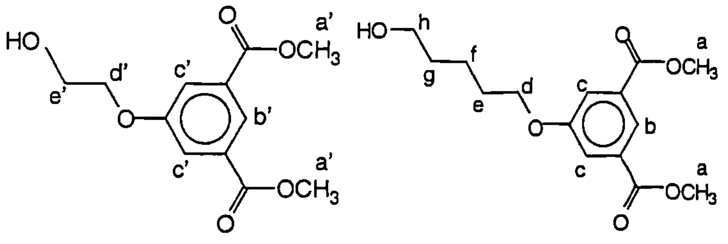


Shift δppm	Integral	Assignment
1.97	2	e, f
3.86	3	a, a'
4.07	1	d
4.39	2	g, d'
4.69	1	e'
7.70, 7.75	2	c, c'
8.22	1	b, b'

Appendix 4. 2: ^{1}H nmr spectrum (400MHz) of the hyperbranched copolymer **CP17**

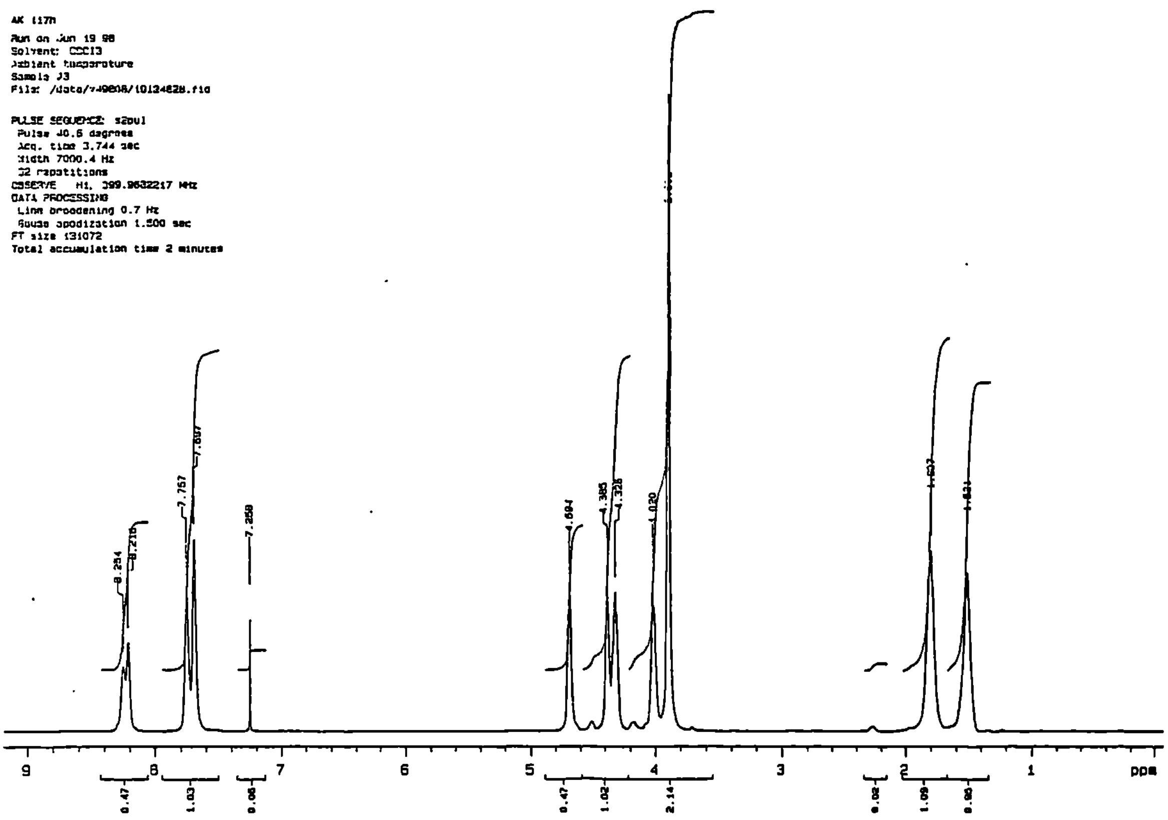


Assignment of ^1H nmr spectrum for the hyperbranched copolymer (**CP18**) prepared from monomers dimethyl 5-(2-hydroxyethoxy)isophthalate and dimethyl 5-(5-hydroxypentoxy)isophthalate, **10**:

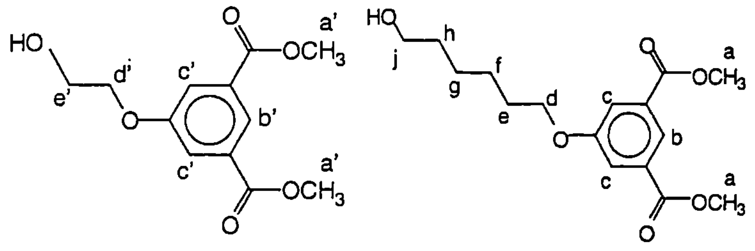


Shift δppm	Integral	Assignment
1.62	1	f
1.86	2	e, g
3.85	3	a, a'
4.04	1	d
4.36	2	h, d'
4.69	1	e'
7.70, 7.76	2	c, c'
8.22, 8.24	1	b, b'

Appendix 4. 3: ^1H nmr spectrum (400MHz) of the hyperbranched copolymer **CP18**

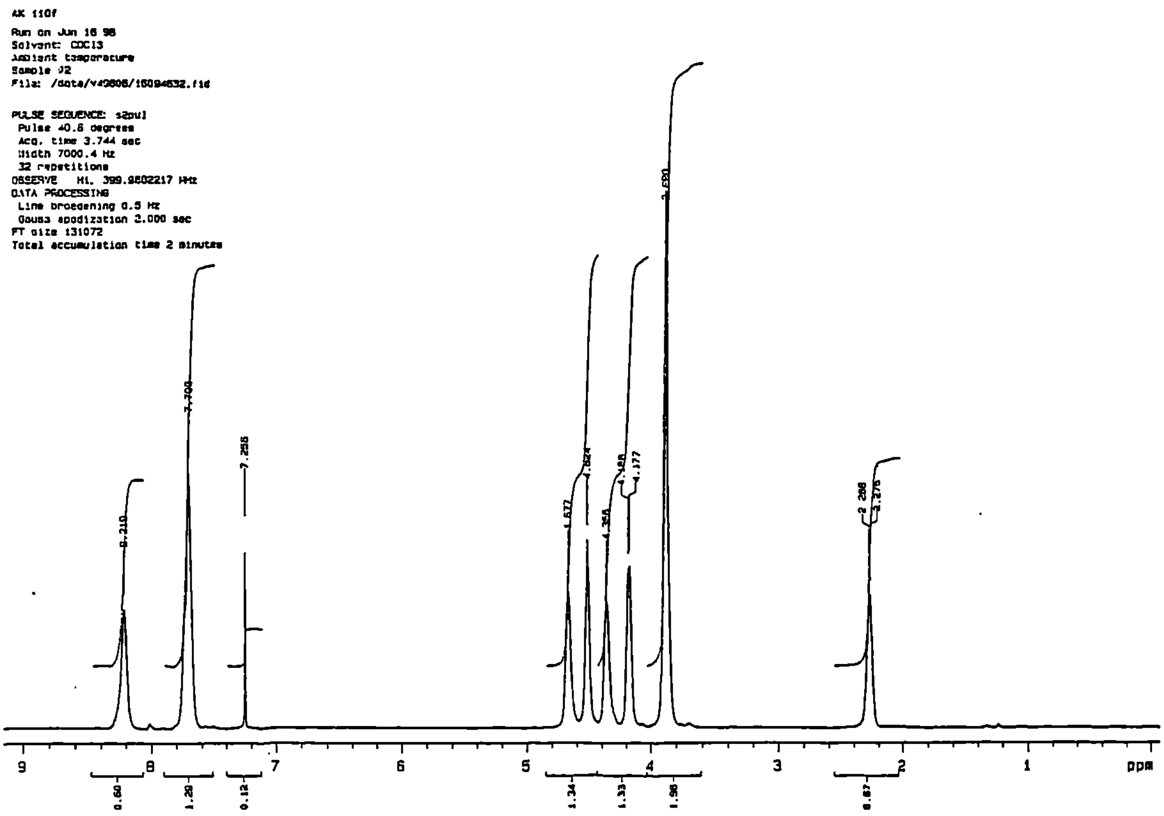


Assignment of ^1H nmr spectrum for the hyperbranched copolymer (**CP19**) prepared from monomers dimethyl 5-(2-hydroxyethoxy)isophthalate and dimethyl 5-(6-hydroxyhexoxy)isophthalate, **11**:



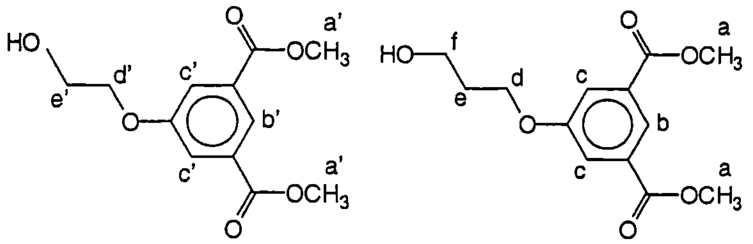
Shift δppm	Integral	Assignment
1.52	2	f, g
1.90	2	e, h
3.91	3	a, a’
4.02	1	d
4.36, 4.39	2	i, d’
4.69	1	e’
7.70, 7.76	2	c, c’
8.22, 8.24	1	b, b’

Appendix 4. 4: ^1H nmr spectrum (400MHz) of the hyperbranched copolymer **CP19**



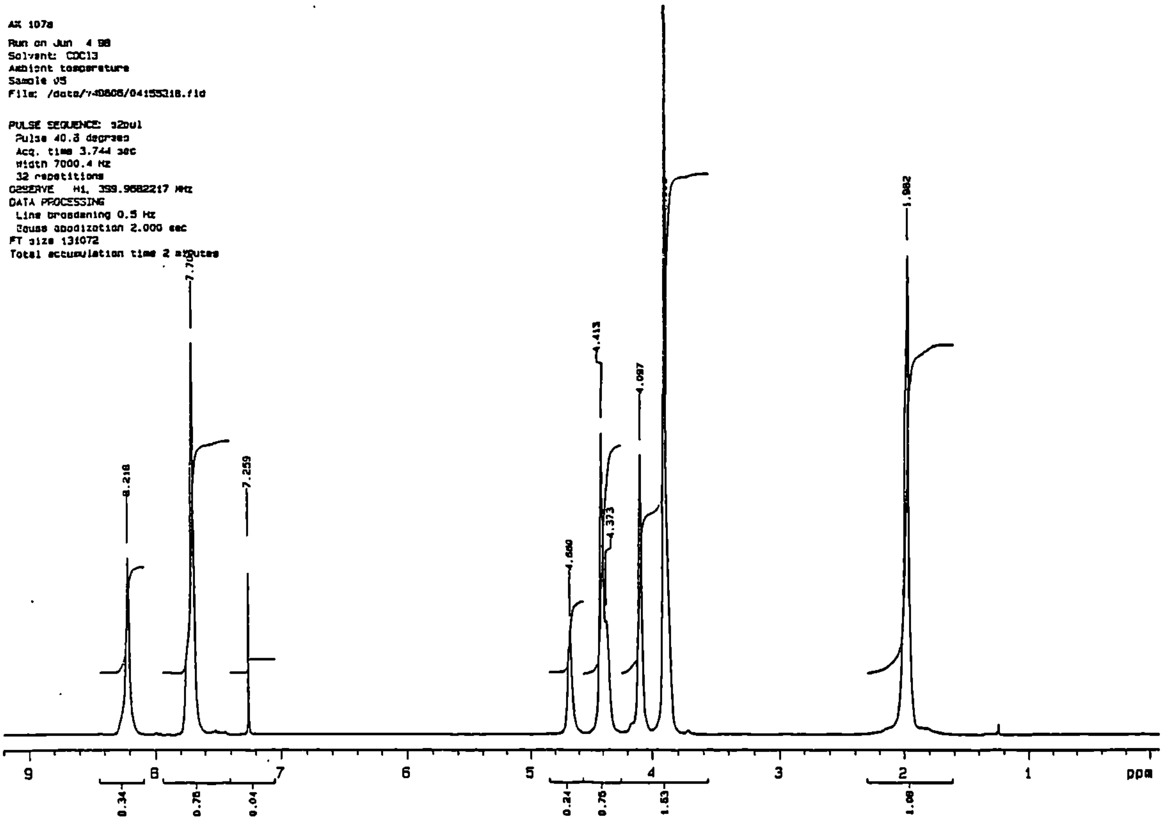
```
AK 110f
Run on Jun 16 98
Solvent: CDCl3
Ambient temperature
Sample #2
File: /data/v43606/16094632.fid

PULSE SEQUENCE: s2pul
 Pulse 40.8 degrees
 Acq. time 3.744 sec
 Width 7000.4 Hz
 32 repetitions
OBSERVE   H1, 399.9602217 MHz
DATA PROCESSING
 Line broadening 0.5 Hz
 Gauss apodization 2.000 sec
FT size 131072
Total accumulation time 2 minutes
```

Assignment of ^{1}H nmr spectrum for the hyperbranched polymer blend (**PB16**) prepared from hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalate) and hyperbranched poly(dimethyl 5-(3-hydroxypropoxy)isophthalate) **12**:

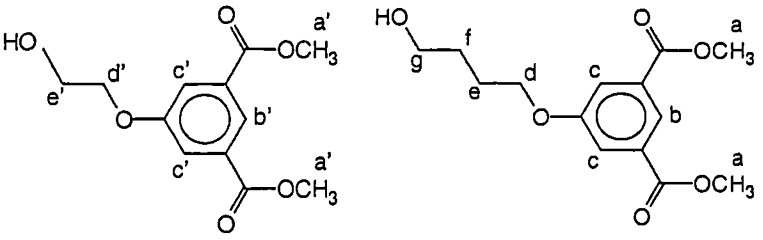


Shift δppm	Integral	Assignment
2.82	1	e
3.89	3	a, a'
4.18	1	d
4.37, 4.52	1	f, d'
4.68	1	e'
7.71	2	c, c'
8.24	1	b, b'

Appendix 4. 5: ^{1}H nmr spectrum (400MHz) of the hyperbranched polymer blend **PB16**

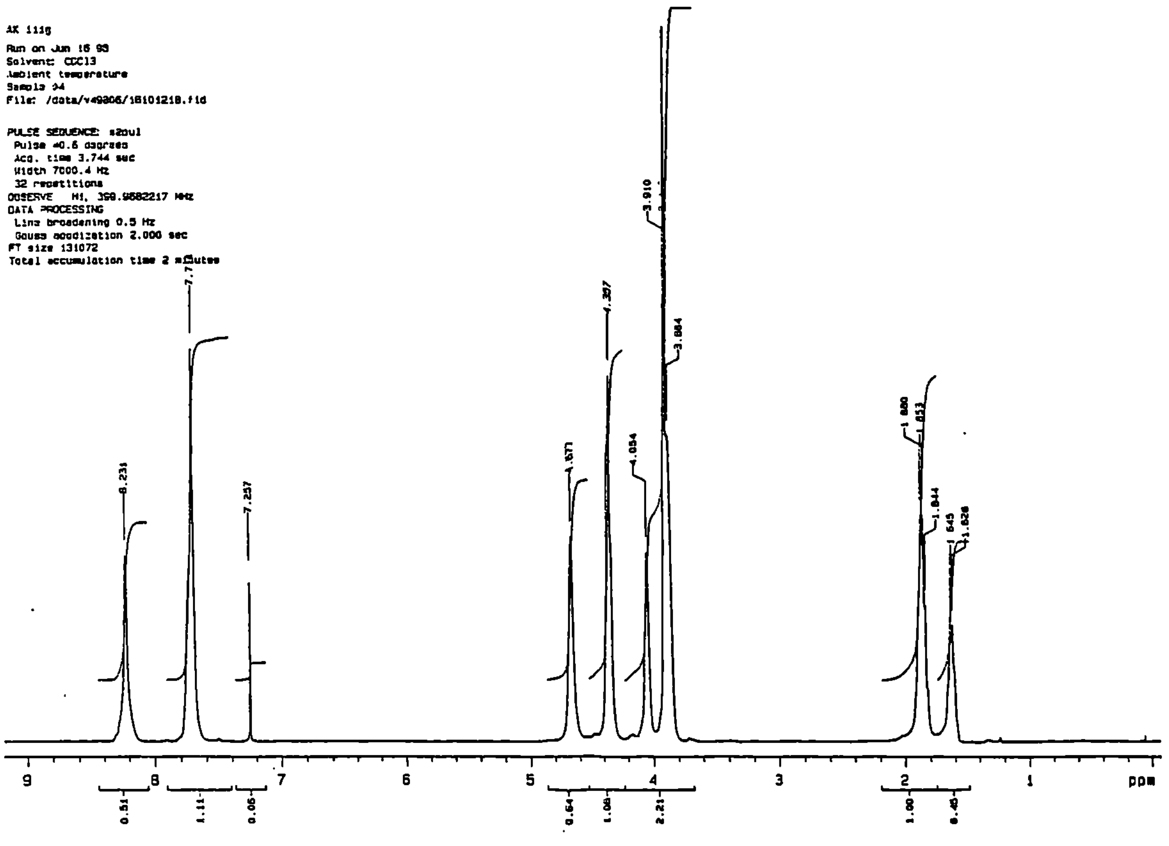


Assignment of ^{1}H nmr spectrum for the hyperbranched polymer blend (**PB17**) prepared from hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalate) and hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophthalate), **13**:

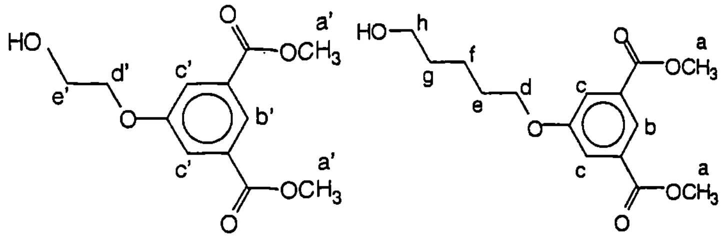


Shift δppm	Integral	Assignment
1.98	3	e, f
3.88	3	a, a’
4.10	1.3	d
4.37, 4.41	2	g, d’
4.68	0.7	e’
7.71, 7.75	2	c, c’
8.22	1	b, b’

Appendix 4. 6: ^{1}H nmr spectrum (400MHz) of the hyperbranched polymer blend **PB17**

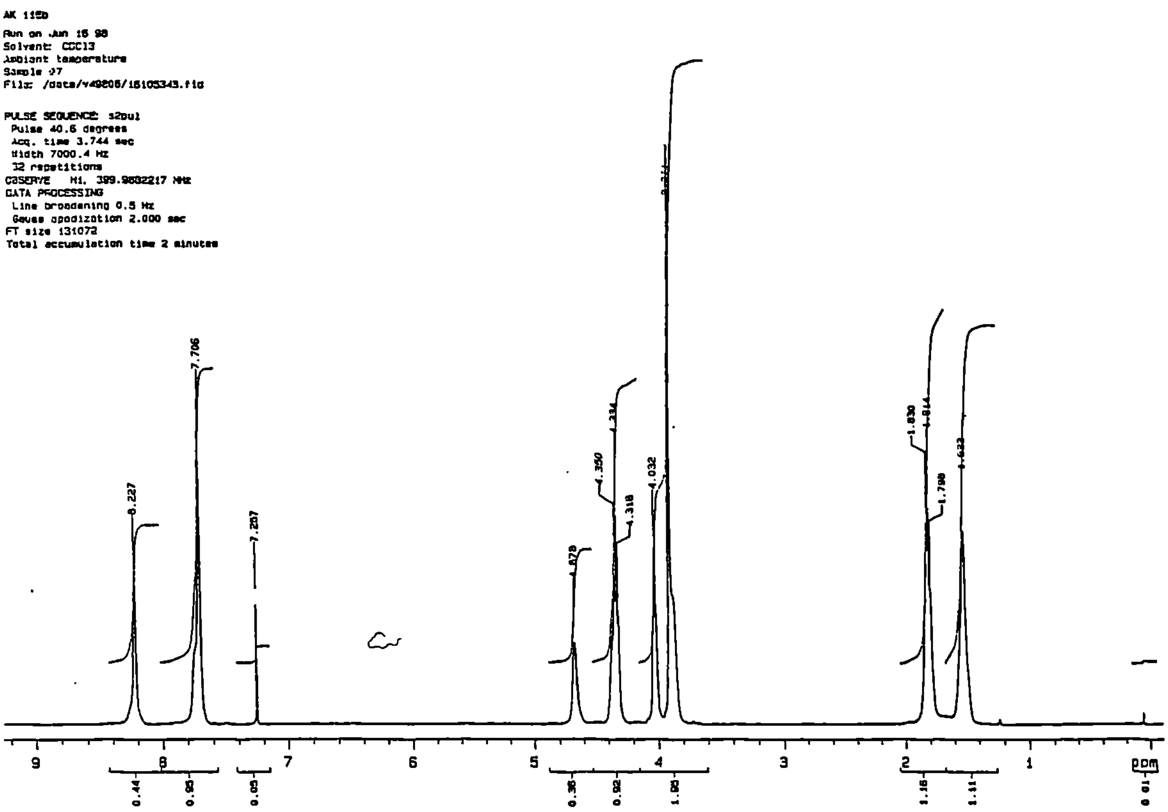


Assignment of ^{1}H nmr spectrum for the hyperbranched polymer blend (**PB18**) prepared from hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalate) and hyperbranched poly(dimethyl 5-(5-hydroxypentoxy)isophthalate), **14**:

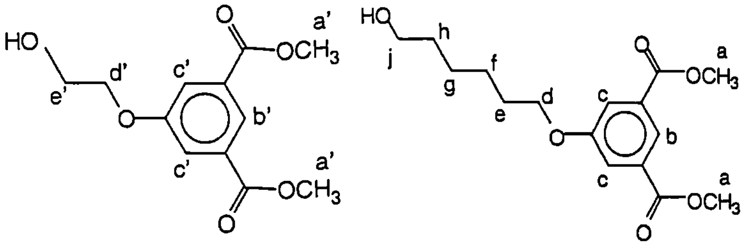


Shift δppm	Integral	Assignment
1.63	1	f
1.87	2	e, g
3.90	3	a, a'
4.05	1	d
4.35	2	h, d'
4.68	1	e'
7.75	2	c, c'
8.23	1	b, b'

Appendix 4. 7: ^{1}H nmr spectrum (400MHz) of the hyperbranched polymer blend **PB18**

