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Catalysis in the synthesis of hyperbranched polyesters

Serguei Daout

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Abstract

An AB_2 monomer, dimethyl 5-(2-hydroxyethoxy)isophthalate was prepared on a scale of 3kg. It was successfully polymerised in the melt and the influence of reaction conditions and catalysts was studied. Structural and physical characterisation of these materials was performed using variety of analytical techniques, including SEC and MALDI-TOF MS. The polymerisations yielded high molecular weight materials with a broad polydispersity. All polymers were cyclised, the proportion of cyclised species increased with time, generally until complete cyclisation was achieved. The polymerisation process conditions were varied and a reaction protocol establishing a degree of reproducibility was achieved. Catalysts were found to promote polycondensation, cyclisation and transesterification reactions. The trends of increase in molecular weights were similar to those observed in uncatalysed reactions. Catalysts based on divalent metals showed a higher activity compared to those based on tri- and tetravalent metals. Qualitatively alcoholysis and cyclisation occurred at about the same rate whether catalysed or uncatalysed and ester-ester interchange was significantly slower under all circumstances. There were only relatively small differences between the effects of the catalysts investigated, apart from Vertec 400AC, which caused very fast reaction and yielded an insoluble product of unidentified structure.

A new route to the synthesis of an A_2B monomer, methyl 3,5-bis(2-hydroxyethoxy)benzoate, was also reported. The monomer was synthesised on a 10g scale and successfully polymerised. The polymer samples were functionalised with acetoxy groups and characterised by SEC and MALDI-TOF MS. Evidences for the presence of polycondensation, cyclisation and ester-ester interchange reactions were observed. Growth in molecular weights and in cyclisation for poly(methyl 3,5-bis(2-hydroxyethoxy)benzoate)s was faster than that for poly(dimethyl 5-(2-hydroxyethoxy)isophthalate)s prepared under same conditions.

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Memorandum

The work reported in this thesis was conducted at the Durham site of the Interdisciplinary Research Centre in Polymer Science and Technology between August 2000 and September 2003. 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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List of Abbreviations

ATRP	Atom transfer radical polymerisation
Bis-MPA	2,2-Bis (hydroxymethyl)propionic acid
B/min	Bubbles per minute
^{o}C/min	Degree of Celsius per minute
CDI	Carbonyl diimidazole
CMS	P-(chloromethyl)styrene
DB	Degree of branching
DMF	Dimethylformamide
DP	Degree of polymerisation
DS	Divinyl sulfone
DTC	N,N-diethylaminodithiocarbamoyl
DTCS	N,N-diethylaminodithiocarbamoylmethylstyrene
DV	Differential Viscometer
Er.	Average experimental error
ES	Electrospray
FC	Fraction of cyclisation
GPC	Gel permeation chromatography
LALLS	Low angle laser light scattering
LS	Light scattering
MALDI-TOF MS	Matrix assisted laser desorption ionisation time of flight mass spectrometry
MALLS	Multi angle laser light scattering
M.pt.	Melting point
MS	Mass spectrometry
MWD	Molecular weight distribution
NLO	Non-linear optics
NMR	Nuclear magnetic resonance
NPA	N-methyl-1,3-propanediamine
PAMAM	Poly(amidoamine)
PEO	Poly(ethylene oxide)
PET	Poly(ethylene terephthalate)
PTP	Proton transfer polymerisation

RALLS	Right angle laser light scattering
RI	Refractive index
R/min	Revolution per minute
ROMBP	Ring opening multi-branching polymerisation
SCVP	Self-condensing vinyl polymerisation
SEC	Size exclusion chromatography
TEMPO	(2,2,6,6-Tetramethylpiperidinyloxy)-based initiators
THF	Tetrahydrofuran
THP	Tetrahydropyran protecting group
TLC	Thin layer chromatography
TPT-b-All	Allyl-terminated poly(13-bromo-1-(4-hydroxyphenyl)-2-(4-hydroxy-4'-p-terphenylyl)tridecane)s
UV	Ultraviolet

Chapter One

Hyperbranched polymers.

1.0 Introduction

In essence, man has always aspired to create materials to meet his needs by shaping or tailoring the properties of existing materials obtained from nature. The drive for polymer scientists to develop new materials is driven by society's wish to substitute conventional materials by plastics and thereby gain advantages in both performance and cost.[1] As polymer science has developed, greater control over the architecture of polymer molecules has been obtained.

"The art and science of macromolecular architecture is based on synthesis, analysis, processing and evaluation of the properties of polymers. The growing specificity of available synthetic methods and the increasing refinement of analytical and physical analysis are gradually providing a deeper insight into the structure-property relationship of polymers, upon which many applications can be based."[2]

When man started to use materials those that were readily available, for example wood, skins and stone, presumably were chosen and adapted for use. Later discoveries made metals, dyestuffs, flavours, perfumes and poisons available for use. The discovery of synthetic polymers is hardly a hundred years old and the impact of these materials is already enormous. By the 1930s, Staudinger had established that the main distinguishing features of polymer science were a consequence of the size of polymer molecules. Soon an industry based on synthetic rubbers, plastics and fibres was established. It became recognised that synthetic materials may be superior to natural materials in their properties, and that they may be used for completely new purposes.[3]

The simplest polymer is one in which all the structural units are connected one to another in a linear sequence. Carothers pointed out that a monomer that joins with only two other monomers, termed bifunctional, gives rise to linear polymers. Monomers with a functionality exceeding two, termed polyfunctional, produce non-linear structures, such as polymer networks, rather than the simple linear chains produced by bifunctional monomers.

Flory, in the 1950s, proposed the use of such polyfunctional monomers and published theoretical analyses of step-growth polymerisation of AB_x monomers. He assumed that A groups reacted with B groups, that there were no cyclisations or other side reactions and, on this basis, was able to predict that these polymers would be uncrosslinked, soluble and of relatively low viscosity. Experimental examination of

AB_x polymers did not begin until fairly recently and was stimulated by the desire to obtain some of the properties of dendrimers by a cheaper and convenient route. The work, which forms the basis of this thesis, is concerned with a study of the synthesis and properties of hyperbranched polymers formed via AB_2 polycondensation. In this chapter the syntheses and properties of dendrimers and hyperbranched polymers will be discussed. Chapters 2, 3 and 4 will deal respectively with the synthesis of the monomers used in this study, their polymerisation with particular emphasis on mechanism and catalysis and finally the characterisation of the products.

Dendrimers and hyperbranched polymers are dendritic macromolecules. The word dendritic originates from the Greek δενδρον – tree, implying their extensive and branched tree-like structure. Dendrimers are globular shaped, perfectly structured, monodisperse molecules. They are composed of structurally regular branches, called dendrons, attached to a central molecule, called the core. Hyperbranched polymers are irregular analogues of dendrons.

The first dendrimers were synthesised in the 1980s. Unfortunately, the laborious synthesis methods, which required repetitive use of protection/deprotection steps, made them commercially unattractive, but it was suggested that if some of the unusual and potentially useful properties of dendrimers are caused by their extensively branched structure and not just by their monodisperse nature, it might be possible to synthesise cheaper and more easily accessible materials with similar structures and hence similar properties. The first publications concerning the synthesis of hyperbranched polymers with properties resembling those of dendrimers date from the 1990s. These new systems had highly branched and polydisperse structures. Various aspects of hyperbranched polymers, such as their controlled degree of branching, high solubility, low viscosity and compatibility with other polymers made them an attractive object for study. However, one of the most important features that makes them attractive is their synthesis via a one-pot process where AB_n monomers are reacted, usually in the presence of a catalyst, to give the desired products.

1.1 Dendrimers

1.1.1 Introduction

Dendrimers have received considerable attention as a new class of polymers since their invention in the 1980s by Tomalia, Denkewalter and Newkome.[4,5,6] They are highly branched three-dimensional polymers with defined molecular weight, structure and size. The structure of dendrimers is different from common polymers, but it is not complicated since they are constructed in a regular way from simpler units. Their molecules possess three distinctive features: an initiator-core region (C), interior region and an exterior region of terminal moieties (B). A core with four functional groups grows in four directions, see Figure 1.1.

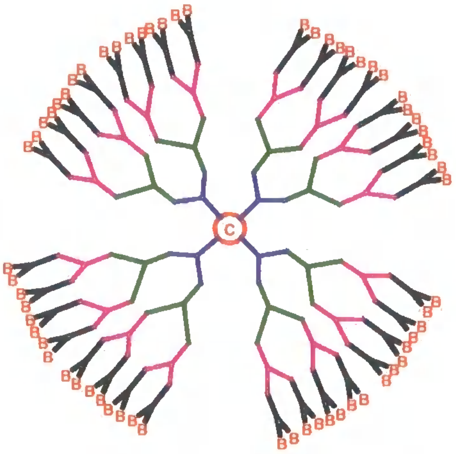


Figure 1.1. A schematic representation of a dendrimer.

One of the four branches is described as a dendron or dendritic wedge. The core is often called a seed, or focal point of the dendrimer. The core and termini are connected via a series of interior segments with tiers of branched cells. They constitute "generations" numbered from the center of the molecule. The generation is the number of branches between the core and the terminal functional group. The core is regarded as generation zero. Thus, Figure 1.1 represents a dendrimer of the fourth generation. The interior zone consists of a sequence of branched units. The ends of the branching sequences are called termini. Unfortunately, it is impossible to show on the picture that dendrimers are three-dimensional molecules, they are often depicted as globular in shape but recent work has shown that they are often quite flexible and can alter their shape as a function of conditions.[7] The structure has a great impact on the properties of dendrimers, due to the large number of end groups. For example, it is assumed that they have no chain entanglements, whereas in linear polymers this feature influences most of the physical properties.