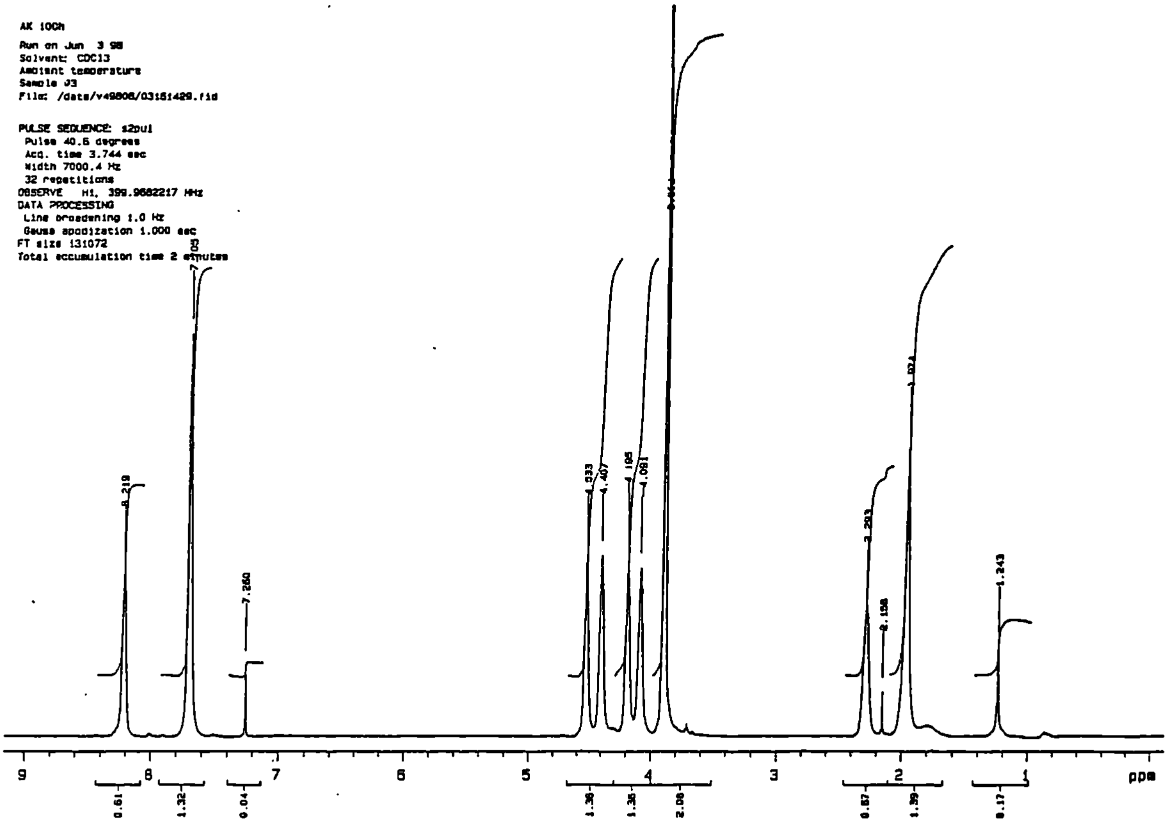


Assignment of ^1H nmr spectrum for the hyperbranched polymer blend (**PB19**) prepared from hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalate) and hyperbranched poly(dimethyl 5-(6-hydroxyhexoxy)isophthalate), **15**:

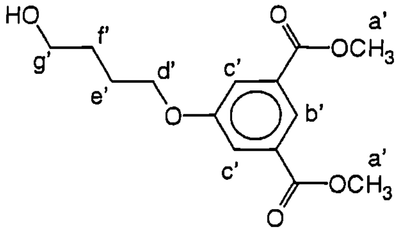


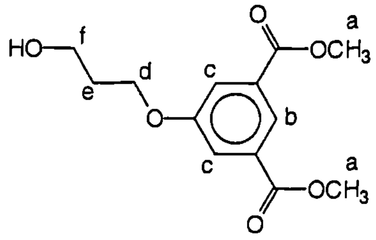
Shift δppm	Integral	Assignment
1.53	2	f, g
1.81	2	e, h
3.91	3	a, a’
4.03	1	d
4.33	2	i, d’
4.68	1	e’
7.71	2	c, c’
8.23	1	b, b’

Appendix 4. 8: ^1H nmr spectrum (400MHz) of the hyperbranched polymer blend **PB19**



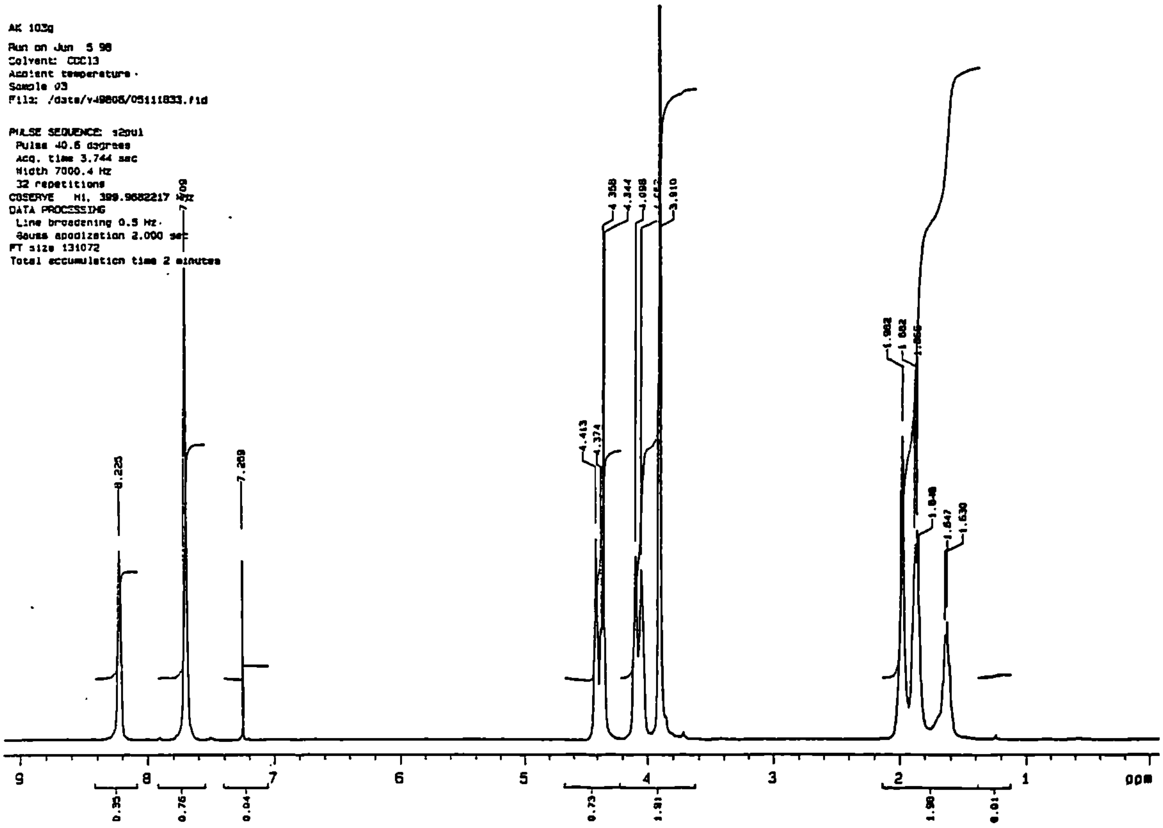
Assignment of ^{1}H nmr spectrum for the hyperbranched copolymer (**CP20**) prepared from monomers dimethyl 5-(4-hydroxybutoxy)isophthalate, **9** and dimethyl 5-(3-hydroxypropoxy)isophthalate, **8**:



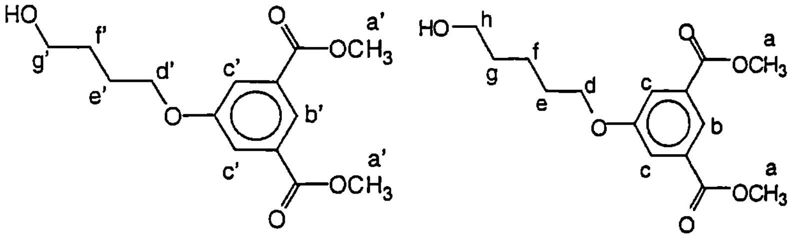


Shift δppm	Integral	Assignment
1.243	0.2	unknown impurity
1.97	2	e', f'
2.29	1	e
3.90	3	a, a'
4.09, 4.19	2	d, d'
4.53, 4.41	2	f, g'
7.71	2	c, c'
8.22	1	b, b'

Appendix 4. 9: ^{1}H nmr spectrum (400MHz) of the hyperbranched copolymer **CP20**

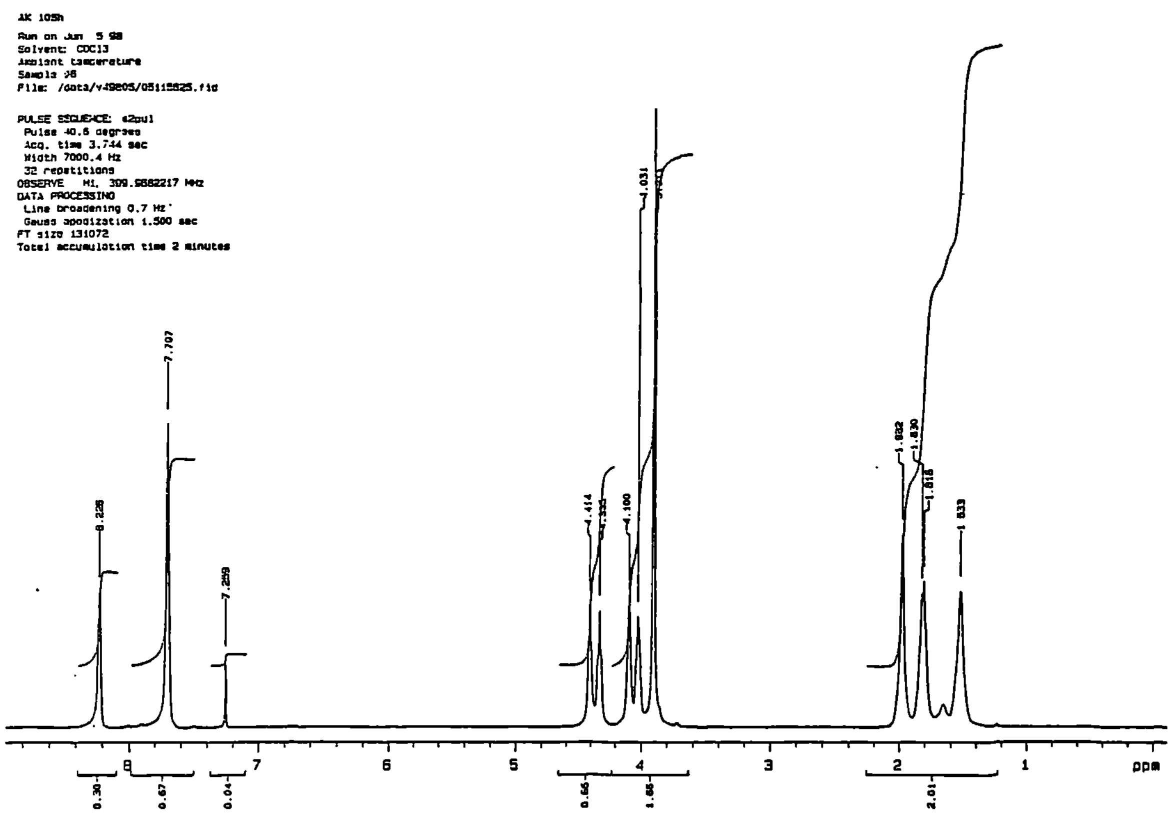


Assignment of ^1H nmr spectrum for the hyperbranched copolymer (**CP21**) prepared from monomers dimethyl 5-(4-hydroxybutoxy)isophthalate, **9** and dimethyl 5-(5-hydroxypentoxy)isophthalate, **10**:

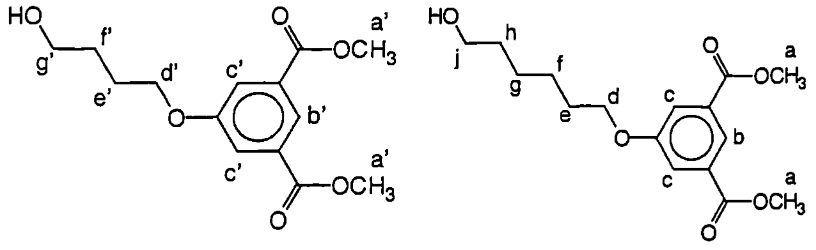


Shift δppm	Integral	Assignment
1.64	1	f
1.86	2	g, e
1.98	2	e', f'
3.91	3	a, a'
4.05, 4.10	2	d, d'
4.35, 4.41	2	h, g'
7.71	2	c, c'
8.23	1	b, b'

Appendix 4. 10: ^1H nmr spectrum (400MHz) of the hyperbranched copolymer **CP21**

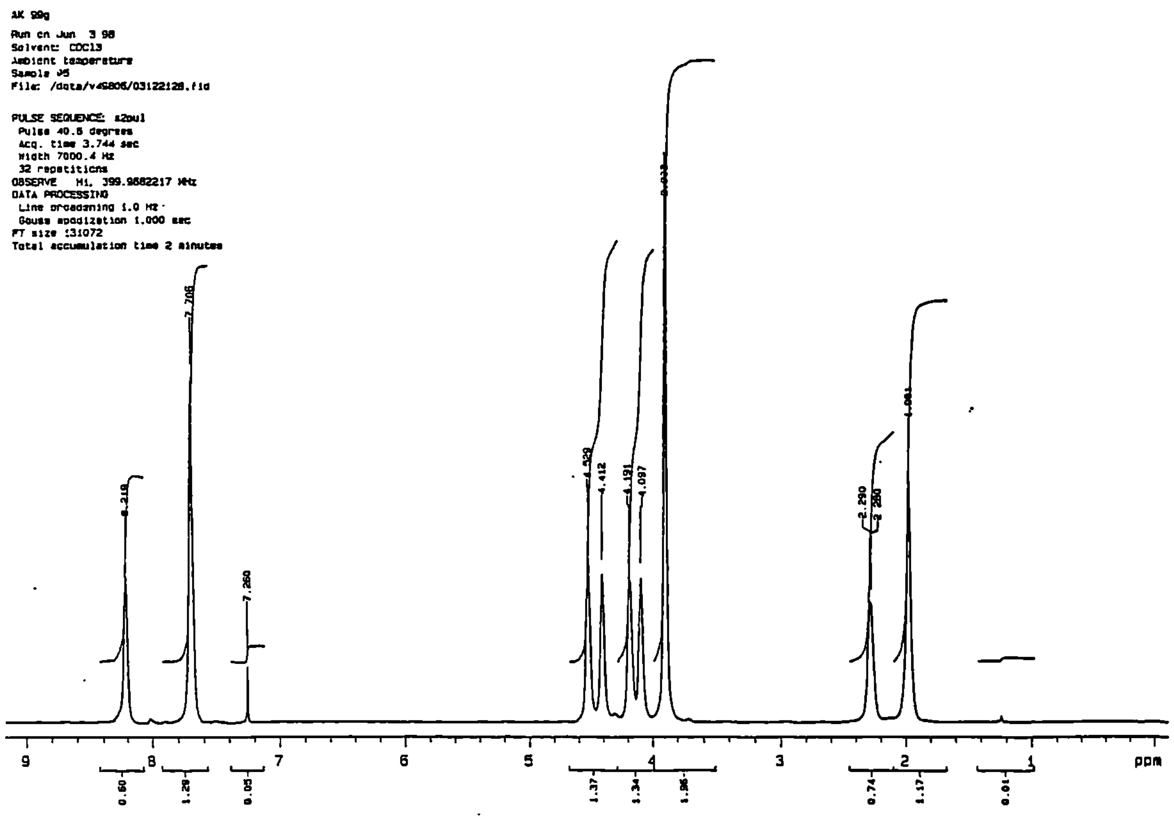


Assignment of ^1H nmr spectrum for the hyperbranched copolymer (**CP22**) prepared from monomers dimethyl 5-(4-hydroxybutoxy)isophthalate, **9** and dimethyl 5-(6-hydroxyhexoxy)isophthalate, **11**:

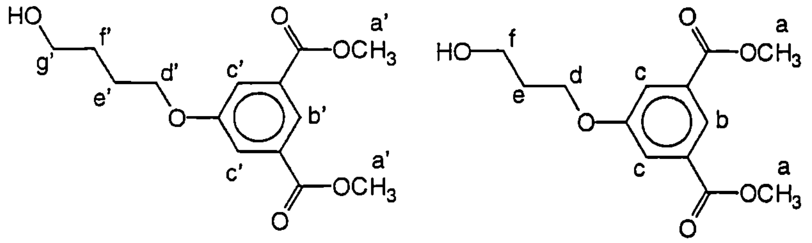


Shift δppm	Integral	Assignment
1.53	2	g, f
1.82	2	e, h
1.98	2	e', f'
3.91	3	a, a'
4.03, 4.10	2	d, d'
4.34, 4.41	2	i, g'
7.71	2	c, c'
8.23	1	b, b'

Appendix 4. 11: ^1H nmr spectrum (400MHz) of the hyperbranched copolymer **CP22**



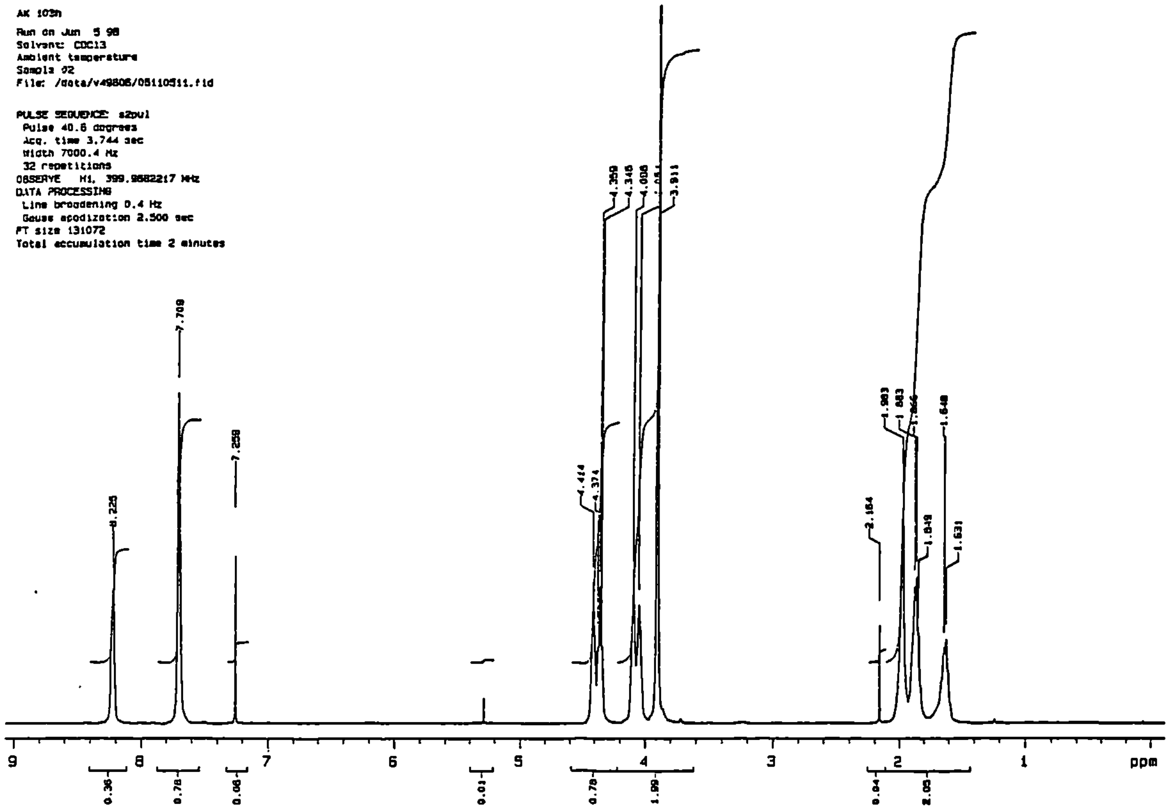
Assignment of ^{1}H nmr spectrum for the hyperbranched polymer blend (**PB20**) prepared from hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophthalate, **13** and hyperbranched poly(dimethyl 5-(3-hydroxypropoxy)isophthalate, **12**:



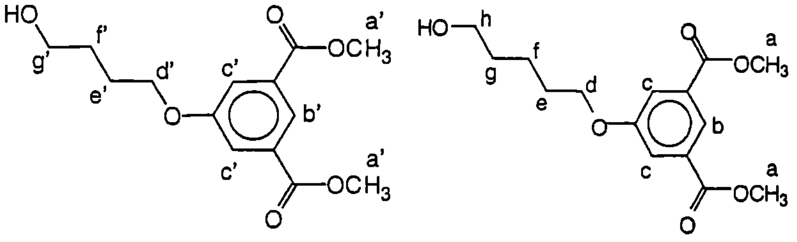
Shift δppm	Integral	Assignment
1.98	2	e', f'
2.29	1	e
3.90	3	a, a'
4.10, 4.19	2	d, d'
4.53, 4.41	2	f, g'
7.71	2	c, c'
8.22	1	b, b'

Appendix 4. 12: ^{1}H nmr spectrum (400MHz) of the hyperbranched polymer blend

PB20



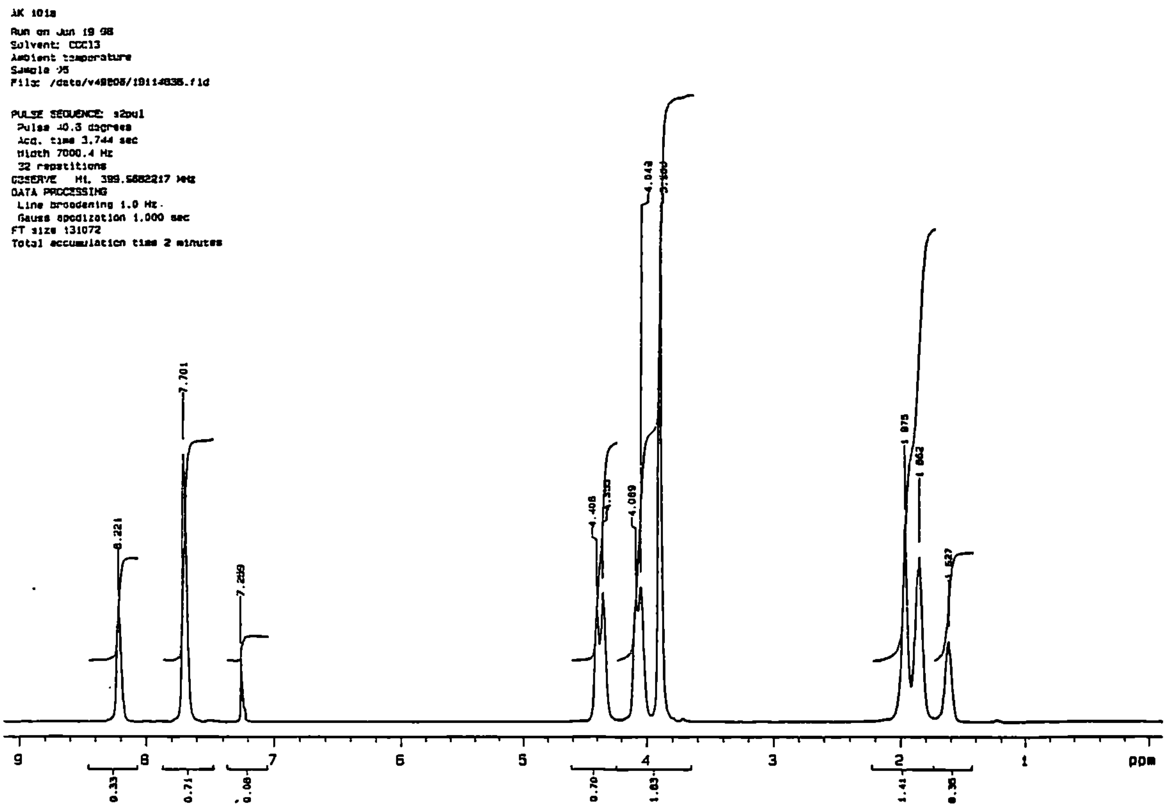
Assignment of ^1H nmr spectrum for the hyperbranched polymer blend (**PB21**) prepared from hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophthalate), **13** and hyperbranched poly(dimethyl 5-(5-hydroxypentoxy)isophthalate), **14**:



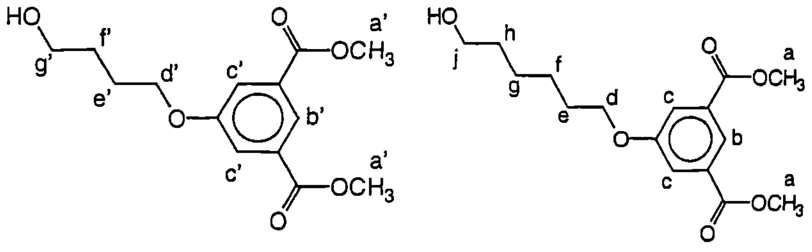
Shift δppm	Integral	Assignment
1.63 1.87	3	g, f e,
1.98	2	e', f'
3.91	3	a, a'
4.05, 4.10	2	d, d'
4.36, 4.41	2	h, g'
7.71	2	c, c'
8.23	1	b, b'

Appendix 4. 13: ^1H nmr spectrum (400MHz) of the hyperbranched polymer blend

PB21



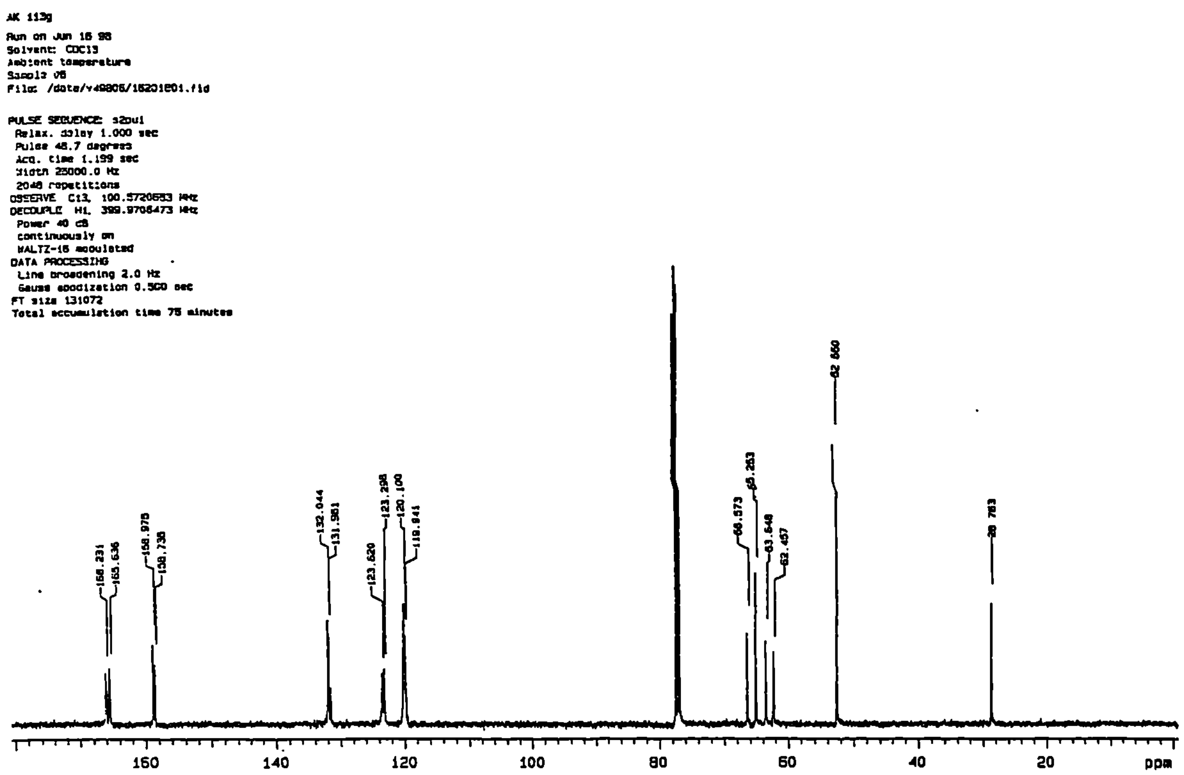
Assignment of ^1H nmr spectrum for the hyperbranched polymer blend (**PB22**) prepared from hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophthalate), **13** and hyperbranched poly(dimethyl 5-(6-hydroxyhexoxy)isophthalate), **15**:



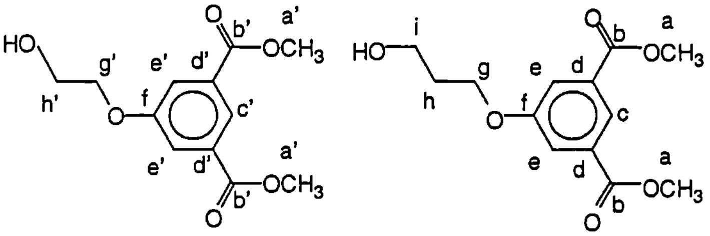
Shift δppm	Integral	Assignment
1.63 1.86	3	g, f e, h
1.98	2	e', f'
3.91	3	a, a'
4.05, 4.09	2	d, d'
4.36, 4.41	2	i, g'
7.71	2	c, c'
8.22	1	b, b'

Appendix 4. 14: ^1H nmr spectrum (400MHz) of the hyperbranched polymer blend

PB22

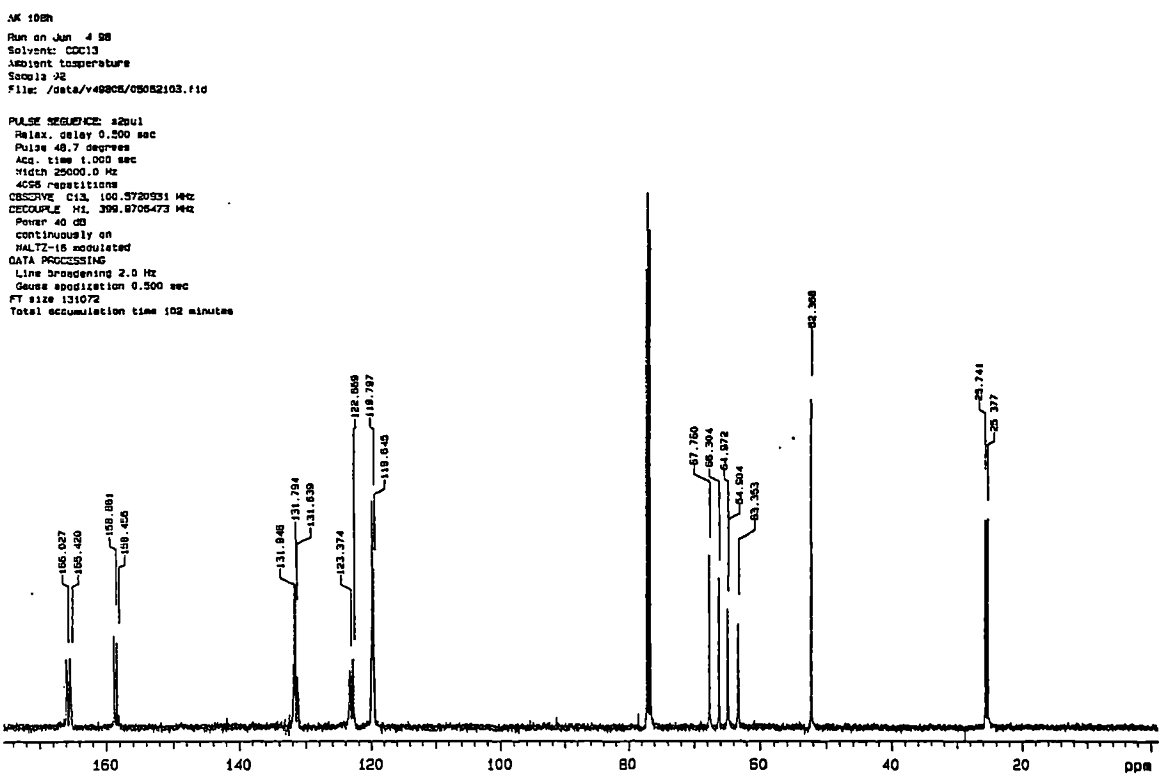


Assignment of ^{13}C nmr spectrum for the hyperbranched copolymer (**CP16**) prepared from monomers dimethyl 5-(2-hydroxyethoxy)isophthalate and dimethyl 5-(3-hydroxypropoxy)isophthalate, **8**:



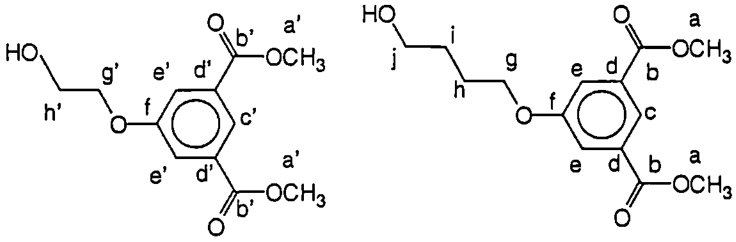
Shift δppm	Assignment
28.6	h
52.6	a, a'
62.2	g
63.4	g'
65.2	i
66.6	h'
120.1 (m)	e, e'
123.4 (m)	c, c'
131.8 (m), 132.0 (m)	d, d'
158.7, 159.0	f, f'
165.6 (m), 166.2 (m)	b, b'

Appendix 4. 15: ^{13}C nmr spectrum (400MHz) of the hyperbranched copolymer **CP16**



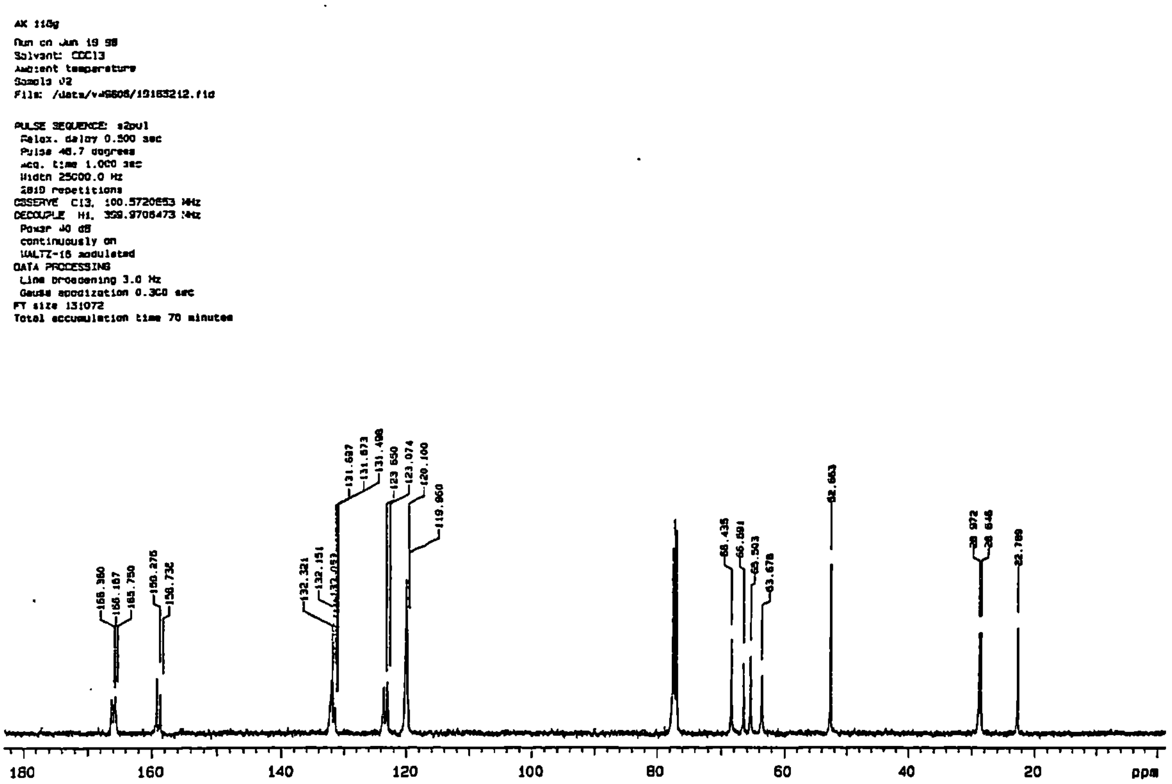
```
AK 108h
Run on Jun  4 98
Solvent: CDCl3
Ambient temperature
Sample #2
File: /data/v498C6/05052103.fid

PULSE SEQUENCE: s2pul
 Relax. delay 0.500 sec
 Pulse 48.7 degrees
 Acq. time 1.000 sec
 Width 25000.0 Hz
 4096 repetitions
OBSERVE  C13, 100.5720931 MHz
DECOUPLE  H1, 399.8706473 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 2.0 Hz
 Gauss apodization 0.500 sec
FT size 131072
Total accumulation time 102 minutes
```

Assignment of ^{13}C nmr spectrum for the hyperbranched copolymer (**CP17**) prepared from monomers dimethyl 5-(2-hydroxyethoxy)isophthalate and dimethyl 5-(4-hydroxybutoxy)isophthalate, **9**:



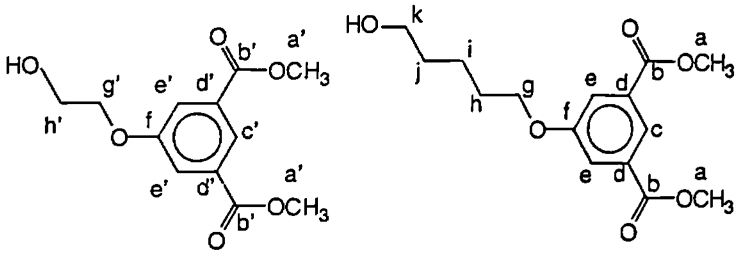
Shift δppm	Assignment
25.7, 25.4	h, i
52.4	a, a'
63.4, 64.9	g, g'
66.3, 67.8	j, h'
119.8 (m)	e, e'
122.4 (m), 123.4 (m)	c, c'
131.9 (m), 131.6 (m)	d, d'
158.4, 158.9	f, f'
165.4 (m), 166.0 (m)	b, b'

Appendix 4. 16: ^{13}C nmr spectrum (400MHz) of the hyperbranched copolymer **CP17**



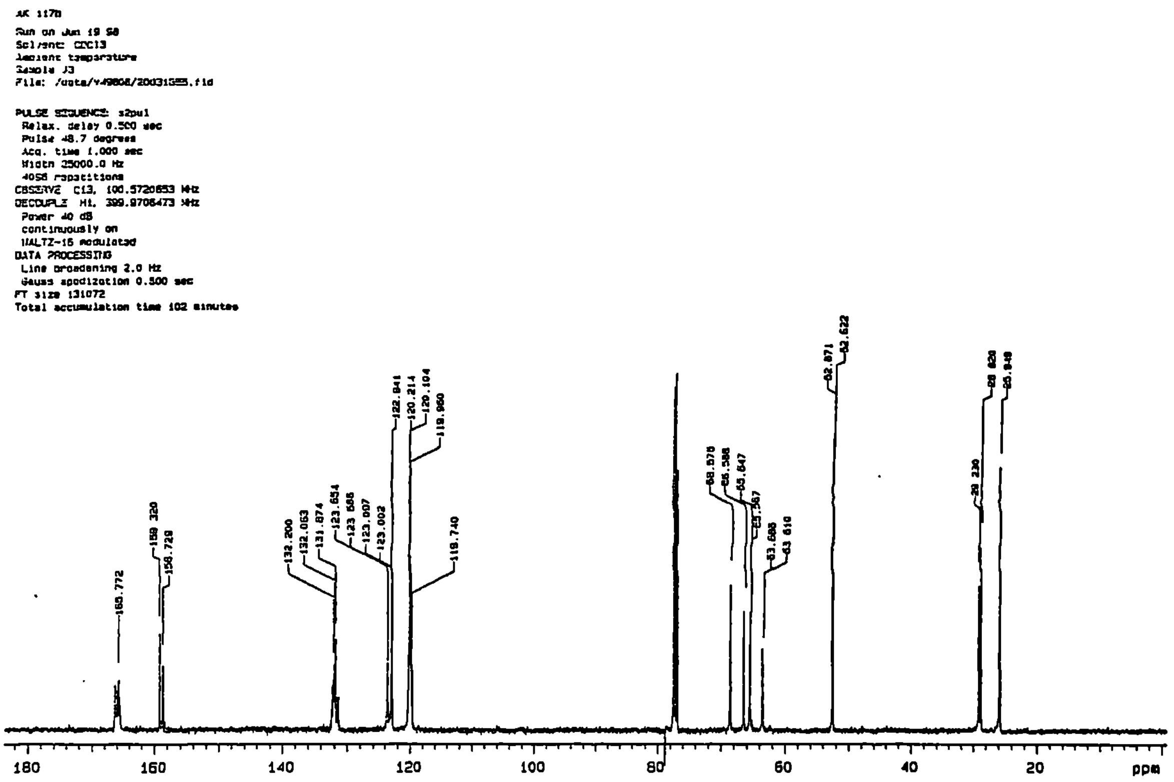
```
AK 118g
Run on Jun 19 98
Solvent: CDCl3
Ambient temperature
Sample 02
File: /data/v4S606/19183212.fid

PULSE SEQUENCE: s2pul
 Relax. delay 0.500 sec
 Pulse 46.7 degrees
 Acq. time 1.000 sec
 Width 25000.0 Hz
 2810 repetitions
OBSERVE C13, 100.5720653 MHz
DECOUPLE H1, 399.9706473 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 3.0 Hz
 Gauss apodization 0.300 sec
FT size 131072
Total accumulation time 70 minutes
```

Assignment of ^{13}C nmr spectrum for the hyperbranched copolymer (**CP18**) prepared from monomers dimethyl 5-(2-hydroxyethoxy)isophthalate and dimethyl 5-(5-hydroxypentoxy)isophthalate, **10**:



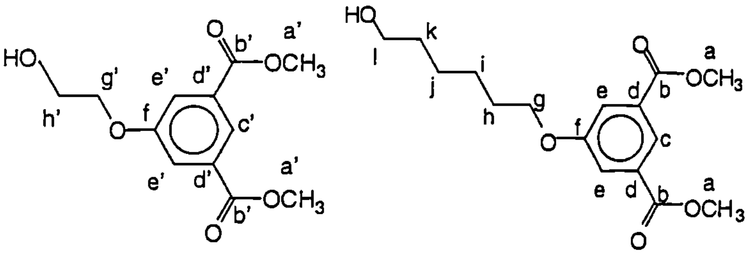
Shift δppm	Assignment
22.8	i
29.0, 28.6	h, j
52.6	a, a'
63.8, 65.5	g, g'
66.6, 68.4	k, h'
120.1, 119.9	e, e'
123.7, 123.1	c, c'
132.1 (m), 131.6(m)	d, d'
158.7, 159.3	f, f'
165.7 (m), 166.3 (m)	b, b'

Appendix 4. 17: ^{13}C nmr spectrum (400MHz) of the hyperbranched copolymer **CP18**



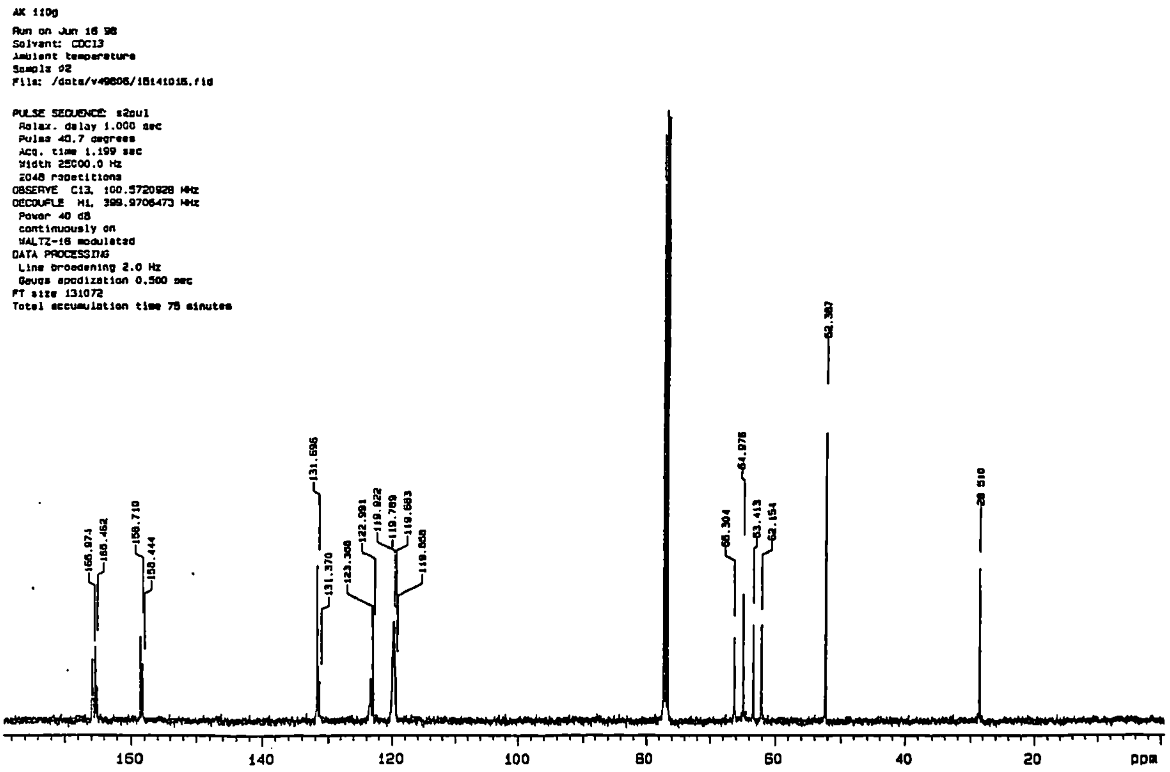
```
AK 117B
Run on Jun 19 98
Solvent: CDCl3
Ambient temperature
Sample J3
File: /data/v49808/20031355.fid

PULSE SEQUENCE: s2pul
 Relax. delay 0.500 sec
 Pulse 48.7 degrees
 Acq. time 1.000 sec
 Width 25000.0 Hz
 4056 repetitions
OBSERVE  C13, 100.5720653 MHz
DECOUPLE  H1, 399.9706473 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 2.0 Hz
 Gauss apodization 0.500 sec
FT size 131072
Total accumulation time 102 minutes
```

Assignment of ^{13}C nmr spectrum for the hyperbranched copolymer (**CP19**) prepared from monomers dimethyl 5-(2-hydroxyethoxy)isophthalate and dimethyl 5-(6-hydroxyhexoxy)isophthalate, **11**:



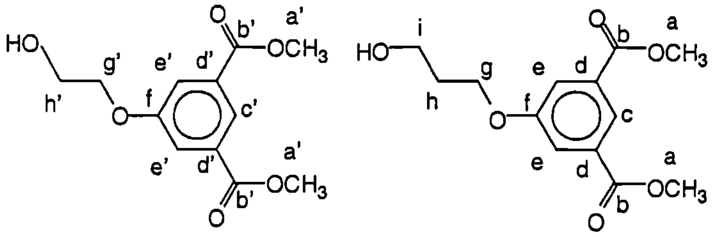
Shift δppm	Assignment
25.9	i j
29.2, 28.9	h, k
52.6	a, a'
63.6, 65.6	g, g'
66.6, 68.6	l, h'
120.1 (m)	e, e'
122.9, 123.6 (m)	c, c'
132.1 (m)	d, d'
158.7, 159.3	f, f'
165.7 (m)	b, b'

Appendix 4. 18: ^{13}C nmr spectrum (400MHz) of the hyperbranched copolymer **CP19**



```
AX 110g
Run on Jun 16 98
Solvent: CDCl3
Ambient temperature
Sample #2
File: /data/v49806/16141016.fid

PULSE SEQUENCE: s2pul
 Relax. delay 1.000 sec
 Pulse 40.7 degrees
 Acq. time 1.199 sec
 Width 25000.0 Hz
 2048 repetitions
OBSERVE  C13, 100.5720928 MHz
DECOUPLE  H1, 399.9706473 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 2.0 Hz
 Gauss apodization 0.500 sec
FT size 131072
Total accumulation time 78 minutes
```