1.1.2 Synthesis of dendrimers

Dendrimer precursors, described as 'cascade' molecules, were reported in 1978 by Vogtle *et al.*[8] They attempted the preparation of an oligomeric nitrile-terminated polyamine by series of Michael additions and subsequent reduction steps with the idea of assembling branches upon branches, see Figure 1.2.

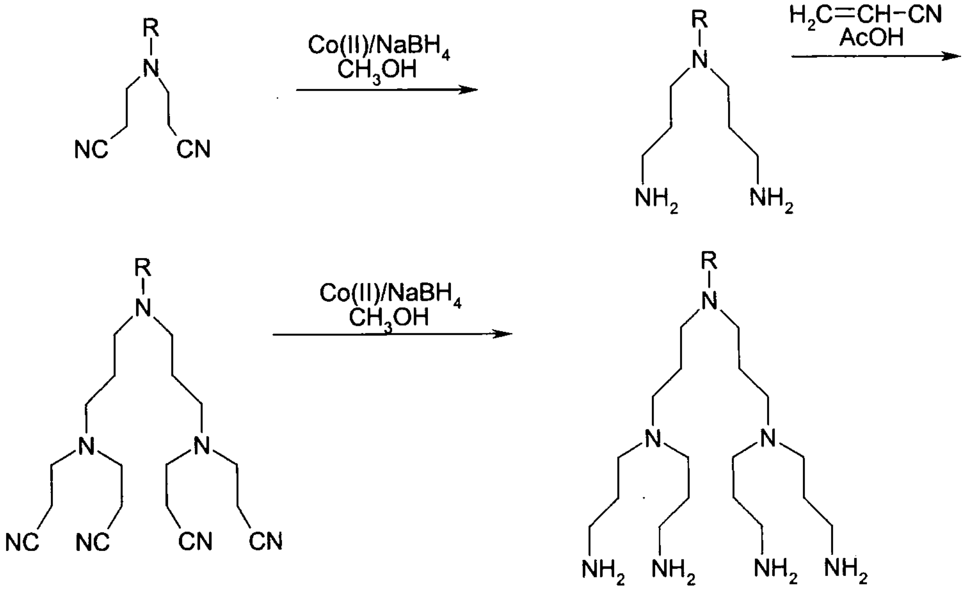


Figure 1.2. Synthesis of branched polyamines by Vogtle.[8]

Unfortunately, problems with the reduction step, incomplete functionalisation of the terminal groups and presence of cyclisation significantly limited the growth of the product.

The first successful synthesis of regular dendrimers, poly(amidoamine)s (PAMAM or starburst dendrimers) was reported by Tomalia in 1985, see Figure 1.3 following page.[4] Tomalia's route involved successive Michael additions to methyl acrylate (see Step 1, Figure 1.3 following page followed by amidation of the ester units, see Step 2, Figure 1.3 following page. In each step large excesses of reagent were required to drive the reaction to completion and the product separation was difficult; however, generations seven and eight were made and characterised, although some defects resulting from incomplete reaction and/or cyclisation were subsequently identified by soft ionization mass spectrometry (Electrospray and MALDI-TOF).

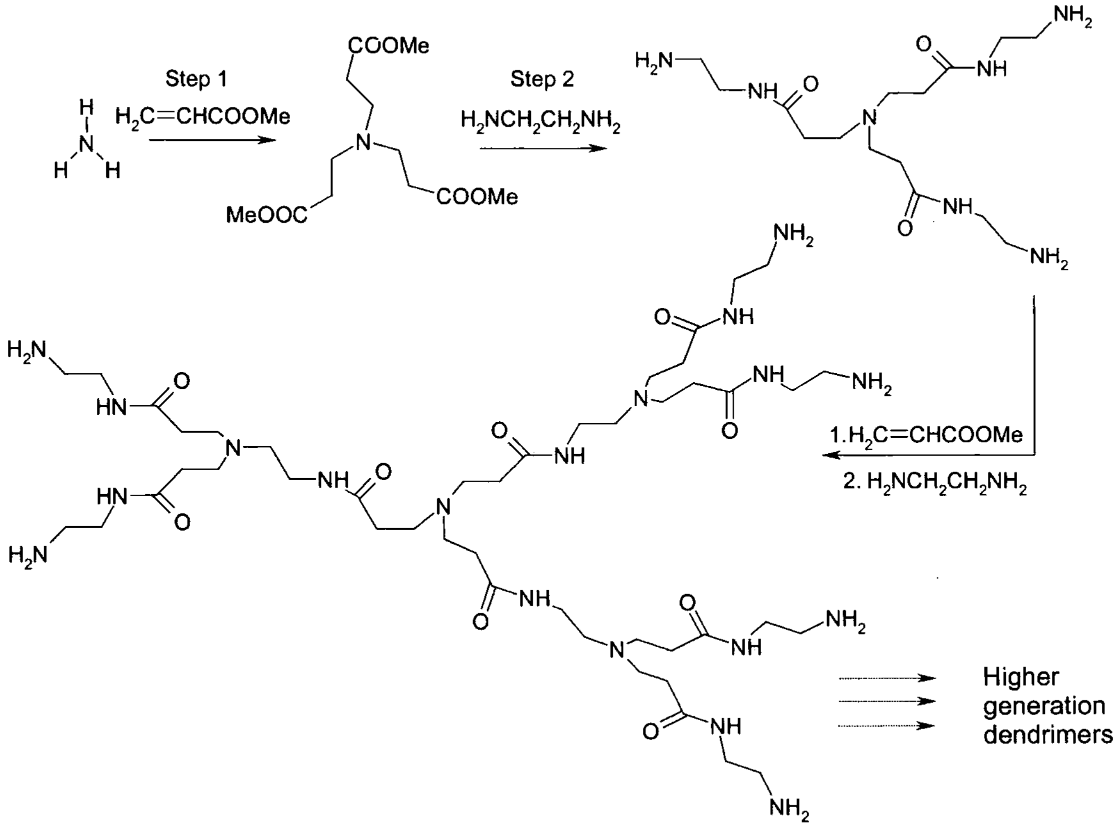


Figure 1.3. Synthetic scheme for starburst or PAMAM dendrimers.[4]

Dendritic poly(propyleneimine)s were prepared in DSM's laboratories using an approach related to Vogtle's method with diaminobutane as the core molecule, see Figure 1.4.[9] The Tomalia and DSM dendrimers are commercially available.

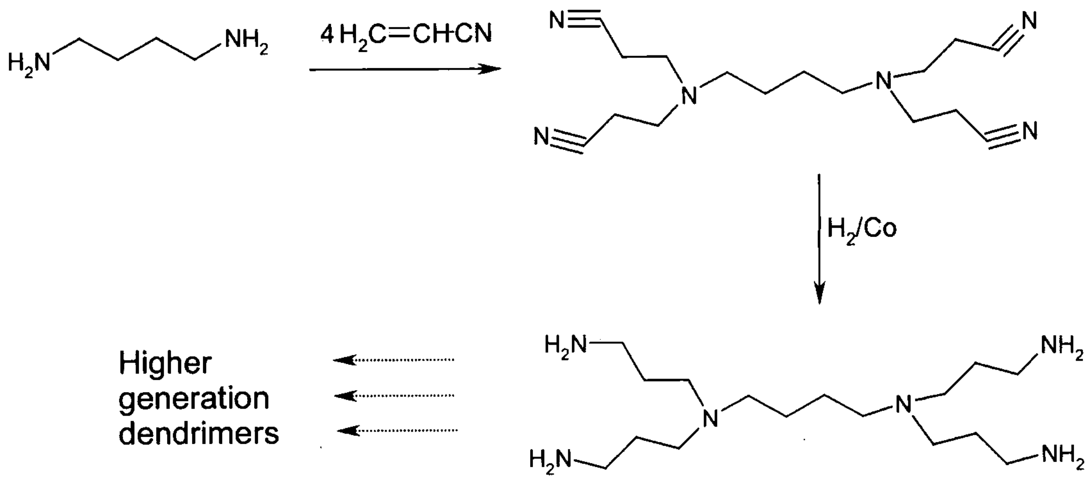


Figure 1.4. Synthetic scheme for poly(propylene imine) dendrimers with diaminobutane as the core molecule.[9]

Newkome *et al.* reported 'arborol' syntheses of water-soluble poly(ether amide)s terminated by hydroxymethyl groups, see Figure 1.5.[6]

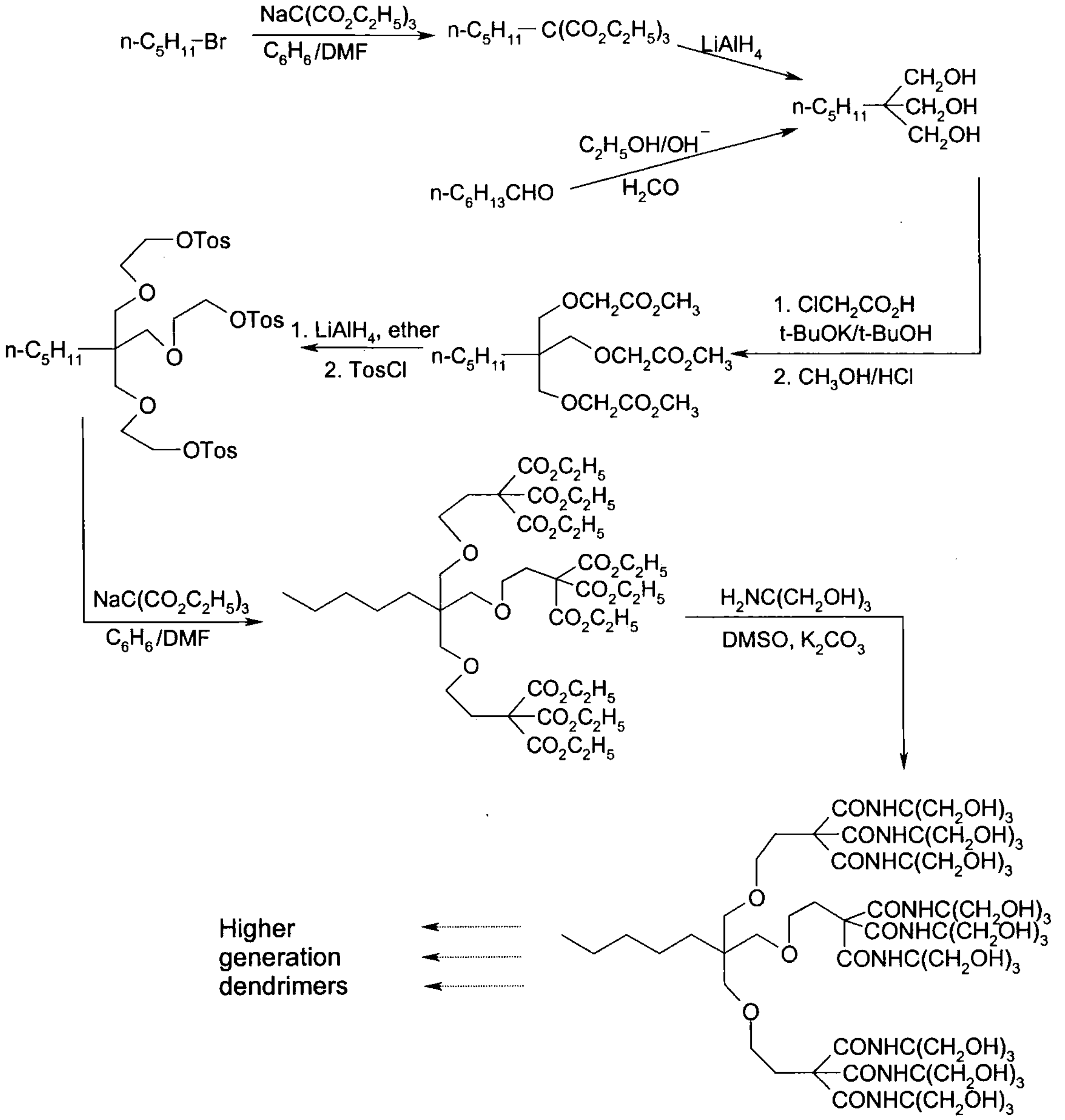


Figure 1.5. Synthetic scheme for poly(ether amide) dendrimers.[6]

They used trifunctional (AB_3) monomers, which resulted in polymers with a higher branching density than the systems developed by DSM and Tomalia.

Most dendrimers have been prepared using one of two distinct strategies. All the dendrimers mentioned above were synthesised via the divergent growth approach. According to this method a central core molecule is reacted with protected branching units sequentially, the process usually involves protection/deprotection steps. The main disadvantage of the method is that during the subsequent growth steps to give higher generations the termini of the dendritic segments become congested which leads to incomplete reaction and structural defects.

In 1990 both Hawker and Frechét *et al.* and Miller and Neenan proposed a new convergent method, see Figure 1.6.[10,11]

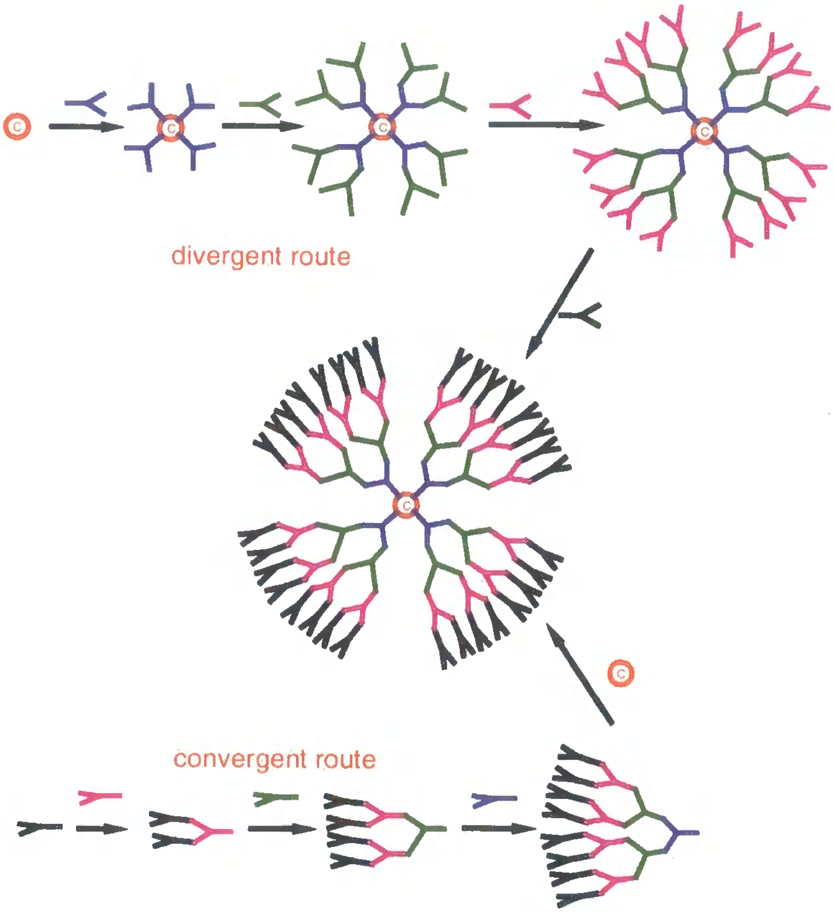


Figure 1.6. Divergent and convergent synthesis approaches.

The convergent method involves the construction of dendrons via coupling of branching units and attaching them in the last step to the core. It is unmatched in its ability to control ultimate macromolecular architecture, though it may be best used to prepare dendrimers of relatively modest size. A serious limitation of this method is that as the size of the molecule increases, functional group at the focal point becomes increasingly sterically hindered. As an example, dendritic structures were synthesised by the convergent approach from 3,5-dihydroxybenzyl alcohols. The first generation dendron was prepared by interaction of the monomer with benzyl bromide in a Williamson ether synthesis. Reaction of the hydroxymethyl group regenerates the benzylic bromomethyl group. Repetition of this two-step alkylation/bromination procedure gives monodisperse reactive dendrons, see Figure 1.7. The same set of reactions may be applied for attachment of such reactive dendrons to a polyfunctional core.

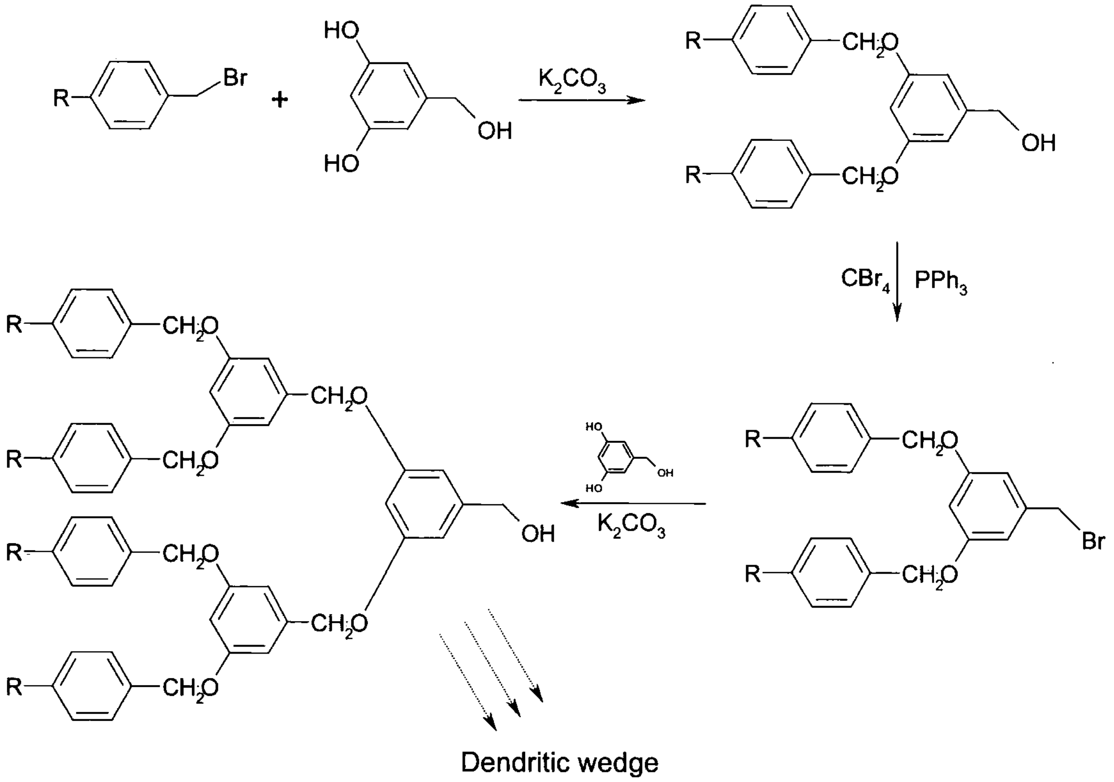


Figure 1.7. The scheme used for dendron synthesis by Hawker and Frechét.[10]

The convergent method allows control over surface functionality, demands a relatively low number of reactive sites for generation growth (usually three) and results in monodisperse products, which can be purified and characterised. These features make this method more attractive than the divergent growth approach, though the products are very sensitive to steric hindrance at the focal point as the size of the molecule increases. Currently both methods are widely used for the synthesis of dendrimers despite the fact that both procedures are quite laborious, time consuming and afford only limited amount of material.