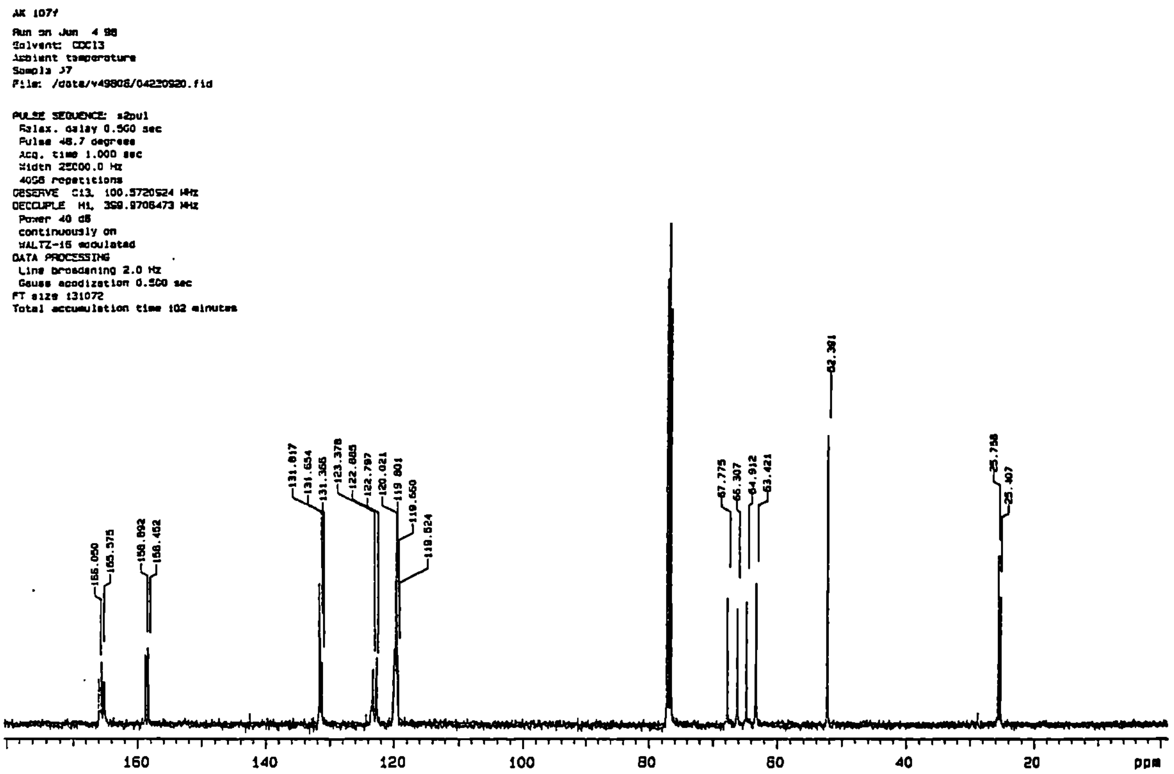
Assignment of ^{13}C nmr spectrum for the hyperbranched polymer blend (**PB16**) prepared from hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalate) and hyperbranched poly(dimethyl 5-(3-hydroxypropoxy)isophthalate), **12**:



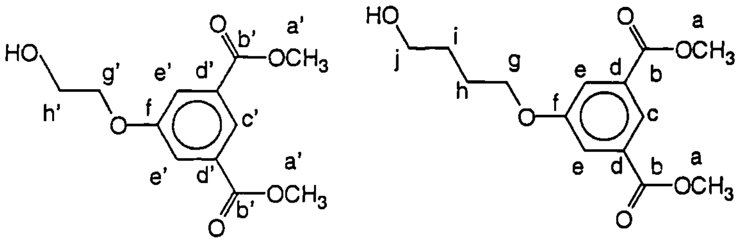
Shift δppm	Assignment
28.5	h
52.4	a, a'
62.2	g
63.4	g'
65.0	i
66.3	h'
119.8 (m)	e, e'
123.4 (m)	c, c'
131.4, 131.7	d, d'
158.4, 158.7	f, f'
165.5 (m), 166.0 (m)	b, b'

Appendix 4. 19: ^{13}C nmr spectrum (400MHz) of the hyperbranched polymer blend

PB16



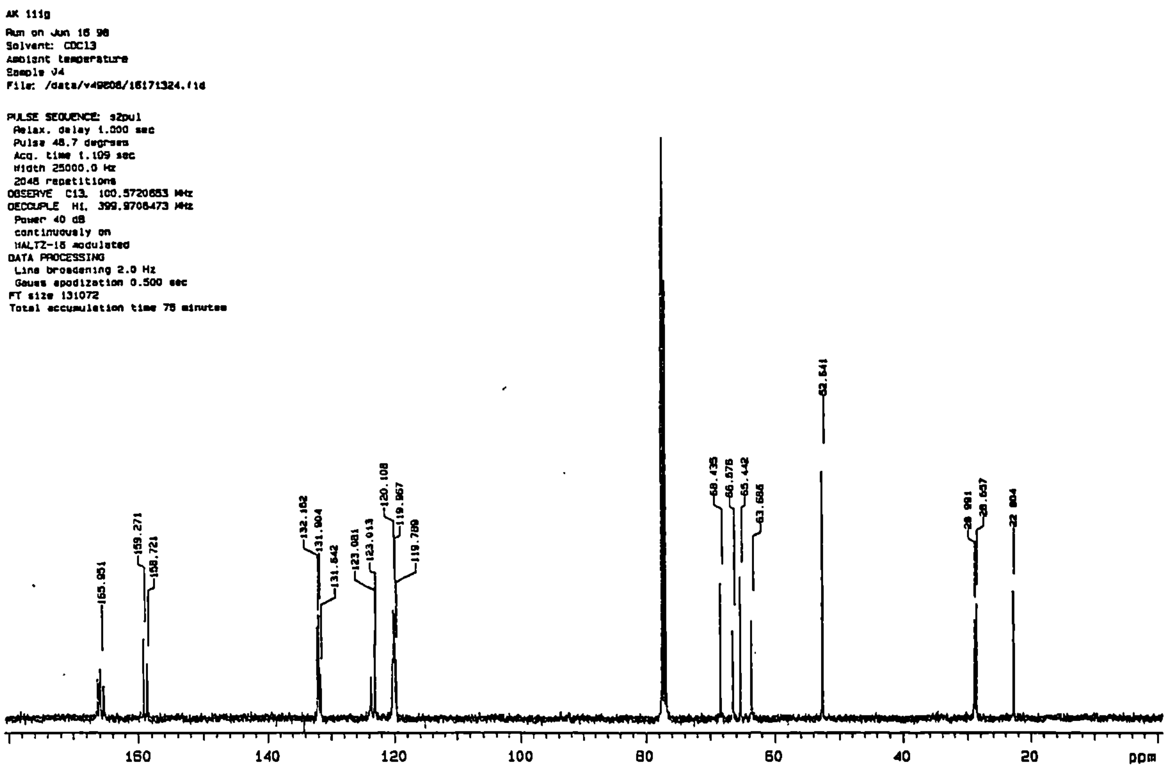
Assignment of ^{13}C nmr spectrum for the hyperbranched polymer blend (**PB17**) prepared from hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalate) and hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophthalate), **13**:



Shift δppm	Assignment
25.7, 25.4	h, i
52.4	a, a'
63.4, 64.9	g, g'
66.3, 67.8	j, h'
119.8 (m)	e, e'
122.8 (m), 123.4 (m)	c, c'
131.4 (m), 131.8 (m)	d, d'
158.5, 158.9	f, f'
165.6 (m), 166.1 (m)	b, b'

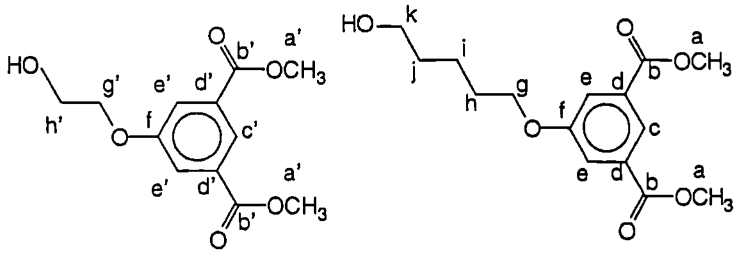
Appendix 4. 20: ^{13}C nmr spectrum (400MHz) of the hyperbranched polymer blend

PB17



```
AK 111g
Run on Jun 16 98
Solvent: CDCl3
Ambient temperature
Sample J4
File: /data/v49806/16171324.fid

PULSE SEQUENCE: s2pul
 Relax. delay 1.000 sec
 Pulse 48.7 degrees
 Acq. time 1.109 sec
 Width 25000.0 Hz
 2048 repetitions
OBSERVE  C13, 100.5720653 MHz
DECOUPLE  H1, 399.9708473 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 2.0 Hz
 Gauss apodization 0.500 sec
FT size 131072
Total accumulation time 75 minutes
```

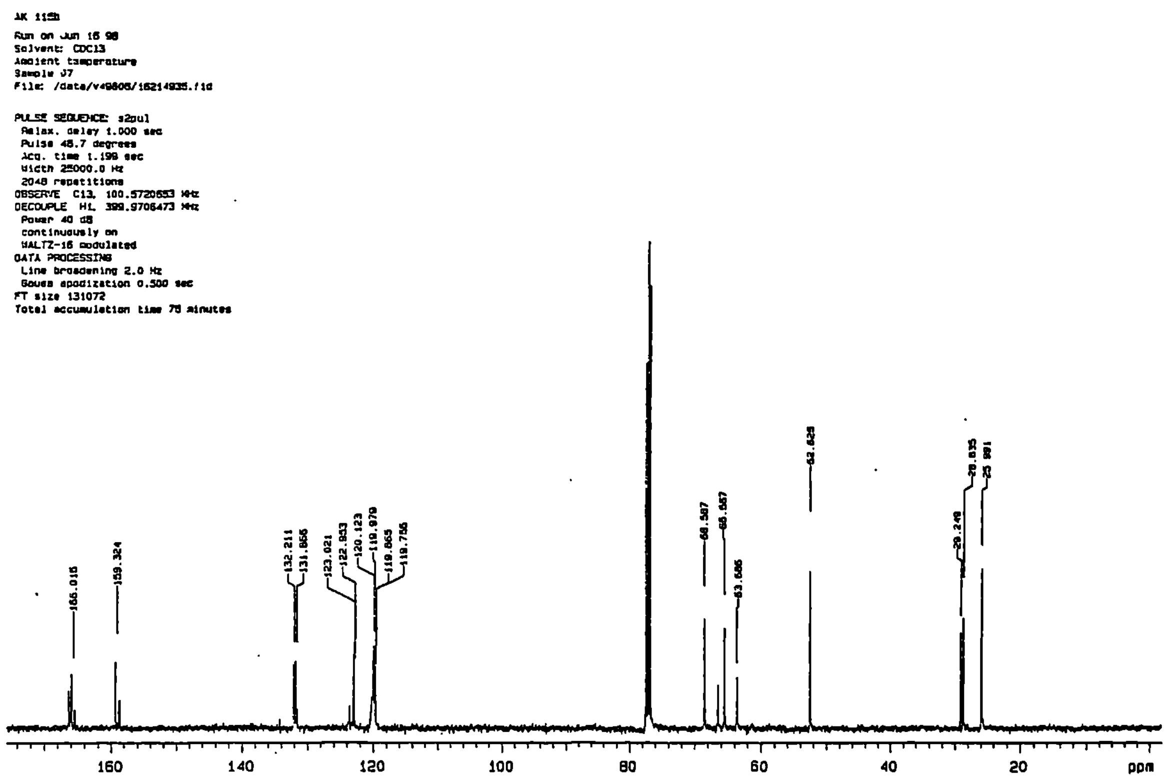
Assignment of ^{13}C nmr spectrum for the hyperbranched polymer blend (**PB18**) prepared from hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalate) and hyperbranched poly(dimethyl 5-(5-hydroxypentoxy)isophthalate), **14**:



Shift δppm	Assignment
22.8	i
29.0, 28.7	h, j
52.6	a, a'
63.7, 65.4	g, g'
66.6, 68.4	k, h'
120.0, (m)	e, e'
123.0, 123.1	c, c'
132.0 (m)	d, d'
158.7, 159.3	f, f'
166.0 (m)	b, b'

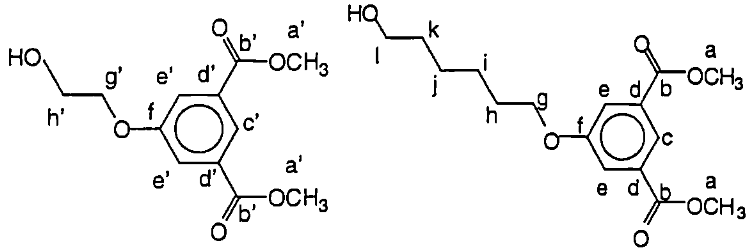
Appendix 4. 21: ^{13}C nmr spectrum (400MHz) of the hyperbranched polymer blend

PB18



```
AK 115b
Run on Jun 16 98
Solvent: CDC13
Ambient temperature
Sample J7
File: /data/v49806/16214935.fid

PULSE SEQUENCE: s2pul
 Relax. delay 1.000 sec
 Pulse 48.7 degrees
 Acq. time 1.198 sec
 Width 25000.0 Hz
 2048 repetitions
OBSERVE  C13, 100.5720653 MHz
DECOUPLE  H1, 399.9706473 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 2.0 Hz
 Gauss apodization 0.500 sec
FT size 131072
Total accumulation time 78 minutes
```

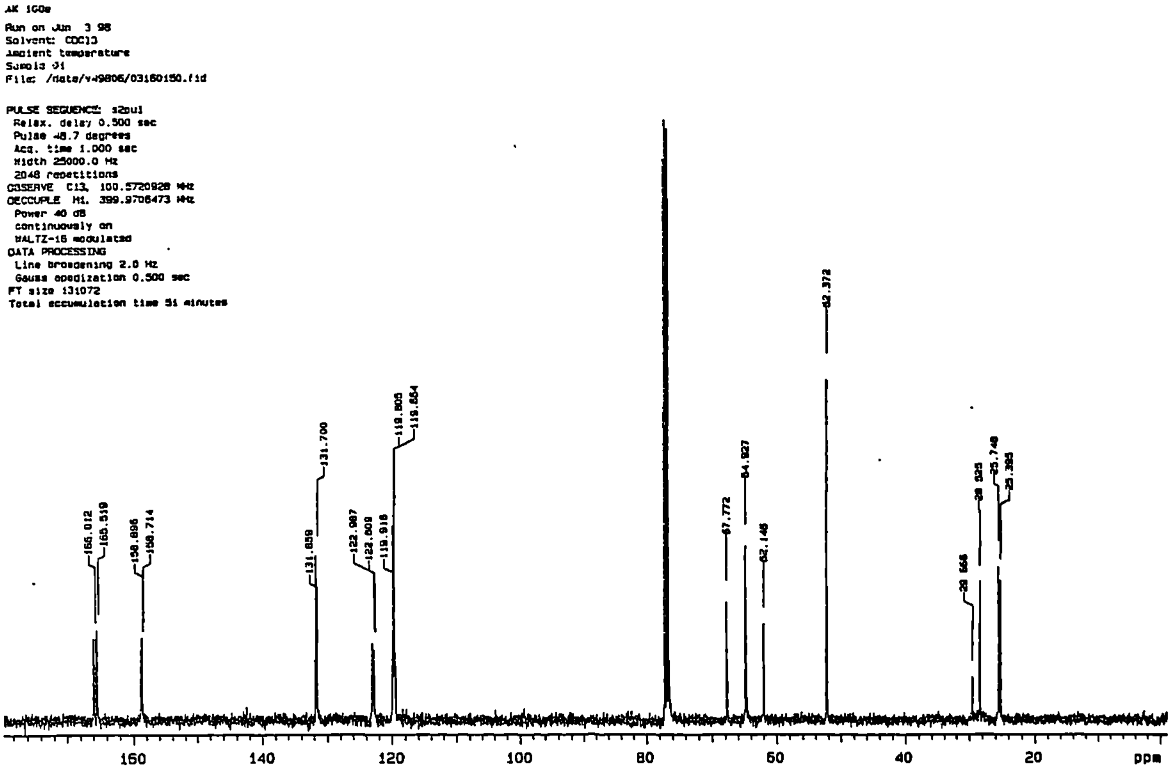
Assignment of ^{13}C nmr spectrum for the hyperbranched polymer blend (**PB19**) prepared from hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalate) and hyperbranched poly(dimethyl 5-(6-hydroxyhexoxy)isophthalate), **15**:



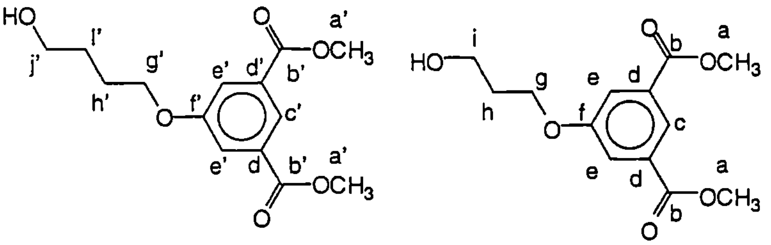
Shift δppm	Assignment
26.0	i j
29.3, 28.9	h, k
52.6	a, a'
63.8, 65.7	g, g'
66.7, 68.6	l, h'
120.0 (m)	e, e'
123.0 (m), 123.7	c, c'
131.9, 132.2	d, d'
158.7, 159.3	f, f`
166.0 (m)	b, b'

Appendix 4. 22: ^{13}C nmr spectrum (400MHz) of the hyperbranched polymer blend

PB19

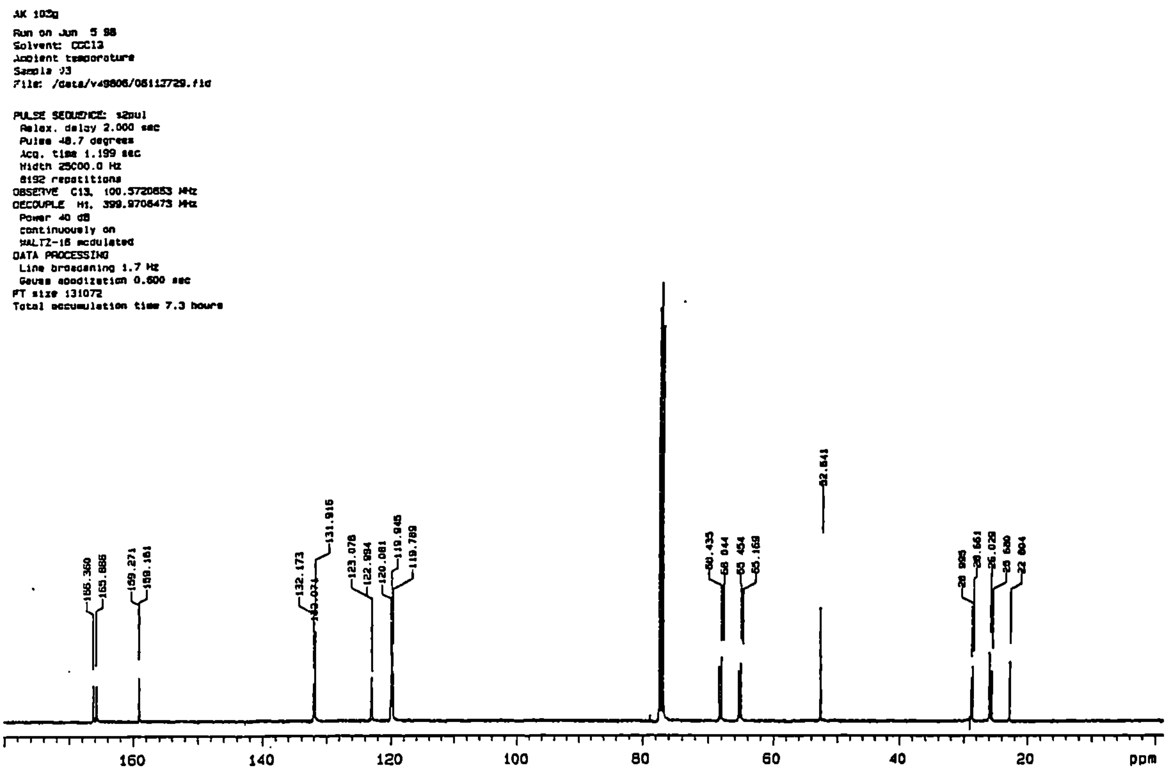


Assignment of ^{13}C nmr spectrum for the hyperbranched copolymer (**CP20**) prepared from monomers dimethyl 5-(4-hydroxybutoxy)isophthalate, **9** and dimethyl 5-(3-hydroxypropoxy)isophthalate, **8**:



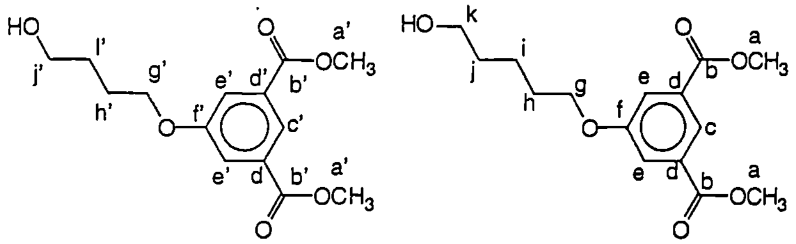
Shift δppm	Assignment
25.4, 25.7	l', h'
28.5	h
29.7	unknown impurity
52.4	a, a'
62.1 64.9 67.8	g' g, j' i
119.8 (m)	e, e'
122.9 (m)	c, c'
131.7 (m)	d, d'
158.7, 158.9	f, f'
165.5, 166.0	b, b'

Appendix 4. 23: ^{13}C nmr spectrum (400MHz) of the hyperbranched copolymer **CP20**



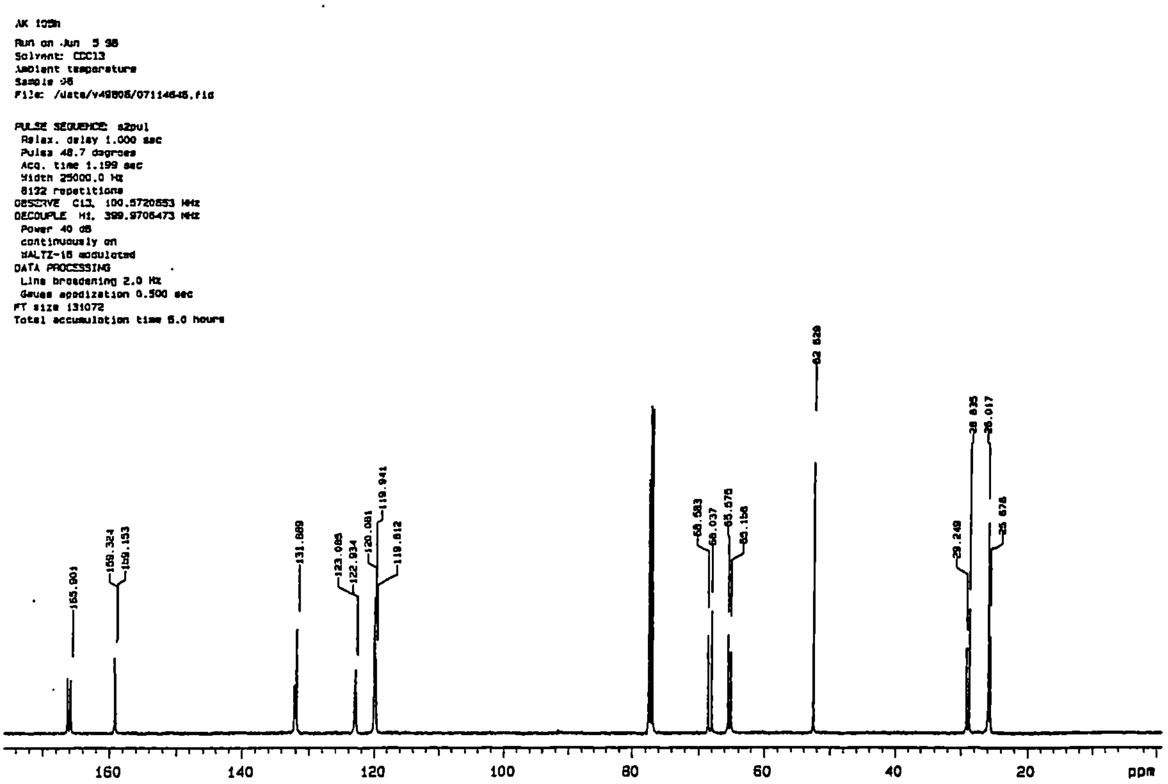
```
AK 103g
Run on Jun  5 98
Solvent: CDCl3
Ambient temperature
Sample 23
File: /data/v49806/06112729.fid

PULSE SEQUENCE: s2pul
 Relax. delay 2.000 sec
 Pulse 48.7 degrees
 Acq. time 1.199 sec
 Width 25000.0 Hz
 8192 repetitions
OBSERVE  C13, 100.5720653 MHz
DECOUPLE  H1, 399.9706473 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.7 Hz
 Gauss apodization 0.600 sec
FT size 131072
Total accumulation time 7.3 hours
```