Several attempts to develop faster dendrimer synthesis; namely, the double-stage convergent growth approach by Frechét and 'double exponential' growth approach by Kawaguchi have been reported.[12,13] These methods have been used to make polyamidoamines, poly(propylene imine)s, aromatic polyethers, polyalkanes, polyphenylenes and polysilane dendrimers.[1,9,10,14,15,16]

The properties of dendrimers as a new class of materials are being studied very thoroughly. As a consequence of their unusual structures they are expected to be significantly different from linear polymers. Modeling studies show that the branch ends on the surface of the dendrimer contain cavities, which may be used for molecular recognition.[17] Dendrimers acting as hosts for guest molecules are called unimolecular micelles.[18] Dendrimers possess an increased solubility compared to analogous linear polymers, which is attributed to their generally amorphous structures and the high number of end groups.[19]

At high generations the space required by the branching units on the surface of the dendrimer exceeds the available space.[20] As a result the molecule approaches the behaviour of a hard sphere, where the crowded surface units shield the interior region. This leads to unusual properties of dendrimers such as a decrease of the intrinsic viscosity, $[\eta]$ with increasing molecular weight.[21] However, computer simulations imply that, the monomer density of a hyperbranched polymer decreases as the distance from the center of mass increases. That is, a hyperbranched polymer does not form a close packed hard shell, but rather forms a soft sphere with voids in the shell.[22] It is well known that the intrinsic viscosity of linear and nonlinear polymers such as stars and branched molecules increases with increasing the molecular weight according to the Mark-Houwink equation, $[\eta]=KM^{\alpha}$, where $[\eta]$ is the intrinsic viscosity, M is the molecular weight, K and α are constants which are related to the polymer type, structure and the conditions of measurement.[23] Linear polymers give a straight-line fit to a plot of $\log[\eta]$ vs. $\log M_w$, in contrast the curve for dendrimers unusually shows a decreasing viscosity with increasing molecular weight above a threshold value of molecular weight, see Figure 1.8 following page.[24]

The $\log[\eta]$ vs. $\log M_w$ for hyperbranched polymers is more difficult to represent in a generalised way. Thus, for example, this research group has reported examples of hyperbranched polyesters where the plot is linear, but with a lower slope than that found for conventional polymers like polystyrene, and an example of core terminated poly(amidoamine) hyperbranched systems with branching ratios close to one which resemble dendrimers in their $\log[\eta]$ vs. $\log M_w$ plots.[25, 26, 27] Thus, the $\log[\eta]$ vs. $\log M_w$ behaviour is variable and may be susceptible to control via control of structure, as suggested in Figure 1.8 following page.

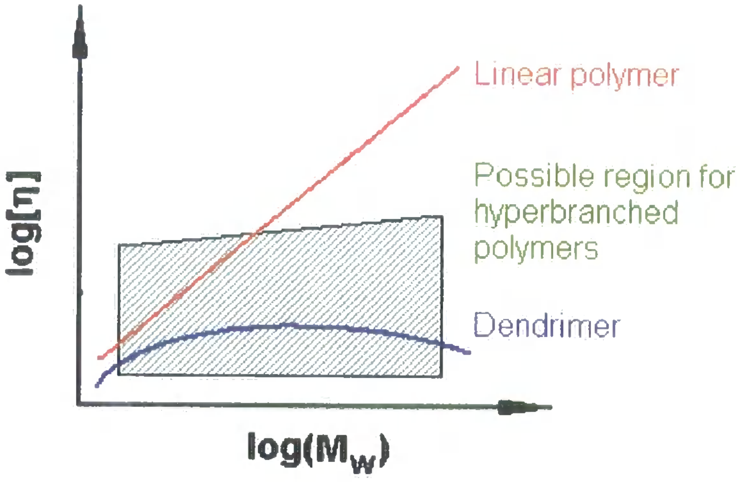


Figure 1.8. Generalised description of intrinsic viscosity as function of molar mass for linear polymers, hyperbranched polymers and dendrimers.

1.2 Hyperbranched polymers

1.2.1 Introduction

Hyperbranched polymers share some of the structural and physical properties of dendrimers. The less laborious synthesis makes them potentially interesting for large-scale production, which demands thorough investigation and additional study. Hyperbranched polymers are usually synthesised in a one-pot procedure where monomers are reacted in the presence of a catalyst. Hyperbranched polymers are reasonably cheap and therefore have a great advantage over dendrimers.

Step-growth polymerisation reactions occur between pairs of mutually reactive functional groups. Difunctional monomers, either of the A-B or a 1:1 mixture of A-A and B-B monomers form linear polymers, see Figure 1.9.

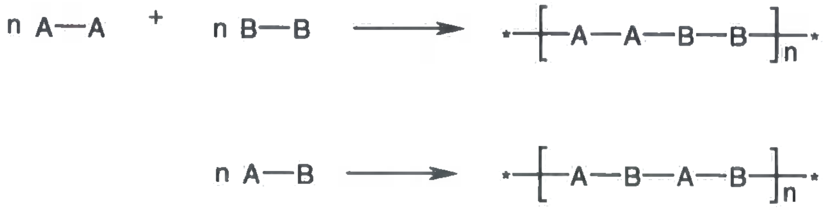


Figure 1.9. Schematic synthesis for linear polymers by step-growth polymerisation.

For example, a mixture of diacid and diol (A-A/B-B), see Reaction 1, Figure 1.10 or ω-hydroxycarboxylic acid (A-B) may be used to form linear polyesters, see Reaction 2, Figure 1.10.

$$HO_2CRCO_2H \quad + \quad HOROH \quad \rightleftharpoons \quad H\!\left(ORO_2CRCO\right)_n\!OH \; + \; (2n-1)H_2O \qquad (1)$$

$$HORCOOH \quad \rightleftharpoons \quad H\!\left(ORCO\right)_n\!OH \quad + \quad (n-1)H_2O \qquad (2)$$

Figure 1.10. Synthetic scheme for linear polyesters formation from a mixture of diacid and diol (Reaction 1) and from ω-hydroxycarboxylic acid (Reaction 2).

After the reaction has occurred the polymer chain remains difunctional and can react further, building longer chains. Each polymer chain grows at a much slower rate than in chain-growth polymerisation, with the degree of polymerisation (DP) linked to the conversion (p) by the equation DP=1/(1-p). This means that even at 95% completion the average degree of polymerisation is only twenty. In order to achieve a reasonable degree of polymerisation a high conversion is necessary. This leads to specific requirements for the reactivity and purity of the monomers.

To allow the synthesis of a hyperbranched rather than a linear polymer, an AB_n monomer must be used instead of an AB monomer or A-A/B-B monomer mixture. During the polymerisation only B groups can react with A groups, but neither A nor B can react with itself. The hyperbranched polymer is built by reactions between monomers and oligomers. It was assumed that each monomer, oligomer and polymer had one A group and n+1 unreacted B groups, where n is the number of repeat units. Hence, large hyperbranched molecules will have a surface dominated by the presence of numerous B groups.

The formation of bonds through the polymer growth reactions is not controlled which results in high polydispersity of the products. Similarly to the formation of linear step-growth polymers, high molecular weight species are not created until the conversion is high and even in samples of high molecular weight polymers, monomers and oligomers are still present. As soon as the degree of polymerisation exceeds two the isomerism becomes possible. The number of B groups to which an A group can be connected is large and as the degree of polymerisation rises, so does the number of possible isomers. Therefore, in a hyperbranched polymer containing only molecules of the same degree of polymerisation a variety of isomeric species would exist.

Flory proposed the theory of branching in 1952. His starting point was the use of an AB_{n-1} monomer, where A and B are functional groups (n-1 is the number of B groups). The argument is most easily understood by consideration of an AB_2 monomer, the polymerisation of this type of monomer results in a product with linear, branched and terminal units unlike the dendrimers where only branched and terminal units are present, see Figure 1.11.

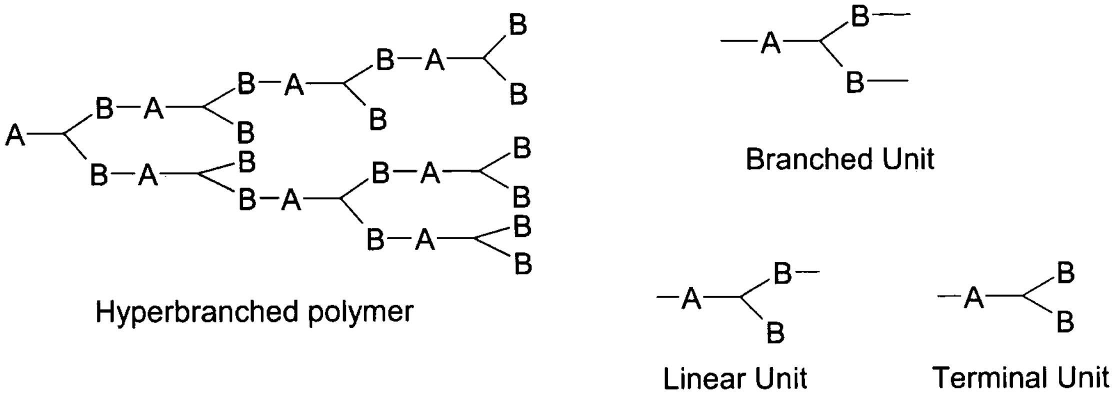


Figure 1.11. Schematic structure of an AB_2 hyperbranched polymer.

During the polymerisation functional A and B groups react with each other to form the polymer linkages or B-A bonds. There are three possible consequences of reaction.[24] All the three functional groups having reacted produce a branched unit. When one of the B groups doesn't take part in the reaction a linear unit is produced. A terminal unit is one in which neither of the B groups has reacted. The unit carrying the only residual A group is called the focal point. Overall, the structure of a hyperbranched molecule lies somewhere between that of a linear polymer and a dendrimer. A common characterising parameter for hyperbranched polymers is the degree of branching (DB). Frechét defined the DB as the ratio of the sum of branched and terminal units to the total number of repeat units, see Equation 1.1.[28]

$$DB = \frac{B+T}{B+L+T}$$

Equation 1.1. Degree of branching of a polymer according to Frechét, where B, L and T are respective fractions of branched, linear and terminal units in a polymer molecule.