Assignment of ^{13}C nmr spectrum for the hyperbranched copolymer (**CP21**) prepared from monomers dimethyl 5-(4-hydroxybutoxy)isophthalate, **9** and dimethyl 5-(5-hydroxypentoxy)isophthalate, **10**:



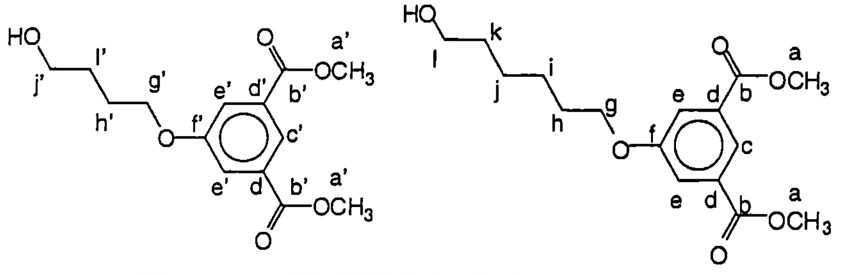
Shift δppm	Assignment
22.8	i
26.0, 25.7	l', h'
29.0, 28.7	j, h
52.6	a, a'
65.2, 65.5 68.0, 68.4	g, g' k, j'
119.9 (m)	e, e'
123.0 (m)	c, c'
132.1 (m)	d, d'
159.2, 159.3	f, f'
165.9, 166.4	b, b'

Appendix 4. 24: ^{13}C nmr spectrum (400MHz) of the hyperbranched copolymer **CP21**



```
AK 109h
Run on Jun  5 98
Solvent: CDCl3
Ambient temperature
Sample 96
File: /data/v49806/07114645.fid

PULSE SEQUENCE: s2pul
 Relax. delay 1.000 sec
 Pulse 48.7 degrees
 Acq. time 1.199 sec
 Width 25000.0 Hz
 8132 repetitions
OBSERVE  C13, 100.5720853 MHz
DECOUPLE  H1, 399.9706473 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 2.0 Hz
 Gauss apodization 0.500 sec
FT size 131072
Total accumulation time 5.0 hours
```

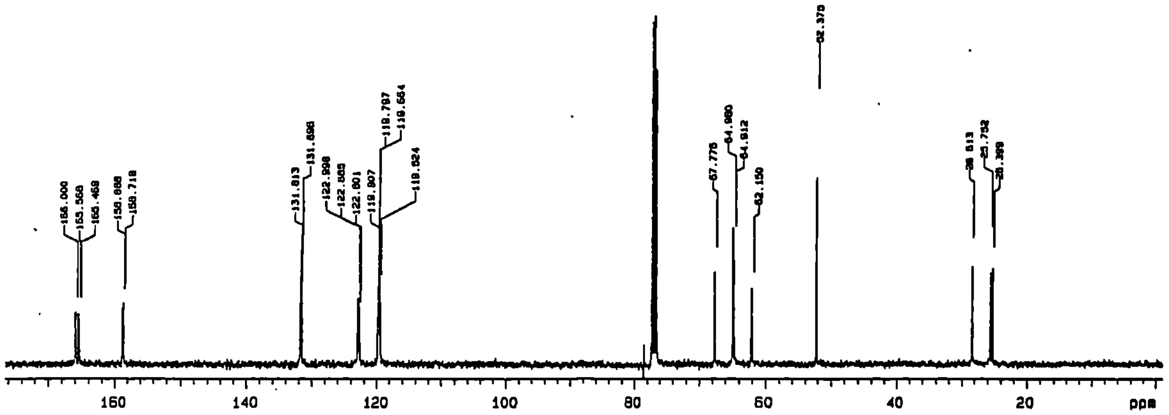
Assignment of ^{13}C nmr spectrum for the hyperbranched copolymer (**CP22**) prepared from monomers dimethyl 5-(4-hydroxybutoxy)isophthalate, **9** and dimethyl 5-(6-hydroxyhexoxy)isophthalate, **11**:



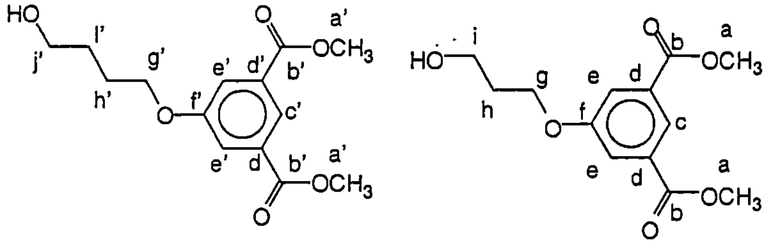
Shift δppm	Assignment
26.0, 25.7 29.0, 28.7	l', h' k, j, i, h
52.6	a, a'
65.2, 65.6 68.0, 68.6	g, g' l, j'
119.9 (m)	e, e'
123.0 (m)	c, c'
131.9 (m)	d, d'
159.2, 159.3	f, f'
165.9, 166.4	b, b'

Appendix 4. 25: ^{13}C nmr spectrum (400MHz) of the hyperbranched copolymer **CP22**

```
AK 99g
Run on Jun  3 98
Solvent: CDCl3
Ambient temperature
Sample J5
File: /data/v49806/03131832.fid

PULSE SEQUENCE: s2pul
 Relax. delay 0.500 sec
 Pulse 48.7 degrees
 Acq. time 1.000 sec
 Width 25000.0 Hz
 2048 repetitions
OBSERVE  C13, 100.5720928 MHz
DECOUPLE  H1, 399.9706473 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 2.0 Hz
 Gauss apodization 0.500 sec
FT size 131072
Total accumulation time 51 minutes
```



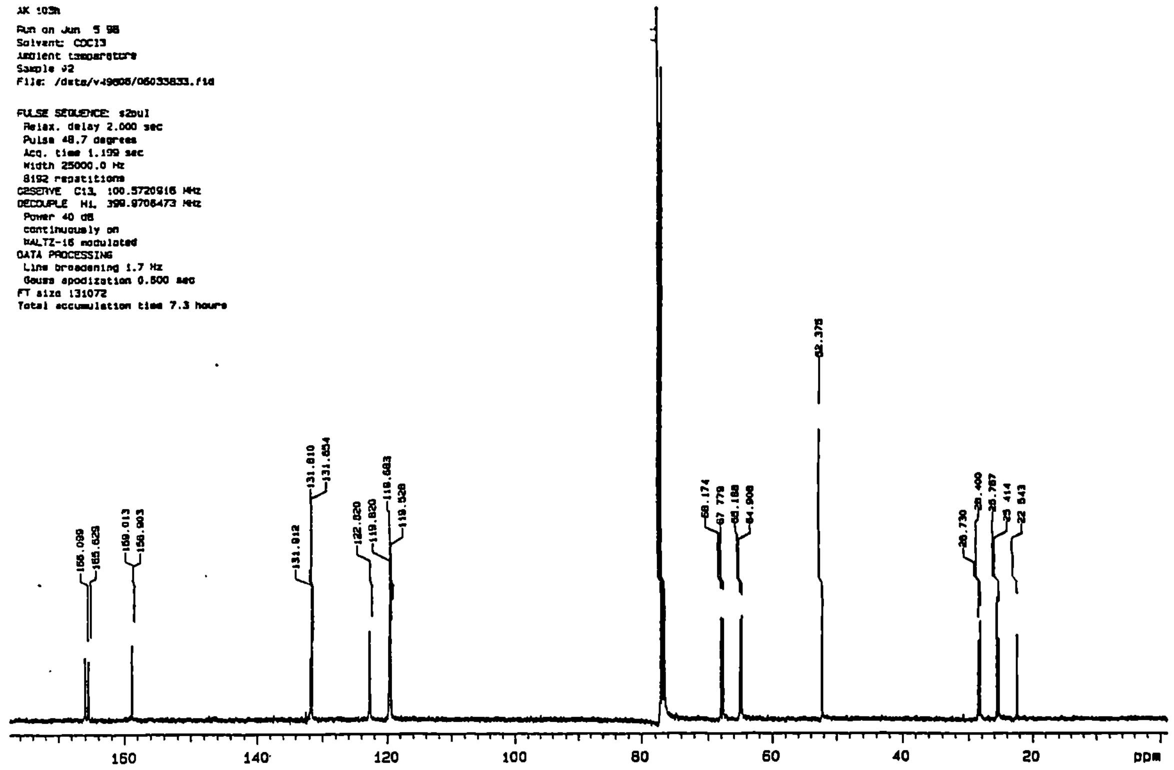
Assignment of ^{13}C nmr spectrum for the hyperbranched polymer blend (**PB20**) prepared from hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophthalate, **13** and hyperbranched poly(dimethyl 5-(3-hydroxypropoxy)isophthalate, **12**:



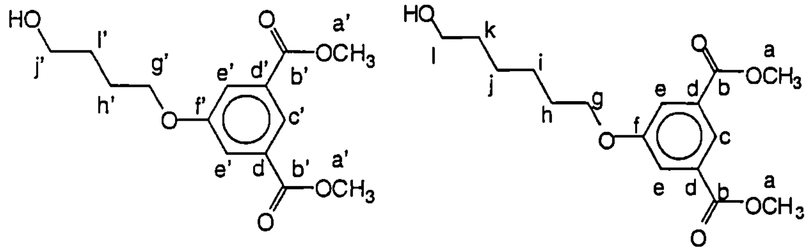
Shift δppm	Assignment
25.4, 25.8	l', h'
28.5	h
52.4	a, a'
62.2	g'
64.9, 65.0 67.8	g, j' i
119.7 (m)	e, e'
122.9 (m)	c, c'
131.7 (m)	d, d'
158.7, 158.9	f, f'
165.5, 166.0	b, b'

Appendix 4. 26: ^{13}C nmr spectrum (400MHz) of the hyperbranched polymer blend

PB20



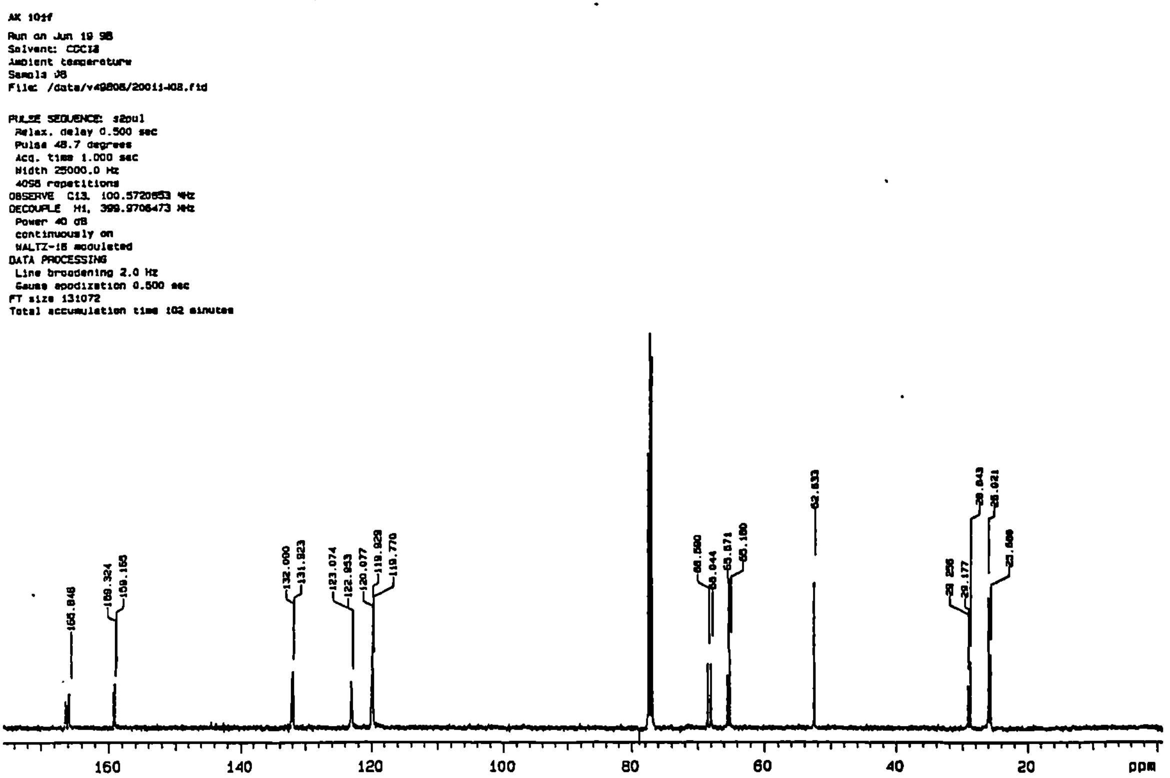
Assignment of ^{13}C nmr spectrum for the hyperbranched polymer blend (**PB21**) prepared from hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophthalate), **13** and hyperbranched poly(dimethyl 5-(6-hydroxypentoxy)isophthalate), **14**:



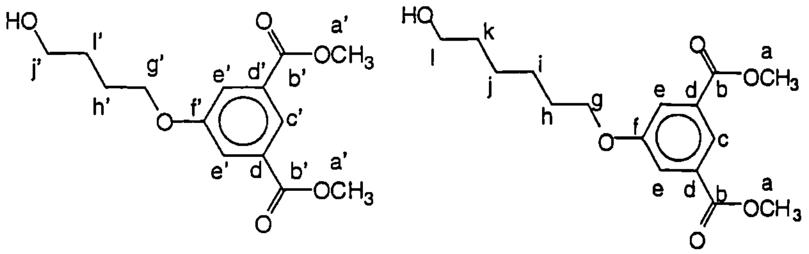
Shift δppm	Assignment
22.5, 25.4, 25.8 28.7, 28.4	l', h' k, j, i, h
52.4	a, a'
65.2, 64.9 68.0, 67.8	g, g' l, j'
119.7 (m)	e, e'
122.8(m)	c, c'
138.1 (m)	d, d'
159.0, 158.9	f, f'
165.6, 166.1	b, b'

Appendix 4. 27: ^{13}C nmr spectrum (400MHz) of the hyperbranched polymer blend

PB21



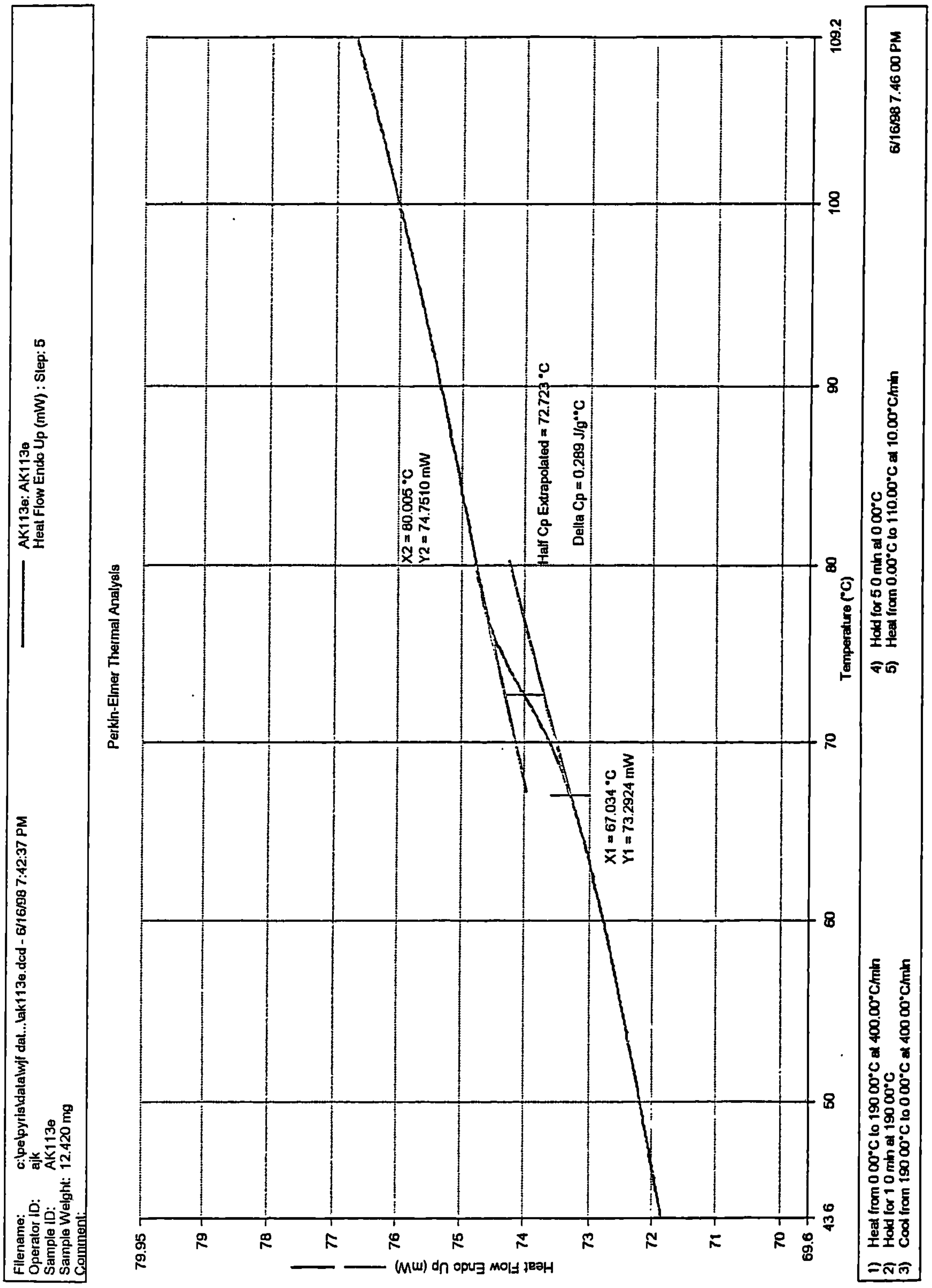
Assignment of ^{13}C nmr spectrum for the hyperbranched polymer blend (**PB22**) prepared from hyperbranched poly(dimethyl 5-(4-hydroxybutoxy)isophthalate), **13** and hyperbranched poly(dimethyl 5-(6-hydroxyhexoxy)isophthalate), **15**:



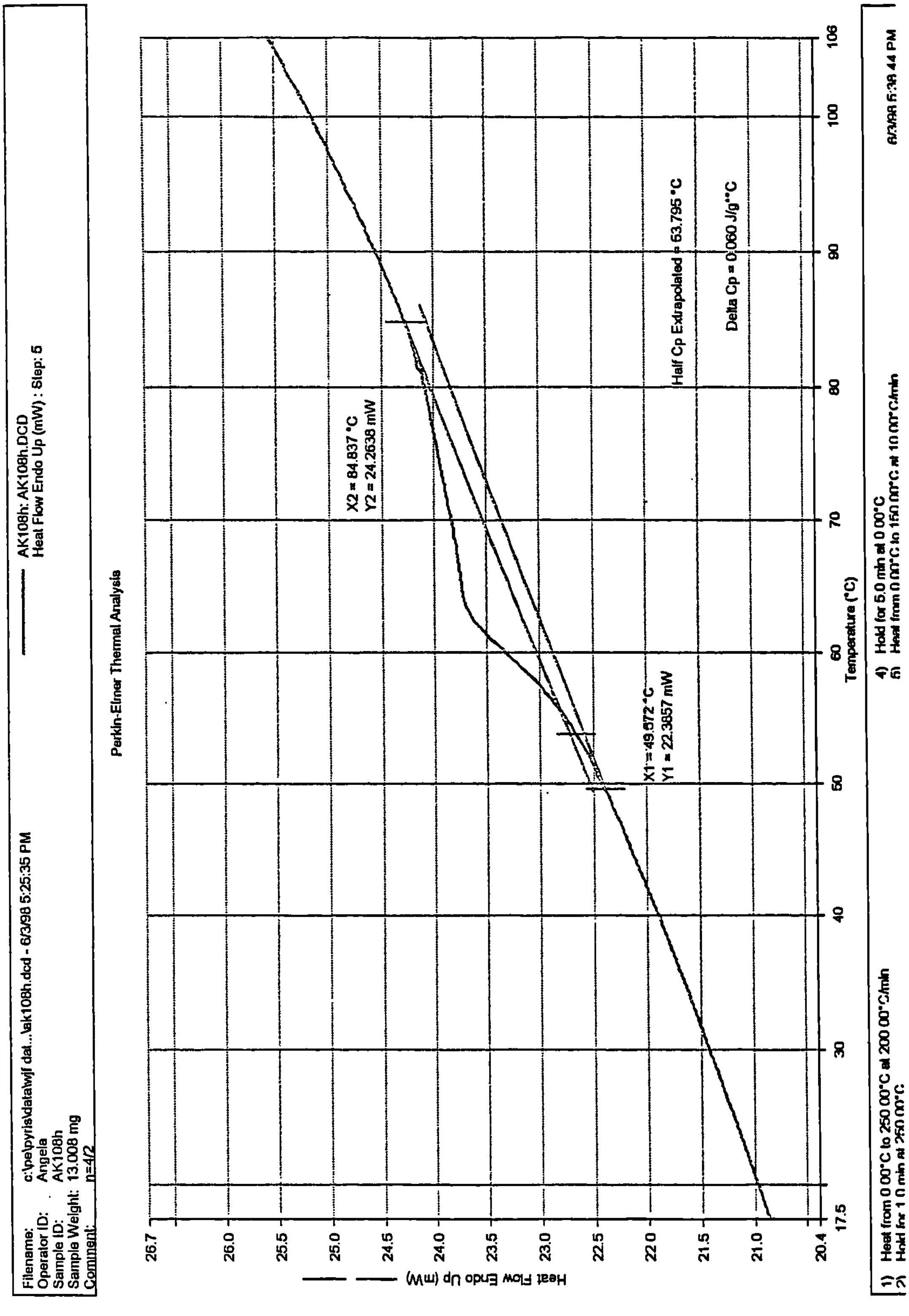
Shift δppm	Assignment
26.0, 25.7 29.3, 28.8	l', h' k, j, i, h
52.6	a, a'
65.2, 65.6 68.0, 68.6	g, g' l, j'
119.9 (m)	e, e'
123.0 (m)	c, c'
132.1 (m)	d, d'
159.2, 159.3	f, f'
165.9 (m), 166.4	b, b'

Appendix 4. 28: ^{13}C nmr spectrum (400MHz) of the hyperbranched polymer blend

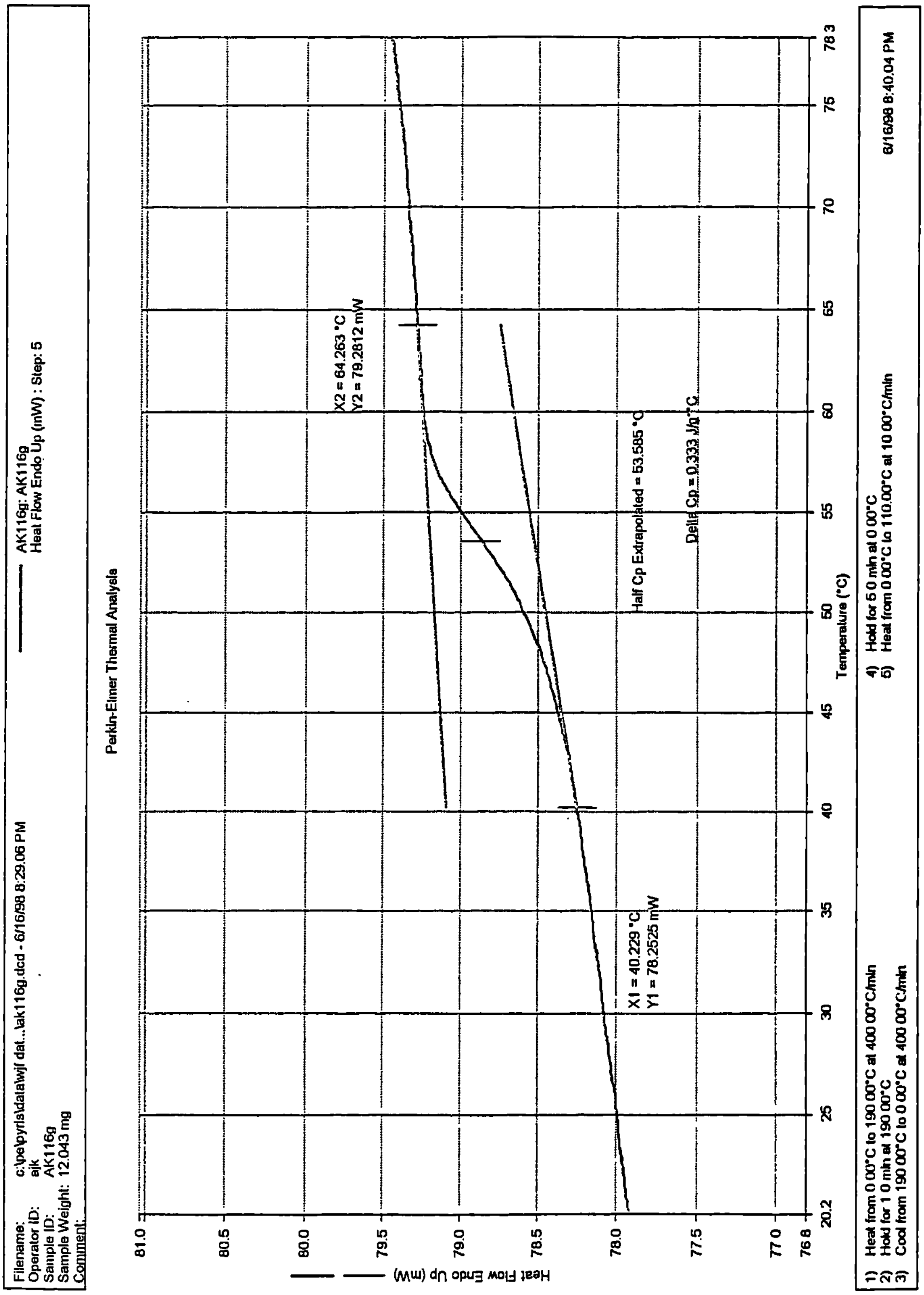
PB22



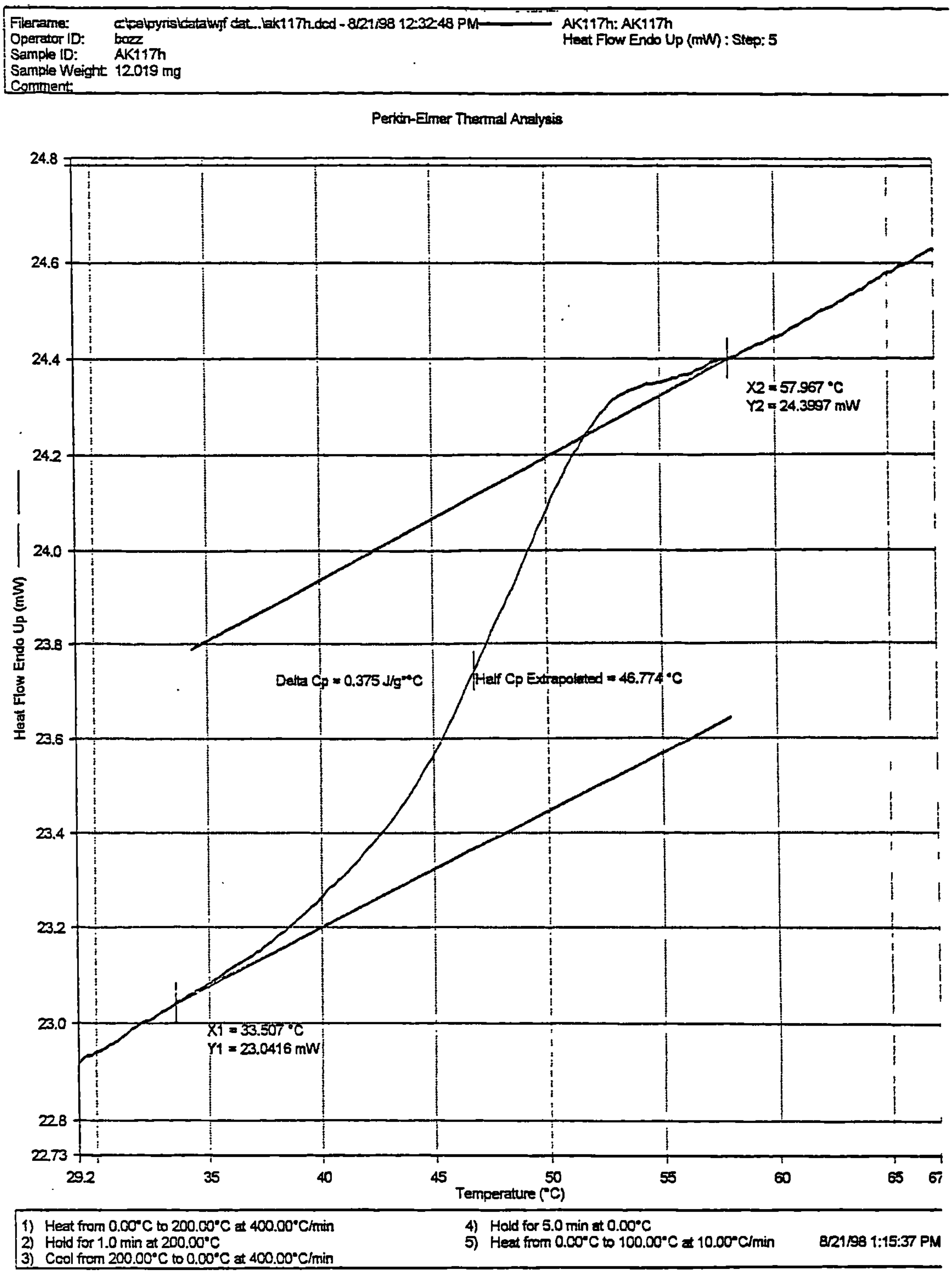
Appendix 4. 29: DSC trace of the hyperbranched copolymer **CP16**



Appendix 4. 30: DSC trace of the hyperbranched copolymer **CP17**



Appendix 4. 31: DSC trace of the hyperbranched copolymer **CP18**



Filename: c:\pe\pyris\data\wjf dat...\ak117h.dcd - 8/21/98 12:32:48 PM
Operator ID: bozz
Sample ID: AK117h
Sample Weight: 12.019 mg
Comment:

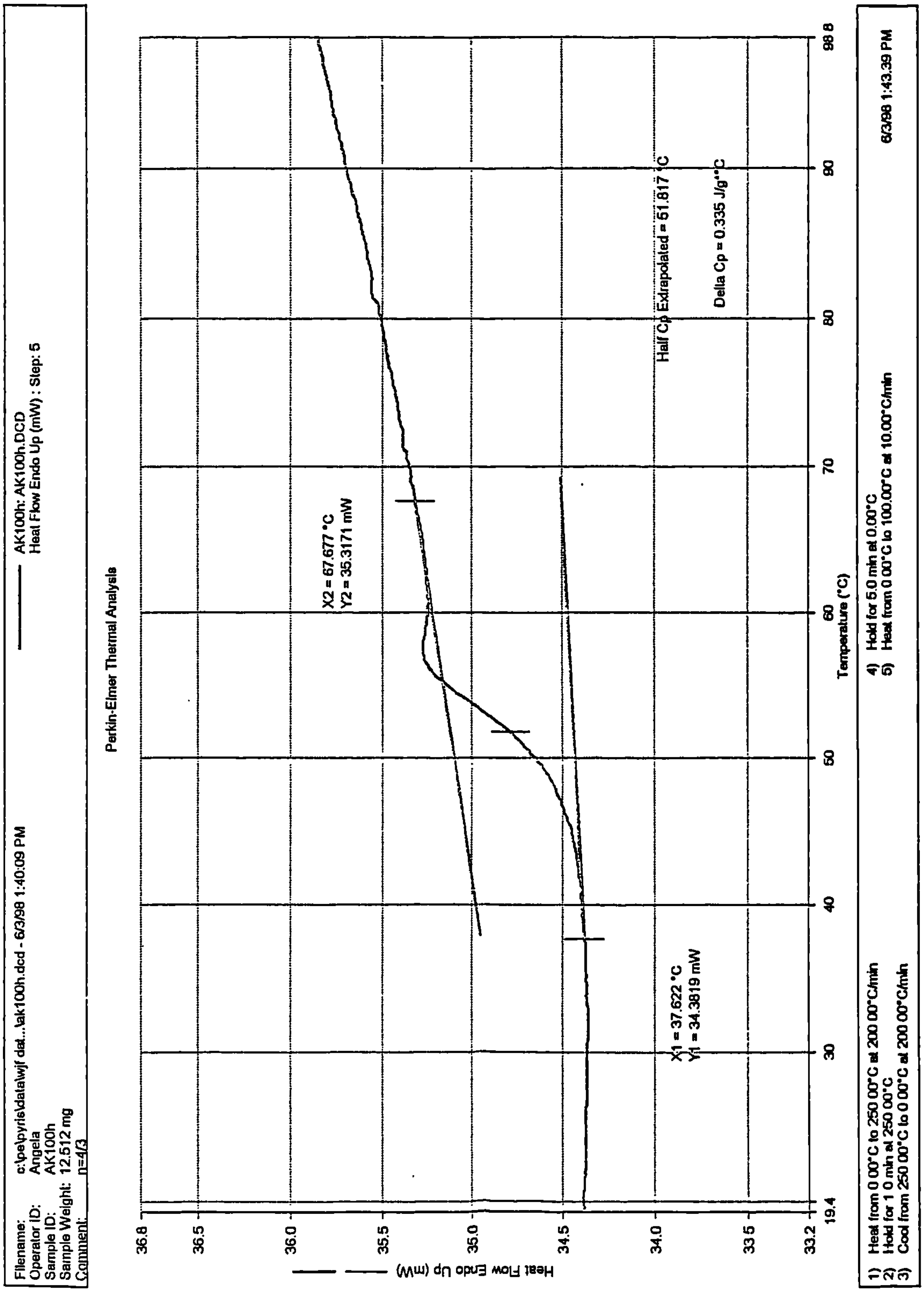
AK117h: AK117h
Heat Flow Endo Up (mW) : Step: 5

Perkin-Elmer Thermal Analysis

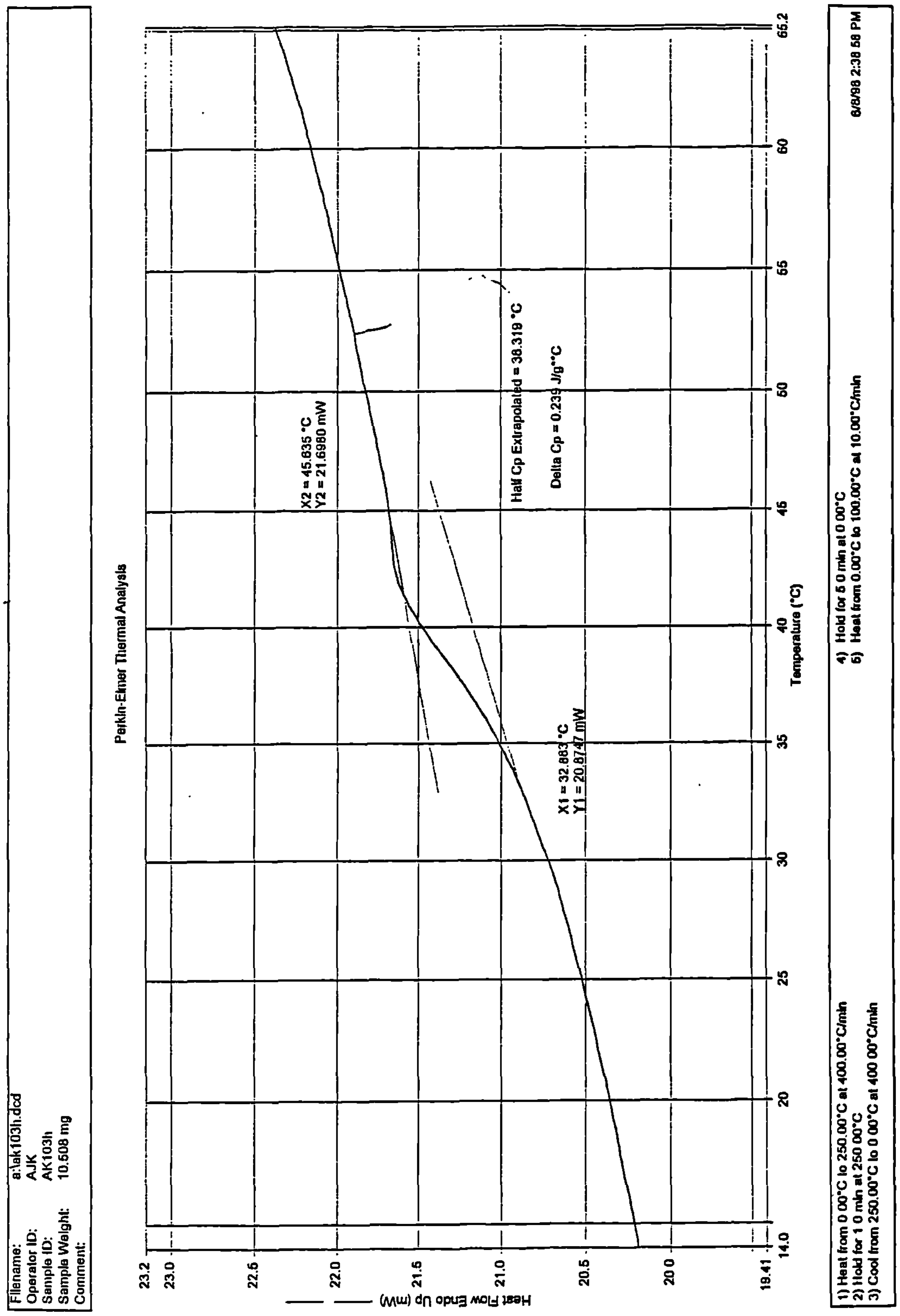
1) Heat from 0.00°C to 200.00°C at 400.00°C/min
2) Hold for 1.0 min at 200.00°C
3) Cool from 200.00°C to 0.00°C at 400.00°C/min
4) Hold for 5.0 min at 0.00°C
5) Heat from 0.00°C to 100.00°C at 10.00°C/min

8/21/98 1:15:37 PM

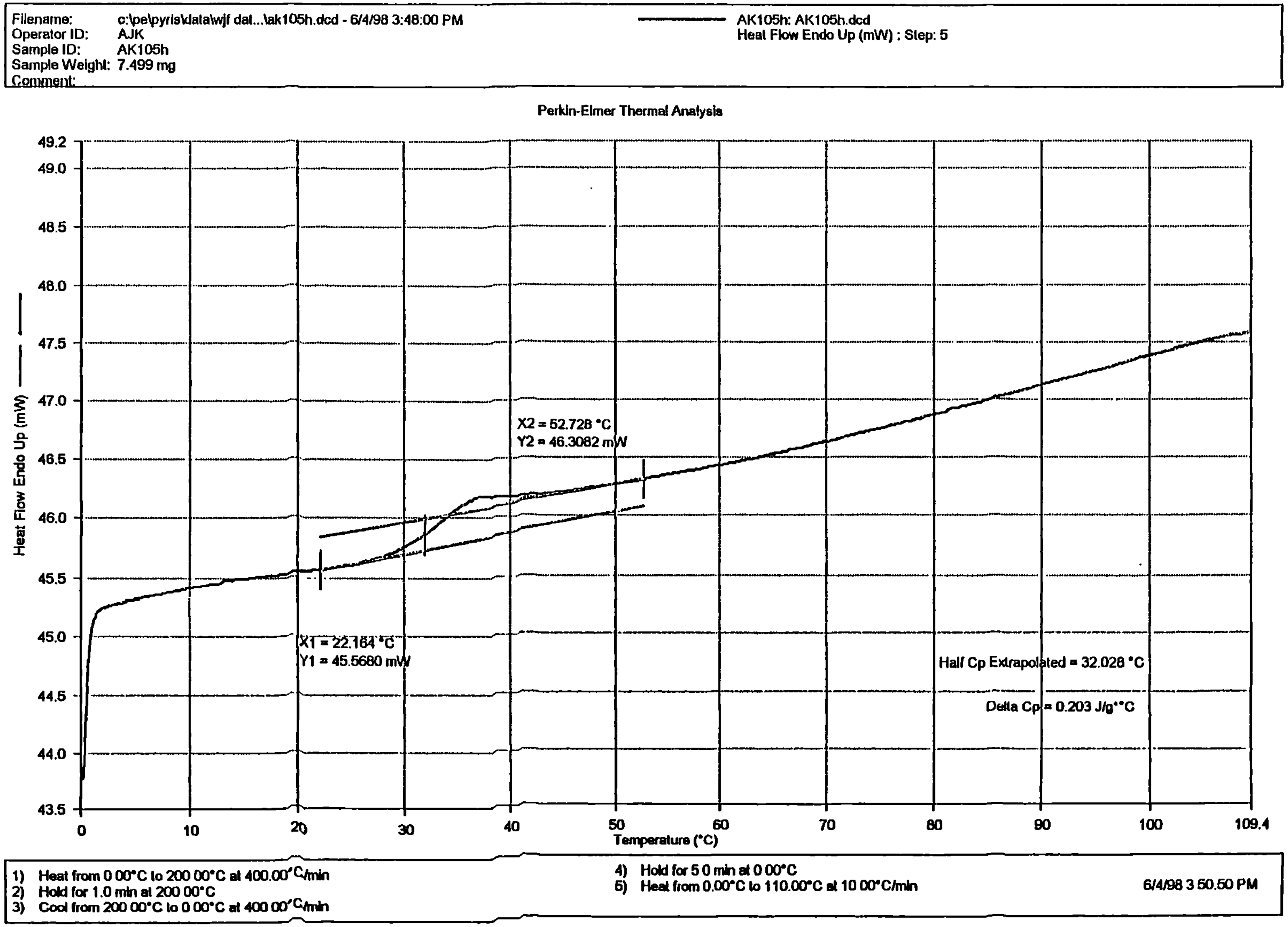
Appendix 4. 32: DSC trace of the hyperbranched copolymer **CP19**



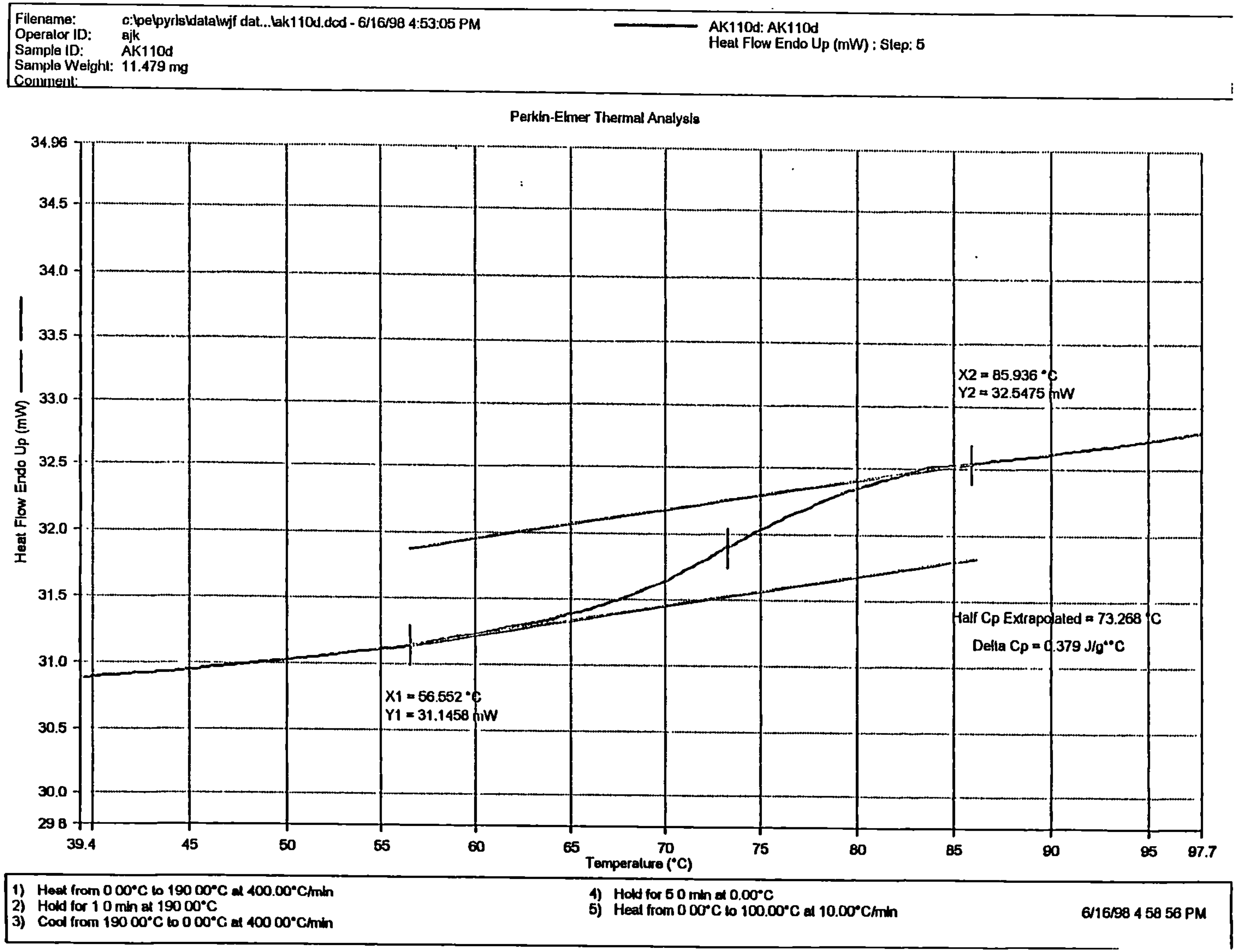
Appendix 4. 33: DSC trace of the hyperbranched copolymer **CP20**