According to Equation 1.1, a linear polymer with no branching units would have DB=0 and a dendrimer, i.e. fully branched macromolecule would have DB=1. The DB values for hyperbranched polymers produced using this formula generally lie between 0.4 and 0.8. Unfortunately this equation cannot be applied to generalised hyperbranched polymers derived from AB_n monomers, where n>2. It also provides extremely high DB values for small molecules; although, in some cases reasonable values have been obtained.[29,30,31] According to a definition proposed by Frey, DB is the actual number of branched units divided by the maximum possible number of branched units (Equation 1.2).[32] When branched units are created from linear units the number of branched units, which can be created is L/2, so the possible number of branched units is (B+L/2) and so in Frey's approach we have Equation 1.2:

$$DB = \frac{B}{B + L/2} = \frac{2B}{2B + L}$$

Equation 1.2. Degree of branching of a polymer according to Frey, where *B* and *L* are respective fractions of the branched and linear units in a polymer molecule.

The DB is usually determined by ^{1}H, ^{13}C, ^{19}F, ^{15}N and ^{29}Si-NMR spectroscopy calibrated using low molecular weight model compounds. Such model compounds have structures similar to the linear, branched and terminal units in the related hyperbranched polymer.[8] Depending on the structure of the unit different chemical shifts are obtained and integration and comparison of relative abundances allows the DB to be calculated using the equations shown above.

1.2.2 Molecular weight distribution

Molecular weight distribution (MWD) are very important characterising parameters for a polymer. Theoretical MWD for hyperbranched polymers were evaluated by Flory in 1952.[23] This statistical study was based on the assumptions of the formation of randomly branched polymers without networks or intramolecular reactions (i.e. no cyclisation) the formation of a typical AB_2 oligomer is shown in Figure 1.12 following page.

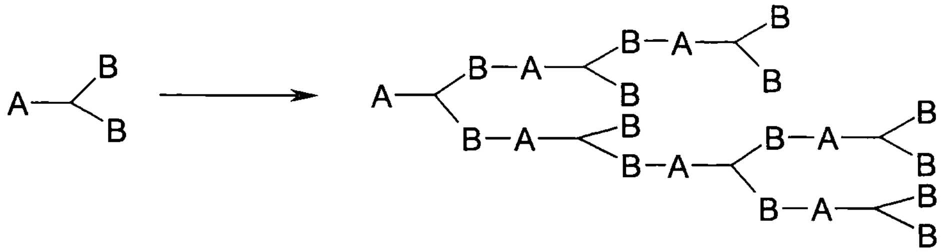
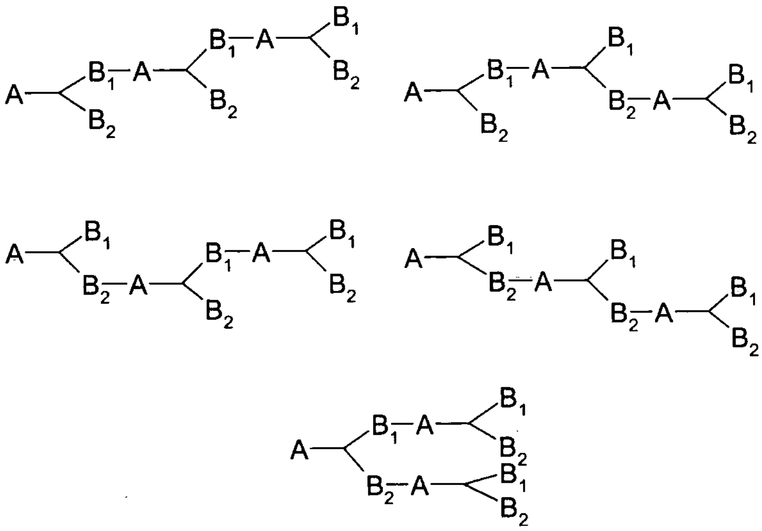
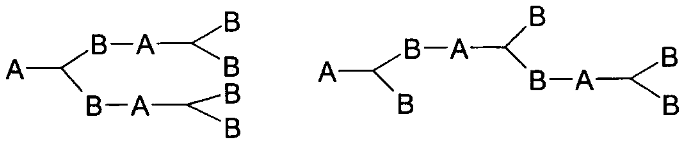


Figure 1.12. An example of a randomly branched AB_2 oligomer.

The functional groups A and B were assumed to be equally reactive independent of their place in a molecule, i.e. in a monomer, oligomer or polymer. Reactions between functional groups of the same molecule were assumed to be forbidden. For a monomer with a functionality f, the resulting AB_{f-1} polymer has one unreacted A group and (f-2)x+1 unreacted B groups, where x is the number of repeat units in the oligomer or polymer. Theoretically there are five possible ways of building a trimer although, if the B groups are identical and free rotation occurs, four of these are experimentally indistinguishable, see Figure 1.13.



Five isomers if B groups are distinguishable



Two isomers if B groups are indistinguishable

Figure 1.13. The difference in the number of isomers if the B groups are distinguishable and if they are not.

An important definition introduced by Flory, is the branching coefficient (α), which is the probability that a functional group of a branching unit reacts with another functional group to produce another branching unit (Equation 1.3):

$$\alpha = \frac{p}{(f-1)}$$

Equation 1.3. Branching coefficient derived by Flory, where *p* is the fraction of A groups, which have reacted, *f-1* is the number of B groups.

The total number of units at the start of the reaction is N_0. As the reaction proceeds the number of unreacted units decreases and at a given time it equals N. Hence the number of A groups that have taken part in the polymerisation is N_0-N. The total number of molecules is N_0(1-p). The number average degree of the polymerisation ($\bar{x}_n$) is defined as the number of monomer residues divided by the total number of molecules (Equation 1.4).

$$\bar{x}_n = \frac{N_0}{N} = \frac{N_0}{N_0(1-p)} = \frac{1}{(1-p)} = \frac{1}{[1-\alpha(f-1)]}$$

Equation 1.4. The number average degree of polymerisation.

As can be seen from Equation 1.3, the critical value of α is α_c= 1/(f-1), since at this point theory predicts that $\bar{x}_n$ tends to infinity. This critical value is unlikely to be reached, since the extent of the reaction, p never reaches unity. The probability that an unreacted A group joins an x-mer structure equals the probability that (x-1) B groups have reacted, whereas (fx-2x+1) B groups have not. This probability is the same for each x-meric configuration (Equation 1.5).

$$P_x = \alpha^{x-1}(1-\alpha)^{fx-2x+1}$$

Equation 1.5. The probability of an A group taking part in the reaction.

The probability that an A group is attached to an x-mer molecule of any structural configuration is given by Equation 1.6 following page:

$$\mathrm{N}_x = \omega_x \alpha^{x-1}(1-\alpha)^{fx-2x+1} = [(1-\alpha)/\alpha]\omega_x \beta^x$$

Equation 1.6. The probability that an A group is attached to an x-mer molecule of any structural configuration, where ω_x is the total number of possible configurations, $\omega_x=(fx-x)!/(fx-2x+1)!x!$, β is a constant for the simplification, $\beta=\alpha(1-\alpha)^{f-2}$.

From the Equation 1.6 another expression for the weight fraction distribution (w_X) and the weight average degree of polymerisation ($\bar{x}_w$) may be derived, the expressions are given in Equations 1.7 and 1.8:

$$w_x = \frac{xN_x}{\Sigma xN_x} = \frac{(1-\alpha)}{\alpha}[1-\alpha(f-1)]x\omega_x\beta^x$$

Equation 1.7. The weight fraction distribution.

$$\bar{x}_w = \frac{\Sigma x^2 N_x}{\Sigma xN_x} = \frac{[1-\alpha^2(f-1)]}{[1-\alpha(f-1)]^2}$$

Equation 1.8. The weight average degree of polymerisation.

Finally, the polydispersity $\bar{x}_w / \bar{x}_n$ may be derived by the combination of the Equations 1.7 and 1.8 (Equation 1.9):

$$\frac{\bar{x}_w}{\bar{x}_n} = \frac{[1-\alpha^2(f-1)]}{[1-\alpha(f-1)]}$$

Equation 1.9. The polydispersity for an AB_2 polymer.

As was stated above, α value is limited to values less than $\alpha = 1/(f-1)$, hence β is always less than unity. As x increases, factors ω_X and β^x change in opposite directions. The decrease of the β^x outweighs the increase of the ω_X, thus N_X and w_X decrease monotonically with x, the latter less rapidly than the former. MWD broaden with the increase in α, as shown in Figure 1.14 following page, and finally merges with x-axis. According to the Equation 1.7, the weight fractions for an AB_2 polymer are 0 at $\alpha=1/2$. The total area under the distribution curve equals one, it follows that under such conditions ($\alpha=\alpha_{max}=0.5$) the MWD is extremely wide.

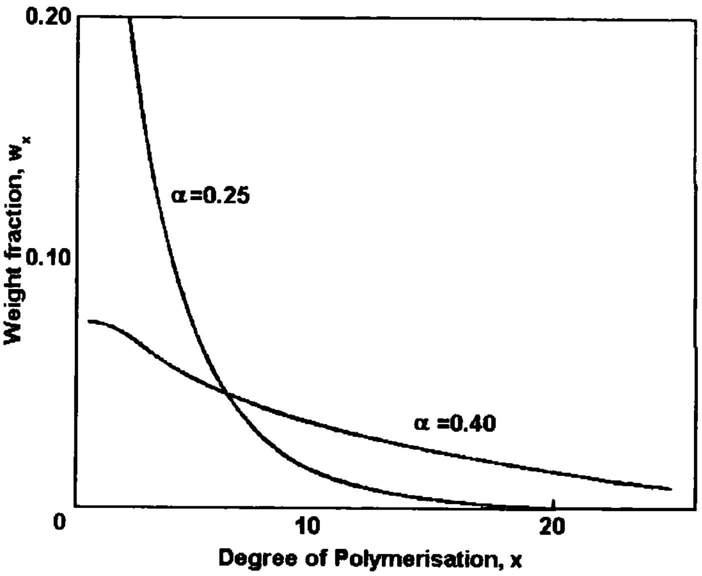


Figure 1.14. The weight fraction distributions for an AB_{f-1} polymer.