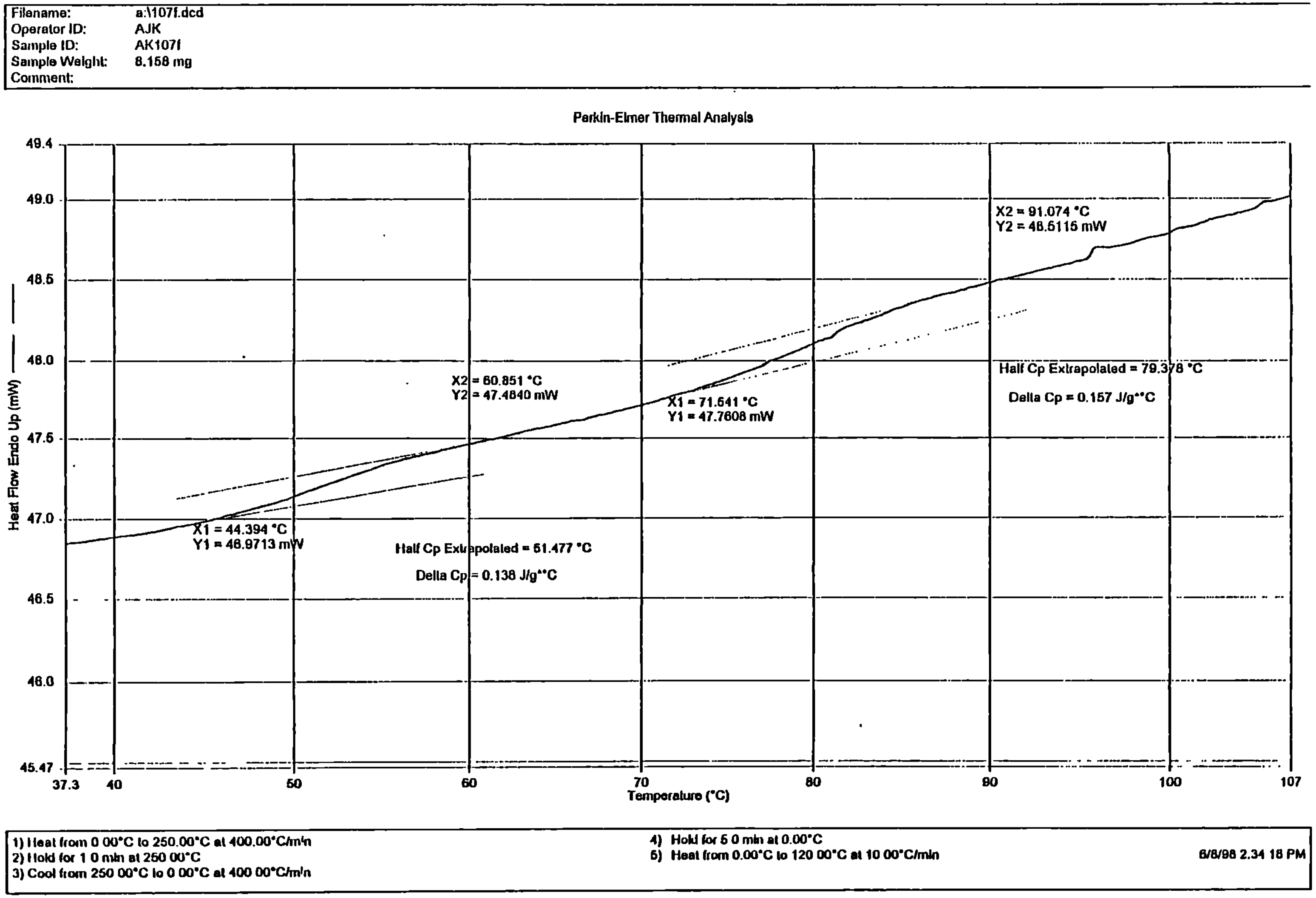
Appendix 4. 34: DSC trace of the hyperbranched copolymer **CP21**



Appendix 4. 35: DSC trace of the hyperbranched copolymer CP22



Appendix 4. 36: DSC trace of the hyperbranched polymer blend **PB16**

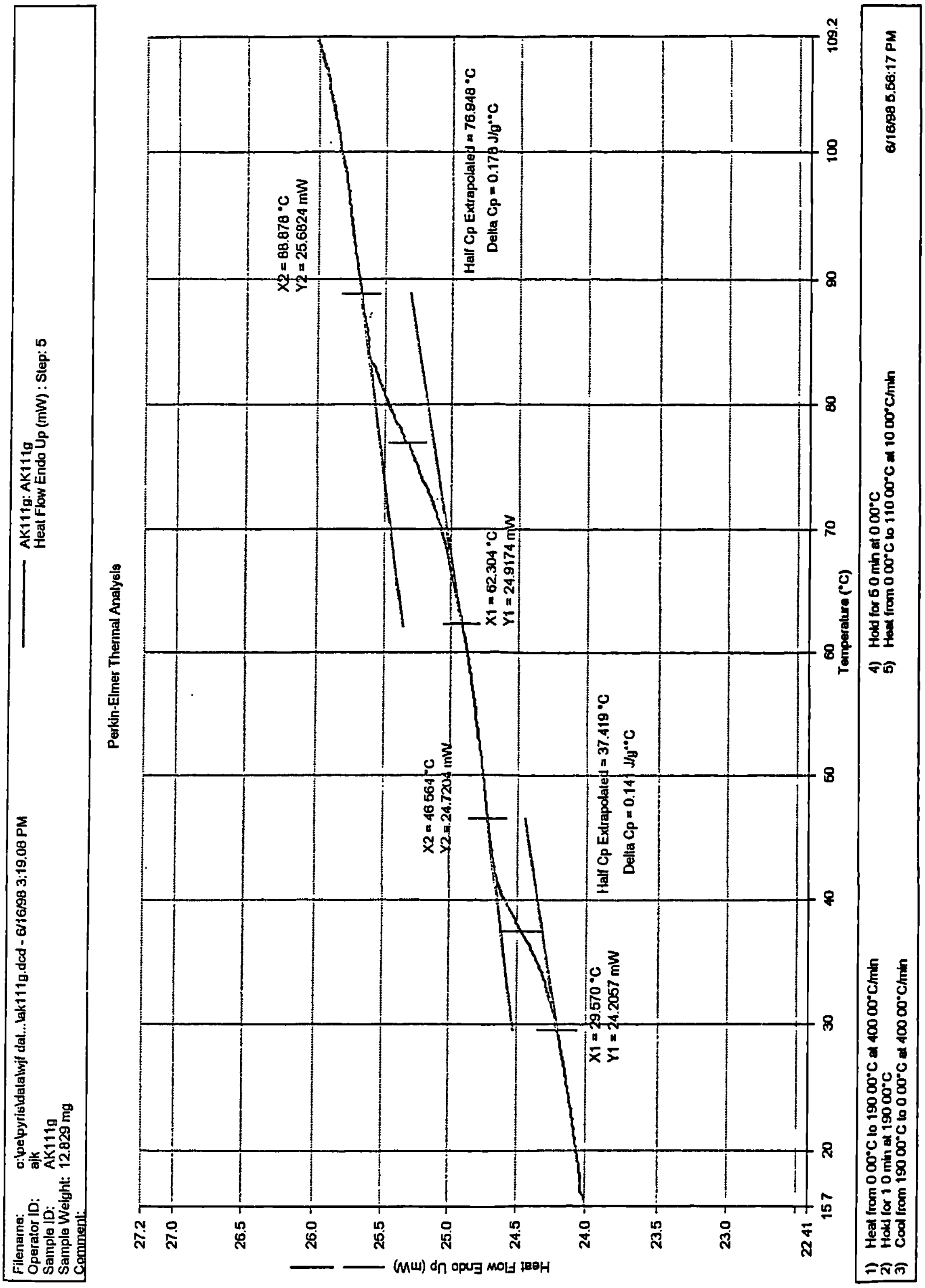


Filename: a:\107f.dcd
Operator ID: AJK
Sample ID: AK107f
Sample Weight: 8.158 mg
Comment:

1) Heat from 0.00°C to 250.00°C at 400.00°C/min
2) Hold for 1.0 min at 250.00°C
3) Cool from 250.00°C to 0.00°C at 400.00°C/min
4) Hold for 5.0 min at 0.00°C
5) Heat from 0.00°C to 120.00°C at 10.00°C/min

6/8/98 2.34 18 PM

Appendix 4. 37: DSC trace of the hyperbranched polymer blend **PB17**


Filename: c:\pe\pyris\data\wjf dat...\ak111g.dcd - 6/16/98 3:19:08 PM
Operator ID: ajk
Sample ID: AK111g
Sample Weight: 12.829 mg
Comment:

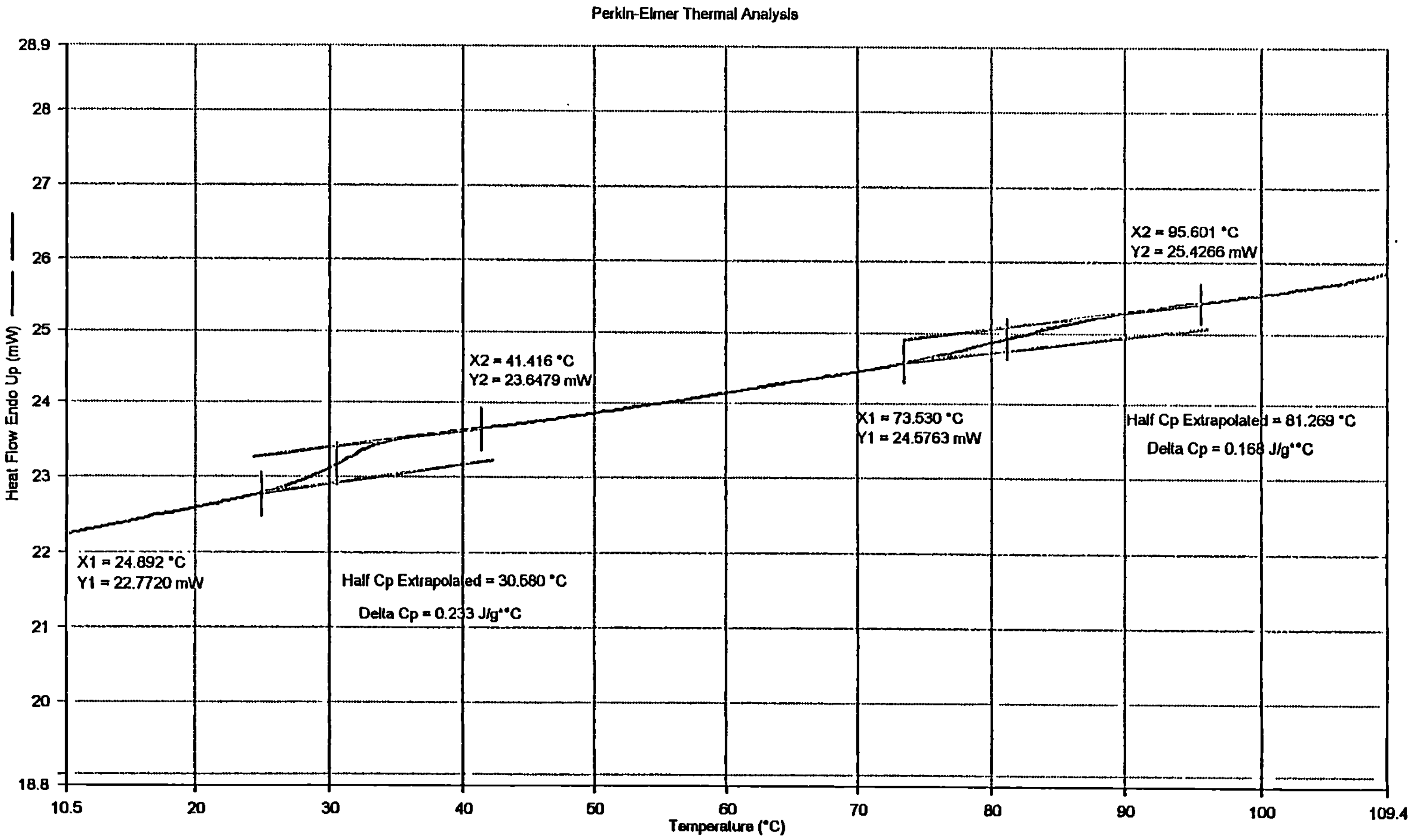
1) Heat from 0.00°C to 190.00°C at 400.00°C/min
2) Hold for 1.0 min at 190.00°C
3) Cool from 190.00°C to 0.00°C at 400.00°C/min
4) Hold for 5.0 min at 0.00°C
5) Heat from 0.00°C to 110.00°C at 10.00°C/min

6/16/98 5:56:17 PM

Appendix 4. 38: DSC trace of the hyperbranched polymer blend **PB18**

Filename: c:\pe\pyris\data\wjf dat...\ak115g.dcd - 6/16/98 6:15:55 PM
Operator ID: ajk
Sample ID: AK115g
Sample Weight: 12.032 mg
Comment:

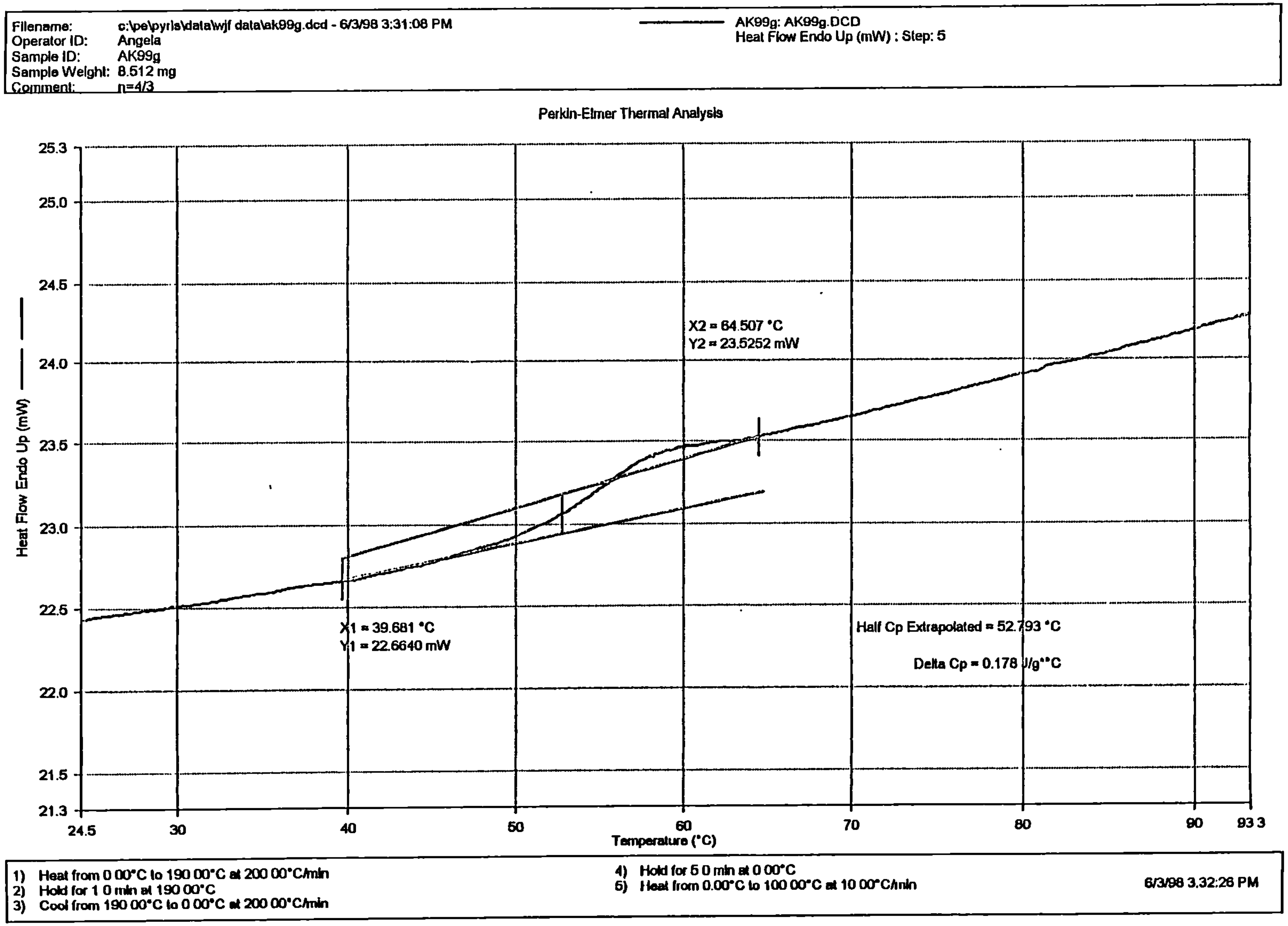
——— AK115g: AK115g
Heat Flow Endo Up (mW) : Step: 5



1) Heat from 0.00°C to 190.00°C at 400.00°C/min
2) Hold for 1.0 min at 190.00°C
3) Cool from 190.00°C to 0.00°C at 400.00°C/min
4) Hold for 5.0 min at 0.00°C
5) Heat from 0.00°C to 110.00°C at 10.00°C/min

6/16/98 6.18.55 PM

Appendix 4. 39: DSC trace of the hyperbranched polymer blend **PB19**



Filename: c:\pe\pyris\data\wjf data\ak99g.dcd - 6/3/98 3:31:08 PM
Operator ID: Angela
Sample ID: AK99g
Sample Weight: 8.512 mg
Comment: n=4/3

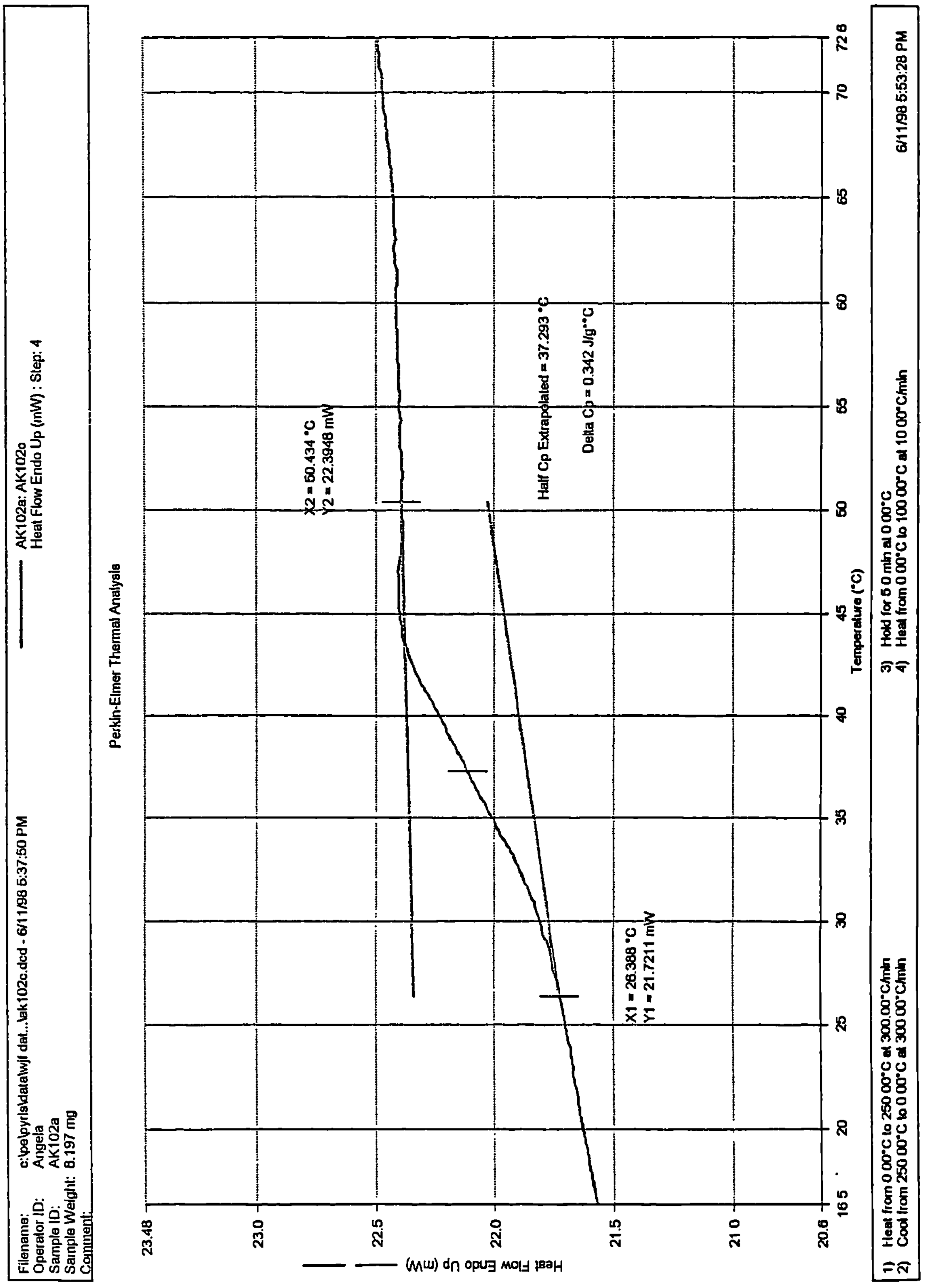
AK99g: AK99g.DCD
Heat Flow Endo Up (mW) : Step: 5

Perkin-Elmer Thermal Analysis

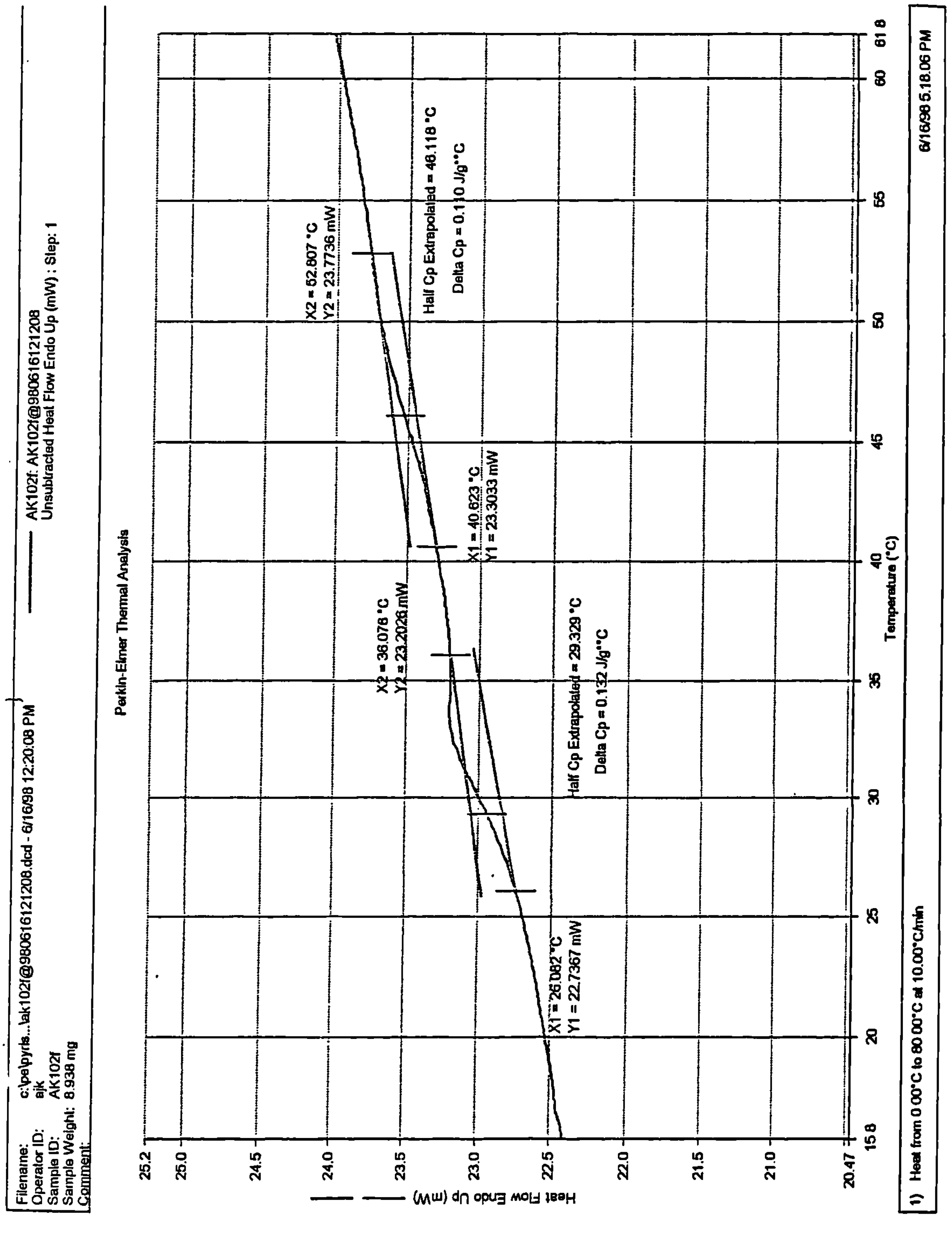
1) Heat from 0.00°C to 190.00°C at 200.00°C/min
2) Hold for 1.0 min at 190.00°C
3) Cool from 190.00°C to 0.00°C at 200.00°C/min
4) Hold for 5.0 min at 0.00°C
5) Heat from 0.00°C to 100.00°C at 10.00°C/min

6/3/98 3:32:26 PM

Appendix 4. 40: DSC trace of the hyperbranched polymer blend **PB20**



Appendix 4. 41: DSC trace of the hyperbranched polymer blend PB21

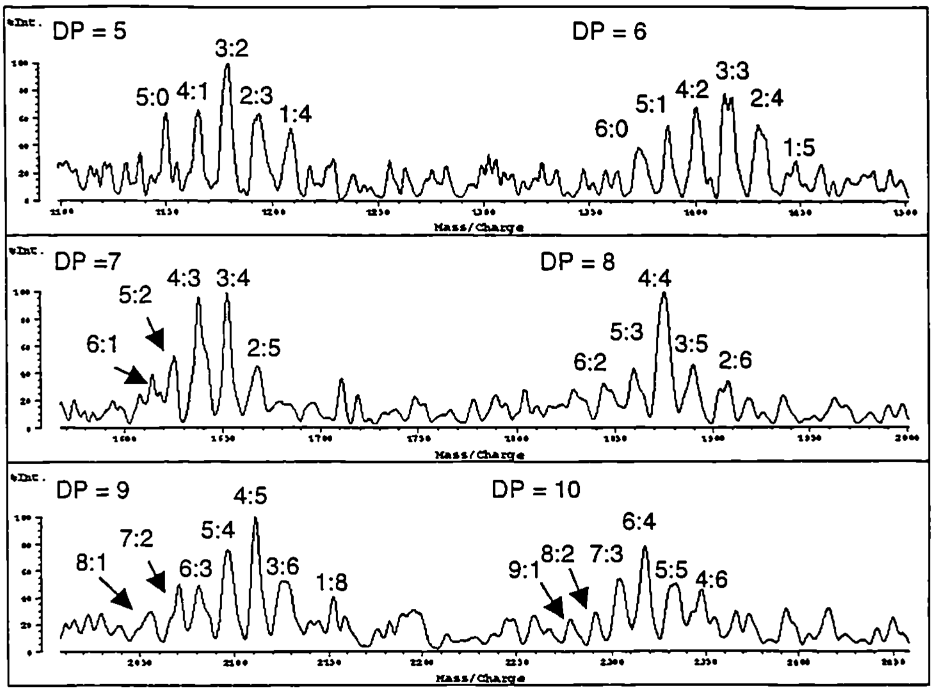


Appendix 4. 42: DSC trace of the hyperbranched polymer blend **PB22**

Appendix 4. 43: Expanded MALDI-TOF mass spectrum obtained for the copolymer **CP16** (KCl doped sample)

The ratios correspond to the ratio of the monomer residue units in the copolymer, i.e. n = 2: n = 3.

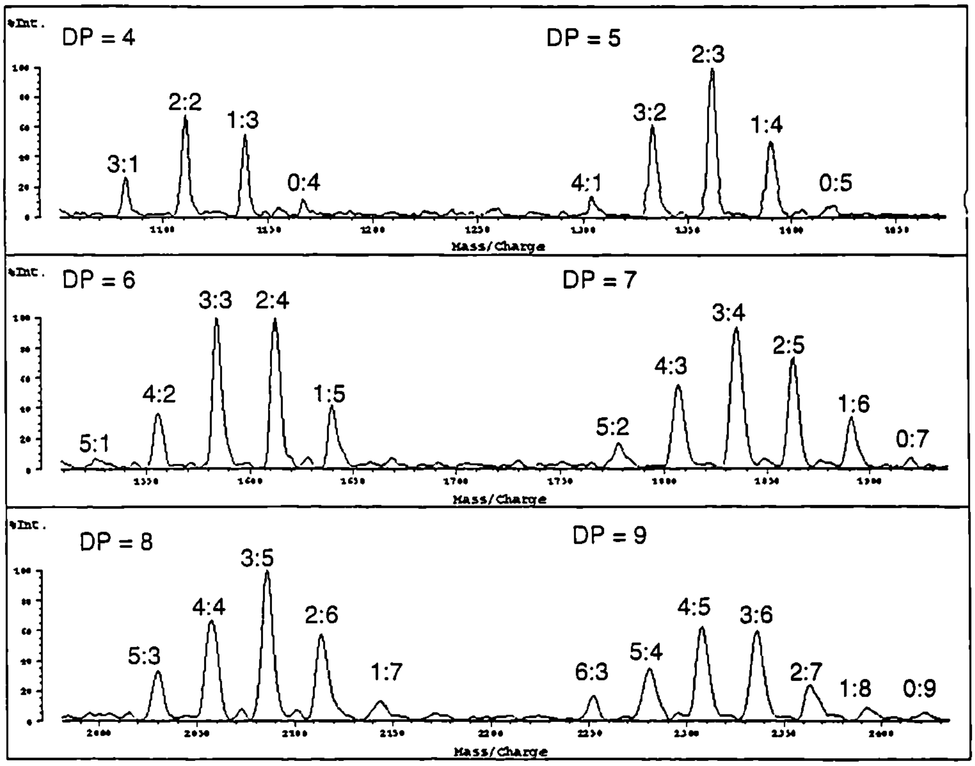
Only cyclised polymers are observed as their K adducts.



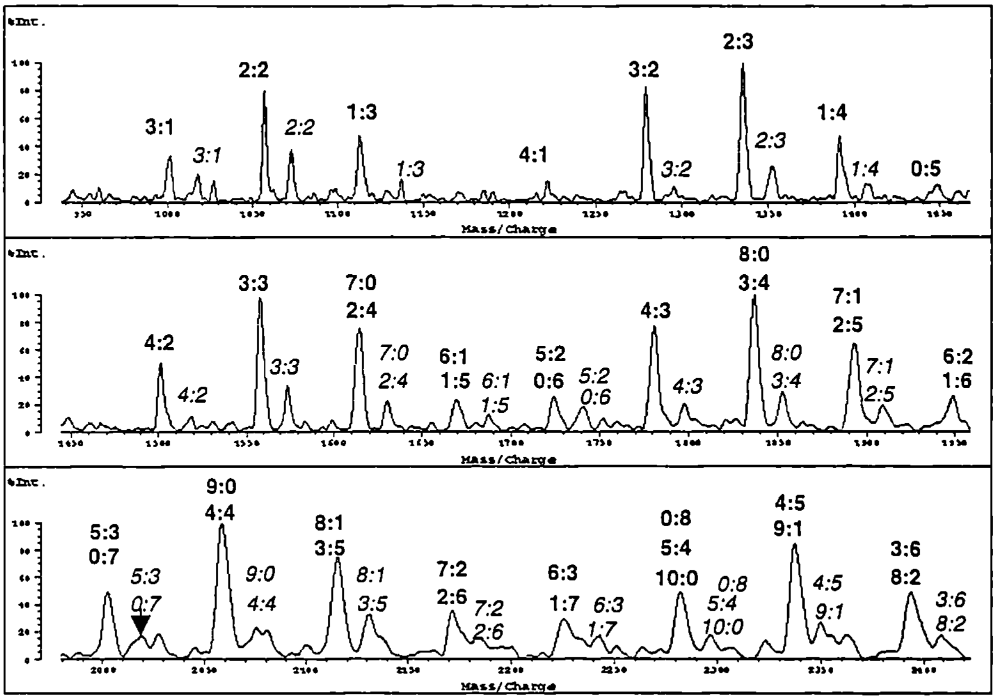
Appendix 4. 44: Expanded MALDI-TOF mass spectrum obtained for the copolymer **CP 17** (CsCl doped sample

The ratios correspond to the ratio of the monomer residue units in the copolymer, i.e. n = 2: n = 4.

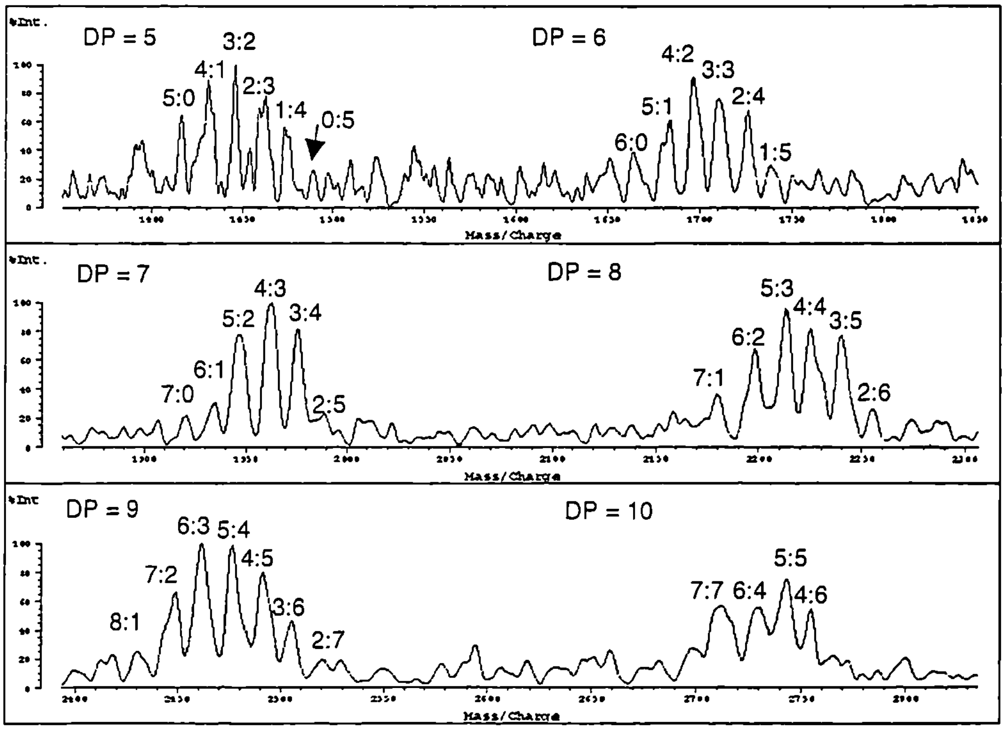
Only uncyclised polymers are observed as their Cs adducts.



Appendix 4. 45: Expanded MALDI-TOF mass spectrum obtained for the copolymer **CP 19** (NaCl doped sample). The ratios correspond to the ratio of the monomer residue units in the copolymer, i.e. n = 2: n =6. Only uncyclised polymers are observed as predominantly their Na adducts (ratios in **bold** type), a minor potassium ion series is observed (ratios in *italics*).



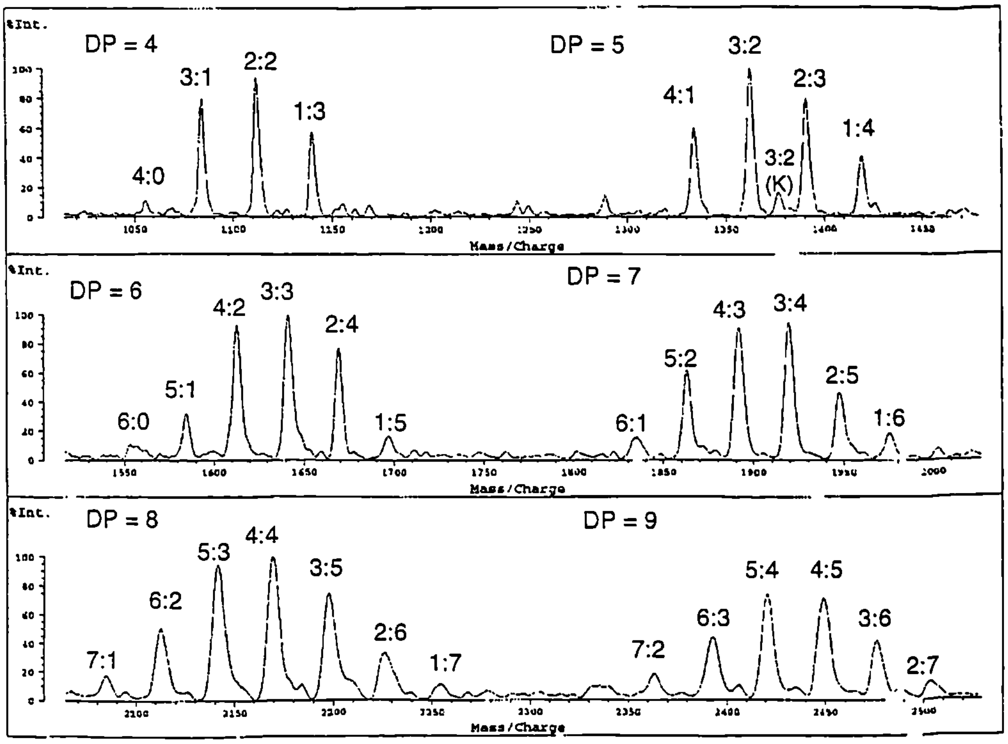
Appendix 4. 46: Expanded MALDI-TOF mass spectrum obtained for the copolymer **CP 21** (CsCl doped sample The ratios correspond to the ratio of the monomer residue units in the copolymer, i.e. n = 4: n = 5. Only uncyclised polymers are observed as their Cs adducts.



Appendix 4. 47: Expanded MALDI-TOF mass spectrum obtained for the copolymer **CP 22** (NaCl doped sample)

The ratios correspond to the ratio of the monomer residue units in the copolymer, i.e. n = 4: n =6.

Only uncyclised polymers are observed as predominantly their Na adducts

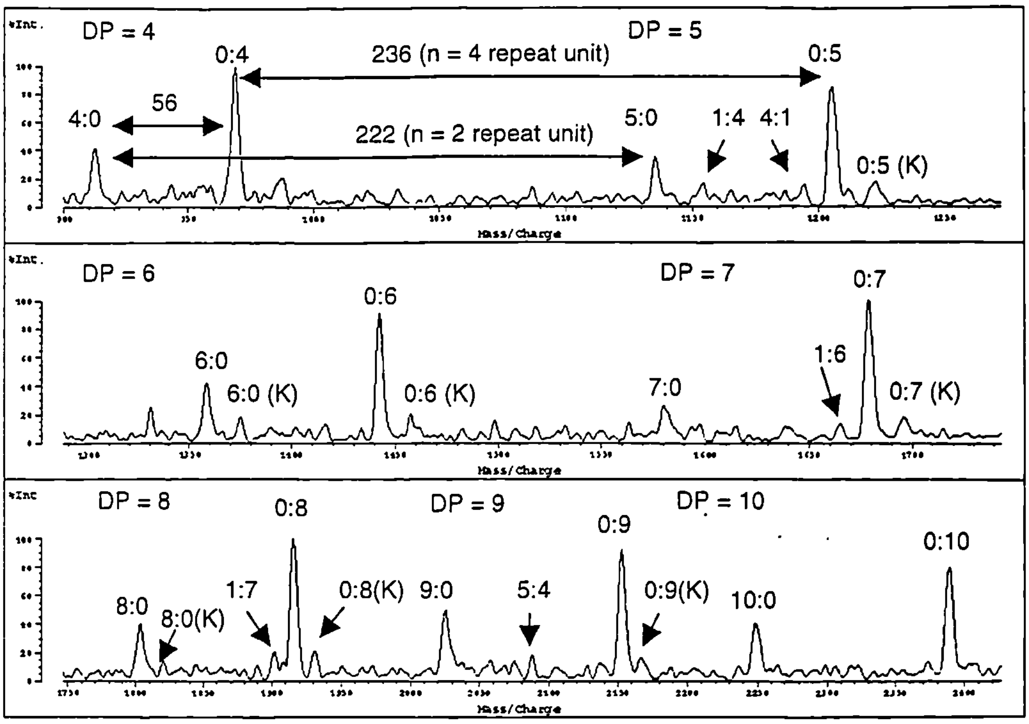


Appendix 4. 48: Expanded MALDI-TOF mass spectrum obtained for the polymer blend **PB 16** (NaCl doped sample).

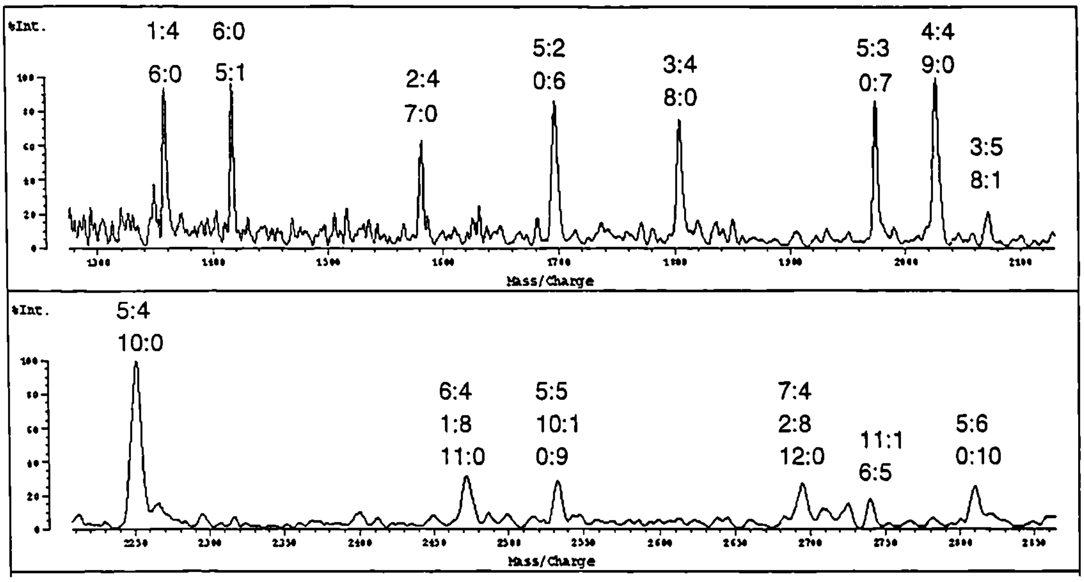
The ratios correspond to the ratio of the monomer residue units in the copolymer, i.e. n = 2: n = 3.

Only cyclised polymers are observed as predominantly their Na adducts,

minor peaks are due to K adducts and are marked on the spectrum(K).



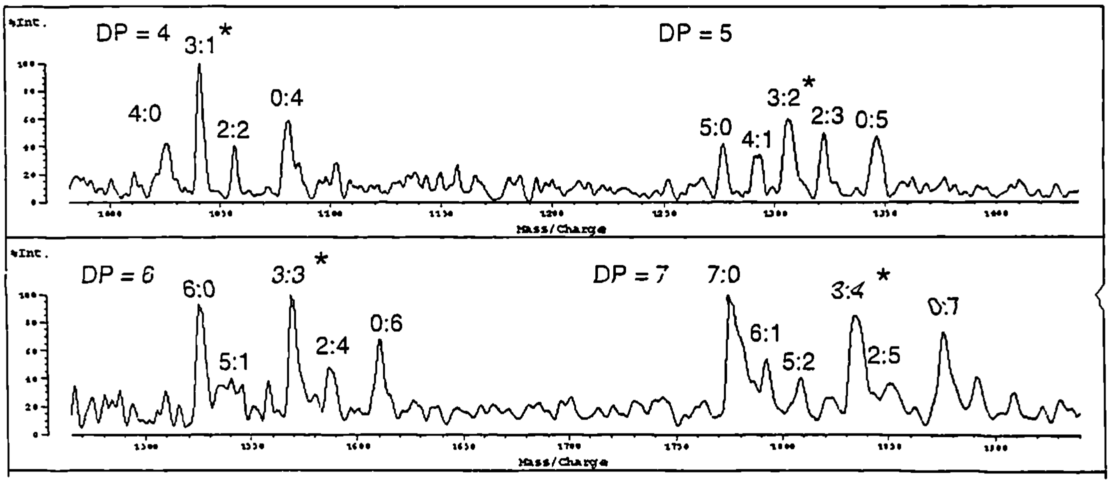
Appendix 4. 49: Expanded MALDI-TOF mass spectrum obtained for the polymer blend **PB 19** (NaCl doped sample). The ratios correspond to the ratio of the monomer residue units in the copolymer, i.e. n = 2: n = 6. Only cyclised polymers are observed as their Na adducts. Assignment of peaks are ambiguous.



Appendix 4. 50: Expanded MALDI-TOF mass spectrum obtained for the polymer blend **PB 21** (NaCl doped sample

The ratios correspond to the ratio of the monomer residue units in the copolymer, i.e. n = 4: n = 5.

Only cyclised polymers are observed as predominantly their Na adducts,



* This ion series is ambiguous since it could also correspond to the homopolymer (**14**), which has undergone an elimination reaction, as discussed in Chapter 5 (i.e. loss of THF from the focal unit).

APPENDIX FIVE

COLLOQUIA, CONFERENCES AND COURSES ATTENDED

Colloquia attended

1995

October 13	Prof. R. Schmutzler, Univ Braunschweig, FRG. Calixarene-Phosphorus Chemistry: A New Dimension in Phosphorus Chemistry
October 18	Prof. A. Alexakis, Univ. Pierre et Marie Curie, Paris, Synthetic and Analytical Uses of Chiral Diamines
November 1	Prof. W. Motherwell, UCL London New Reactions for Organic Synthesis
November 8	Dr. D. Craig, Imperial College, London New Strategies for the Assembly of Heterocyclic Systems

1996

January 10	Dr Bill Henderson, Waikato University, NZ Electrospray Mass Spectrometry - a new sporting technique
January 17	Prof. J. W. Emsley, Southampton University Liquid Crystals: More than Meets the Eye
February 7	Dr R.B. Moody, Exeter University Nitrosations, Nitrations and Oxidations with Nitrous Acid
February 28	Prof. E. W. Randall, Queen Mary & Westfield College New Perspectives in NMR Imaging
October 9	Professor G. Bowmaker, University Aukland, NZ Coordination and Materials Chemistry of the Group 11 and Group 12 Metals : Some Recent Vibrational and Solid State NMR Studies

October 16	Professor Ojima, Guggenheim Fellow, State University of New York at Stony Brook Silylformylation and Silylcarbocyclisations in Organic Synthesis
October 22	Professor B. J. Tighe, Department of Molecular Sciences and Chemistry University of Aston Making Polymers for Biomedical Application - can we meet Nature's Challenge?
October 23	Professor H. Ringsdorf (Perkin Centenary Lecture), Johannes Gutenberg Universitat, Mainz, Germany Function Based on Organisation
November 18	Professor G. A. Olah, University of Southern California, USA Crossing Conventional Lines in my Chemistry of the Elements
December 3	Professor D. Phillips, Imperial College, London "A Little Light Relief" -

1997

January 16	Dr Sally Brooker, University of Otago, NZ Macrocycles: Exciting yet Controlled Thiolate Coordination Chemistry
January 22	Dr Neil Cooley, BP Chemicals, Sunbury Synthesis and Properties of Alternating Polyketones
February 12	Dr Geert-Jan Boons, University of Birmingham New Developments in Carbohydrate Chemistry
February 18	Professor Sir James Black, Foundation/King's College London My Dialogues with Medicinal Chemists
February 26	Dr Tony Ryan, UMIST Making Hairpins from Rings and Chains

October 8	Prof. E. Atkins, Department of Physics, University of Bristol Advances in the control of architecture for polyamides: from nylons to genetically engineered silks to monodisperse oligoamides
October 21	Prof. A. F. Johnson, IRC, Leeds Reactive processing of polymers: science and technology
November 5	Dr Mimi Hii, Oxford University Studies of the Heck reaction
November 11	Prof. V Gibson, Imperial College, London Metallocene polymerisation
November 26	Prof. R.W. Richards, University of Durham, Inaugural Lecture A random walk in polymer science

1998

January 28	Dr Steve Rannard, Courtaulds Coatings (Coventry) The synthesis of dendrimers using highly selective chemical reactions
March 4	Prof. T.C.B. McLeish, IRC of Polymer Science Technology, Leeds University The polymer physics of pyjama bottoms (or the novel rheological characterisation of long branching in entangled macromolecules)

Conferences and courses attended

1996

April 10-12	Aspects of Contemporary Polymer Science, MACRO Group UK Famil Meeting, Manchester
Jul 29-Aug 2	International Conference on Recent Advances in Polymer Synthesis, Y

1997

April 10-12	MACRO Group UK Spring Meeting for Younger Researchers, Leeds
July 2-6	EPSRC Graduate Schools Programme, Sheffield
July 21-25	3rd International Conference on Materials Chemistry, Exeter
Sept 17-19	IRC Industrial Club Meeting, Leeds

1998

January	IRC Polymer Physics and Engineering Courses, Leeds and Bradford Universities
April 6-9	RSC National Congress and Young Researchers Meeting, Durham
July 12-17	IUPAC, World Polymer Congress, 37th International Symposium on Macromolecules, Gold Coast, Australia
Sept	IRC Industrial Club Meeting, Durham