This is also reflected by the number average degree of polymerisation $\bar{x}_n$ and weight fraction distribution w_x. As α approaches 0.5 both values approach infinity, but $\bar{x}_w$ approaches it faster, consequently the polydispersity $\bar{x}_w / \bar{x}_n$ approaches infinity too. This is in direct contrast to step-growth polymerisation of an AB monomer, where as the extent of reaction approaches one the polydispersity becomes closer to two, see Figure 1.15.[33]

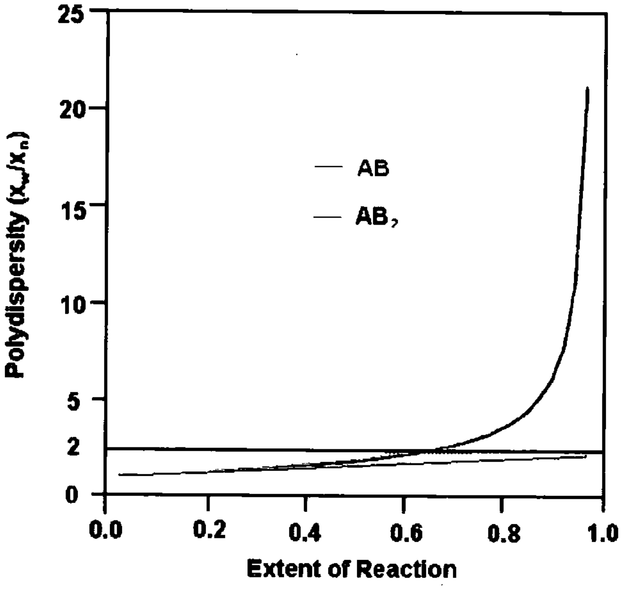


Figure 1.15. Theoretical variation of polydispersity with the extent of reaction for branched AB_2 and linear AB polymers.

1.2.3 Synthesis of hyperbranched polymers

Most hyperbranched polymers are prepared from AB_2 monomers by polycondensation.[19] There are also studies based on AB_3, AB_4, AB_6 and AB_8 monomers. These types of monomers are used to achieve more accelerated growth of the polymer and higher DB values compared to AB_2 monomers. One of the pioneering studies in this field is due to Mathias and Carothers. They used a hydrosilation reaction to obtain highly branched polymers containing silane and siloxane groups.[34] Later attempts were made to synthesise AB_4, AB_6 and AB_8 monomers, see Figure 1.16.[35,36,37,38]

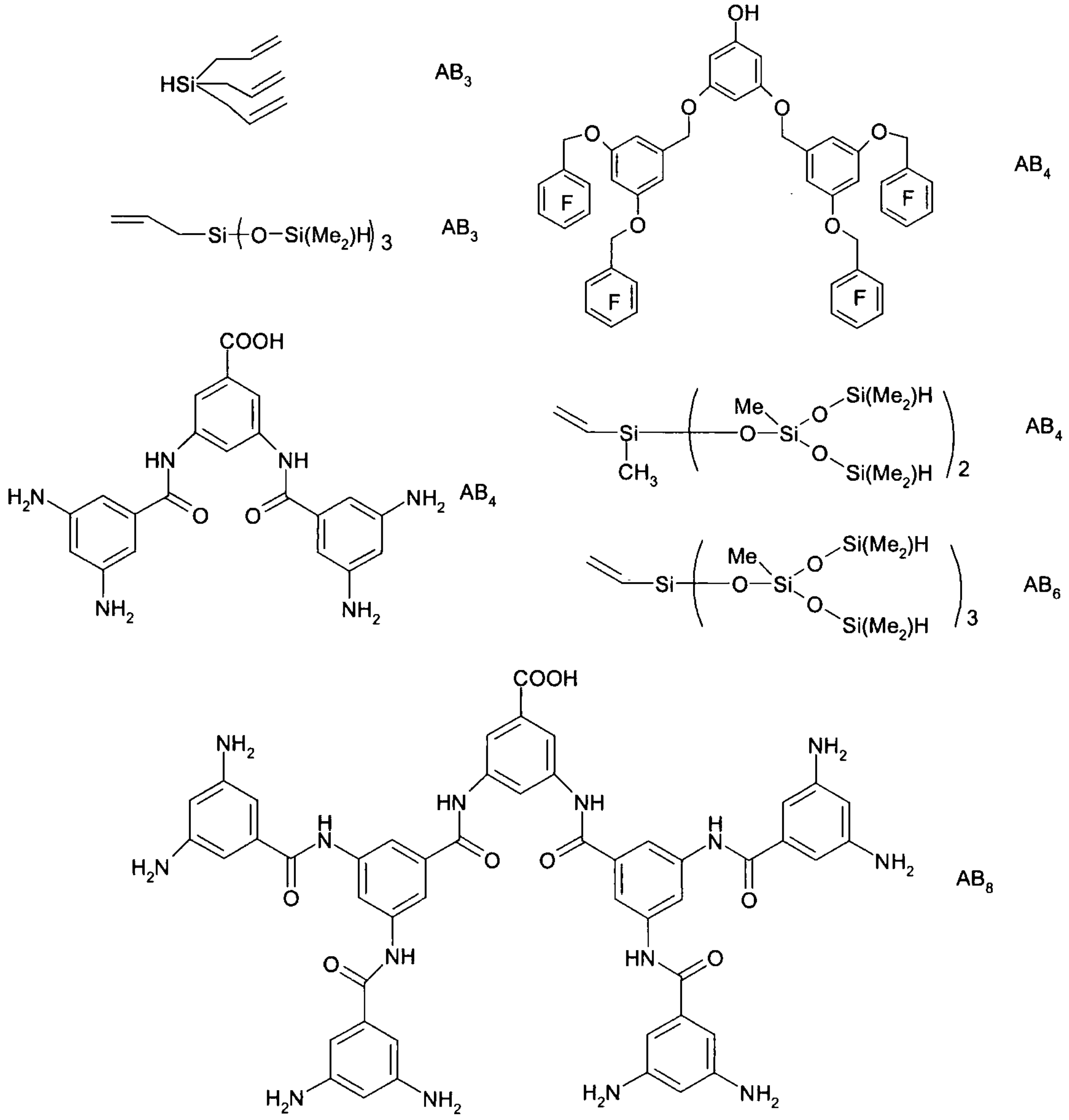


Figure 1.16. Examples of AB_3, AB_4, AB_6 and AB_8 monomers.

Malmström and Hawker produced AB_3 and AB_4 monomers by insertion of either dendritic or linear fragments into an AB_2 monomers.[39,40] Hawker proved that AB_3 and AB_4 monomers could be used to control degree of branching in poly(ether ketone)s, see Figure 1.17.

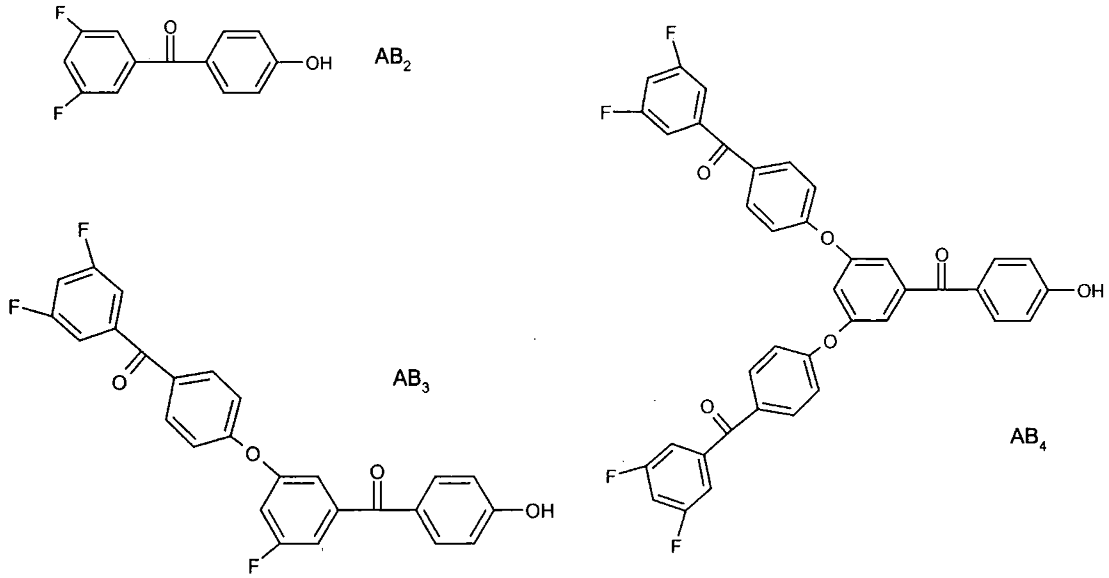


Figure 1.17. AB_2, AB_3 and AB_4 monomers used by Hawker for the synthesis of poly(ether ketone)s.

Kennedy and then Nuyken used m-/p-(chloromethyl)styrene as an initiator and observed a side reaction leading to a product with higher than calculated molecular weight.[41,42] Later, Frechét *et al.* reported the homopolymerisation of such molecules resulting in hyperbranched polymers and termed this process as "self-condensing vinyl polymerisation" (SCVP).[43]

The monomers employed in SCVP are termed as inimers, since they act both as monomers and as cationic initiators, see Figure 1.18.

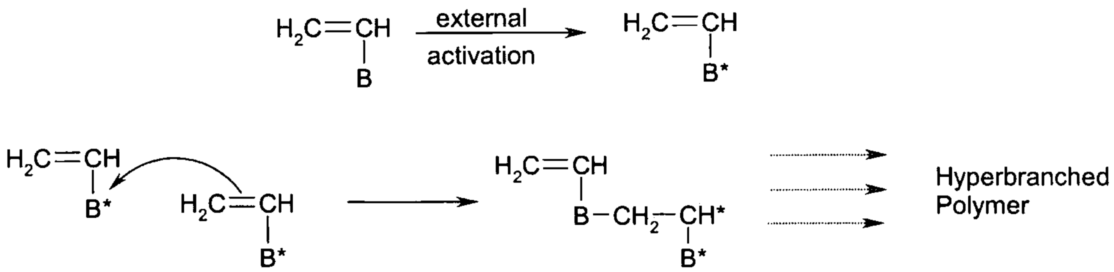


Figure 1.18. A scheme for self-condensing vinyl polymerisation.

For example, chlorine abstraction from p-(chloromethyl)styrene forms a carbocation or a radical depending on the initiation mechanism, i.e. heterolytic or homolytic bond breaking. The reaction proceeds via addition of the activated p-(chloromethyl)styrene to a double bond, giving a dimer with two C-Cl bonds capable of further activation and reaction to generate a hyperbranched structure, see Figure 1.19.

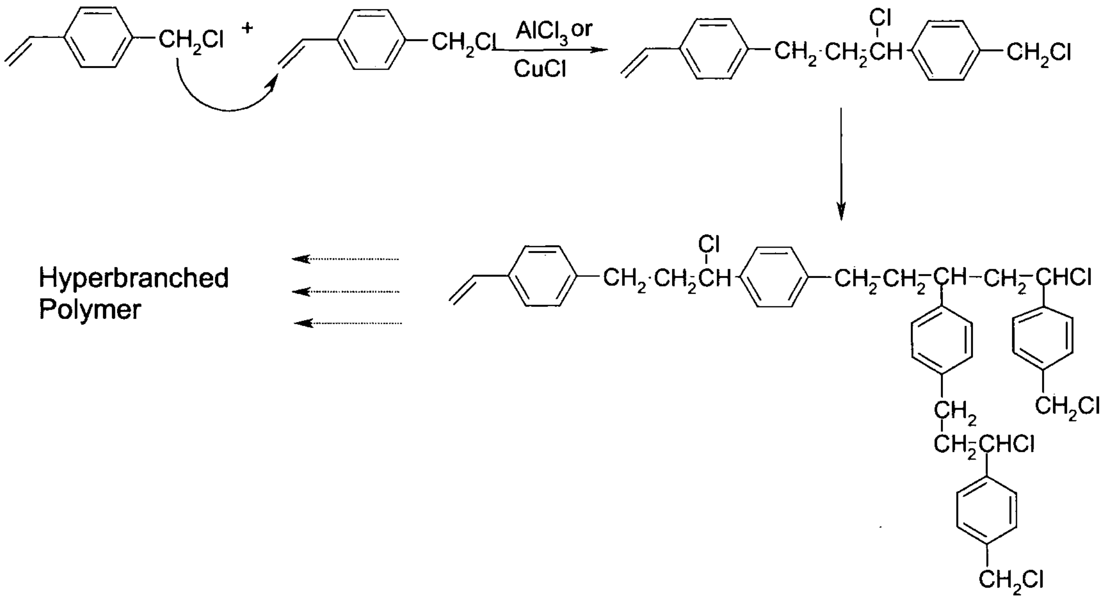


Figure 1.19. A scheme of self-condensing vinyl polymerisation of p-(chloromethyl)styrene.

Terminal, linear and branching units are formed during addition of monomer units to each other. Due to the different rate constants of the reactions occurring the kinetics of SCVP are different from conventional chain-growth polymerisation leading to polymers with a higher polydispersity.[44]

Broad MWD provided by SCVP could be due to coupling of growing chains. It was supposed that larger molecules consume monomer at the expense of the smaller ones. Introduction into the system of a small amount of a core-forming multifunctional initiator ($f \geq 2$) and slow monomer addition leads to polymers with narrow MWD.[45]

A similar route to hyperbranched polymers using self-addition free radical vinyl polymerisation of N,N-diethylaminodithiocarbamoylmethylstyrene (DTCS) was studied by Ishizu.[46] DTCS contains a polymerisable styrene group and an initiating/propagating DTC group. Photolysis of the monomer produces the initiating benzyl and inactive DTC radicals. The benzyl radical adds to the vinyl group of the second monomer molecule to produce a dimer. The dimer corresponds to an AB_2 monomer with a polymerisable vinyl group and two propagating sites. The dimer grows further by these reactions and finally a hyperbranched polymer is obtained, see Figure 1.20.

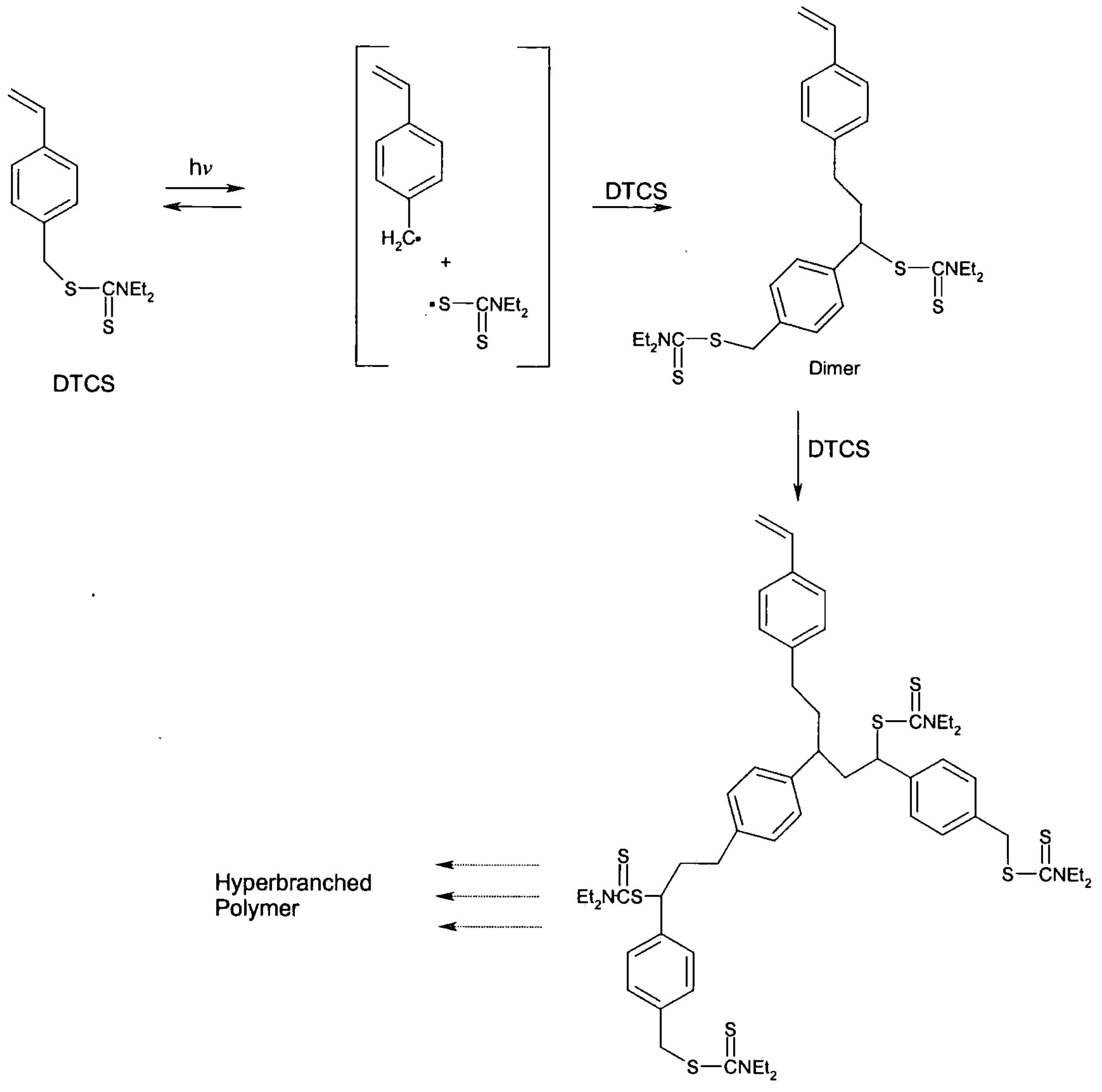


Figure 1.20. A scheme of self-addition free radical vinyl polymerisation.

TEMPO mediated vinyl polymerisation combines SCVP and free radical polymerisation. Hawker reported the use of (2,2,6,6-TEtraMethylPiperidinylOxy)-based initiators (TEMPO) in the synthesis of hyperbranched polymers.[47] The TEMPO monomers possess a styrene group and a nitroxide group linked to a substituted benzylic carbon atom, see Figure 1.21 following page.

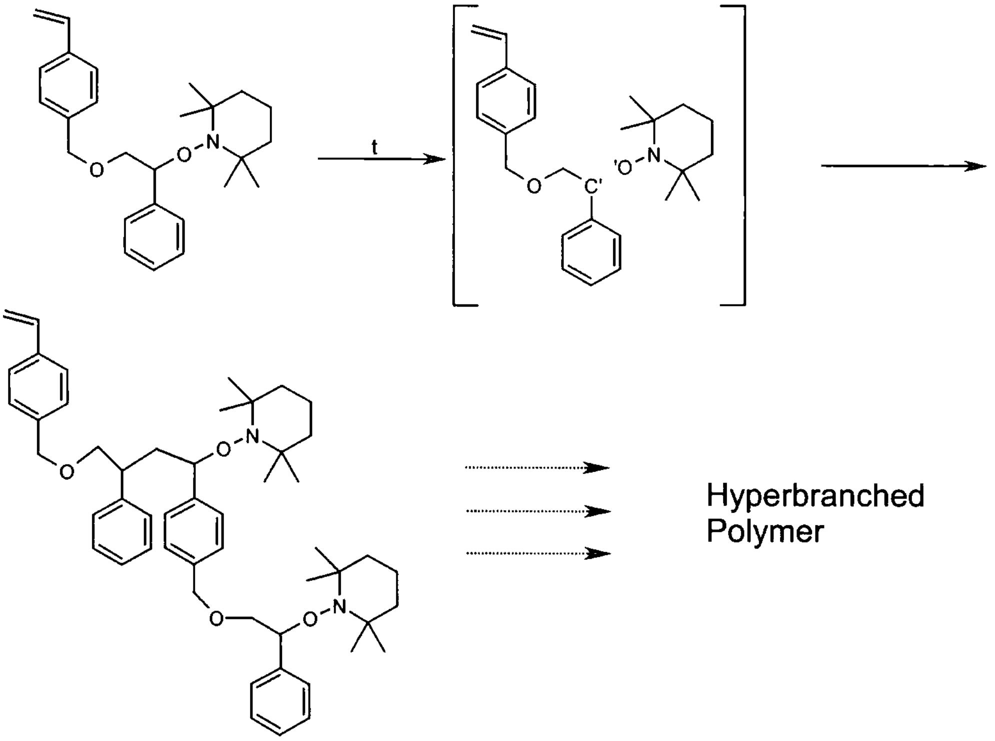


Figure 1.21. An example of the TEMPO mediated vinyl polymerisation.

Thermal activation of the monomer produces a propagating benzylic radical, which forms a dimer after recombination with a nitroxide radical. The dimer has one double bond and two initiating/propagating sites. Monomers and oligomers interact with the growing molecule to form the hyperbranched polymer.

Copolymerisation of vinyl monomers with specific amounts of the TEMPO monomer resulted in polymers with controlled branching densities. Matyjaszewski and co-workers have attached TEMPO-based stable radicals to dendrimers of variable size to control the radical polymerisation of styrene, vinyl acetate and methacrylates.[48]

Graft and dendrigraft products were derived by "living" free radical polymerisation followed by "living" atom transfer radical polymerisation (ATRP).[49] Hyperbranched polystyrenes, polyacrylates and polyacrylamides have been recently synthesised by one-pot ATRP.[50,51,52,53]

Hyperbranched polystyrenes were prepared from p-(chloromethyl)styrene (CMS) in the presence of CuCl and 2,2-bipyridyl. CMS can be copolymerised with styrene by ATRP, producing a branched copolymer, with the DB controlled by the concentration of CMS and the reaction time. Simulation studies were performed on the synthesis of copolymers from AB* inimer and a conventional vinyl monomer.[54] One of the latest examples of ATRP is the synthesis of star-shaped and dendrimer-like copolymers from styrene and ethylene oxide.[55]

Recently Suzuki synthesised hyperbranched polyamines with controlled molecular weight and polydispersities via ring opening multi-branching polymerisation (ROMBP).[56] Frey *et al.* successfully applied ROMBP to hydroxyepoxides.[57] The controlled anionic polymerisation of glycidol, termed as "proton-transfer polymerisation" (PTP), with alkoxide initiator was analogous to the polymerisation of propylene oxide, see Figure 1.22.

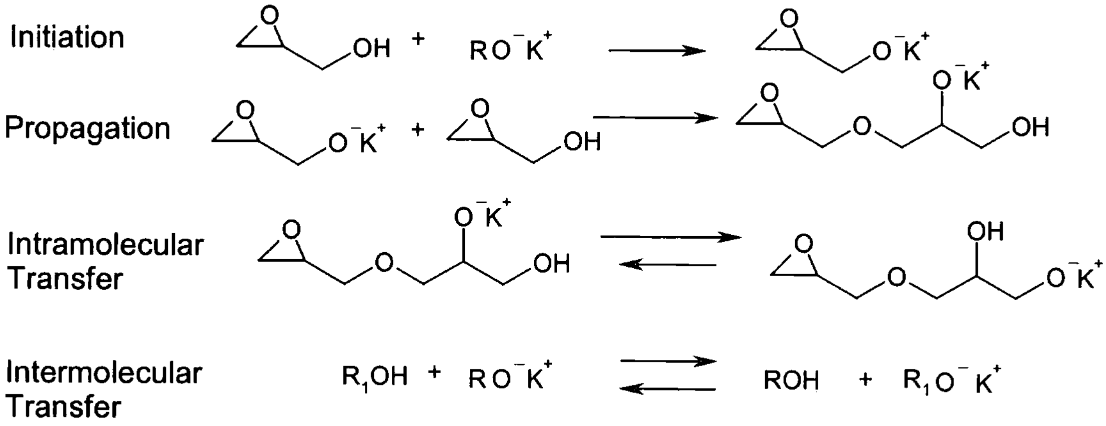


Figure 1.22. Mechanism of a PTP reaction of glycidol.

The product, a hyperbranched aliphatic polyether with hydroxyl end groups was of low polydispersity (below 1.25) and of DB=0.53-0.59. Later, Frechét synthesised hyperbranched polyesters from glycidol-based monomers by the same method.[58] Voit prepared poly(ether amide)s via nucleophilic ROMBP route.[59] Hult reported the synthesis of hydroxy terminated polyethers using the same approach.[60] Hyperbranched polyesters, prepared in a single step by ring opening polymerisation were found to be suitable for templating nanostructures in organosilicates. The porous films generated by the thermolysis of the products, possessed low dielectric constants and low refractive indices.[61] One of the disadvantages of the one-step polymerisation is the loss of control of molecular weight, resulting in a broad molecular weight distribution.[62] Moore overcame this problem using solid support in the synthesis of hyperbranched poly(3,5-di-*tert*-butylphenyl)acetylene)s.[63] This method prevents cyclisation, provides only one focal point per molecule, eases purification, allows control over molecular weight and narrows polydispersity.

Hyperbranched polyimides were synthesised via A_2+B_3 polymerisation.[64] Film forming properties of polymers produced from tri(phthalic anhydride) and tri(phthalic acid methyl ester) (B_3) with 1,4-phenylenediamine (A_2) were studied by Hao.[65]

Gao *et al.* polymerised a BB`$_2$ monomer, N-methyl-1,3-propanediamine (NPA) with an A_2 monomer, divinyl sulfone (DS) to give hyperbranched polymers with amino end groups and sulfone groups in the interior region, see Figure 1.23.[66]

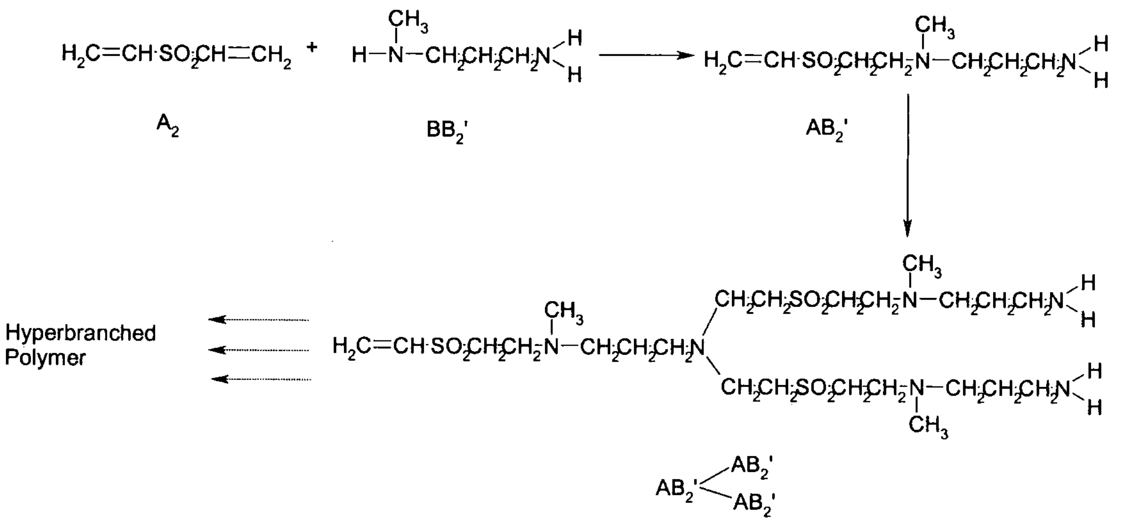


Figure 1.23. A scheme for the synthesis of hyperbranched polysulfones-amine.

During polymerisation, the vinyl groups of DS react with the secondary amino groups of NPA generating a new AB`$_2$ monomer. Further polyadditions of the monomer result in higher oligomers and finally in a hyperbranched poly(sulfone amine). The cyclisation is thought to be negligible, since the polymers produced possess high molecular weights and narrow molecular weight distribution (<1.3). The molecular weight of the polymers increases with increasing initial molar ratio of DS to NPA, while the inherent viscosity decreases, which could be a result of high DB values. A hyperbranched poly(amide-imide) was synthesised via A_2+B`B_2 approach by Chang.[67]

Trollsas prepared branched polymers by the polymerisation of A-polymer-B_2 monomers.[68] The polymer chains of the macromonomer contain no branching units but as they are terminated by A and B groups they can be polymerised to yield macromolecular hyperbranched polymers. The molecular weight of macromonomers can be substantial, so polymers of high molecular weights are easily obtained. A series of hyperbranched poly(ε-caprolactones) were synthesised from the condensation polymerisation of AB_2 macromonomers, which were in turn formed from the ring-opening polymerisation of ε-caprolactone, either initiated by benzyl alcohol followed by capping with a protected diol and deprotection, or by initiation with a diol followed by deprotection, see Figure 1.24.[69]

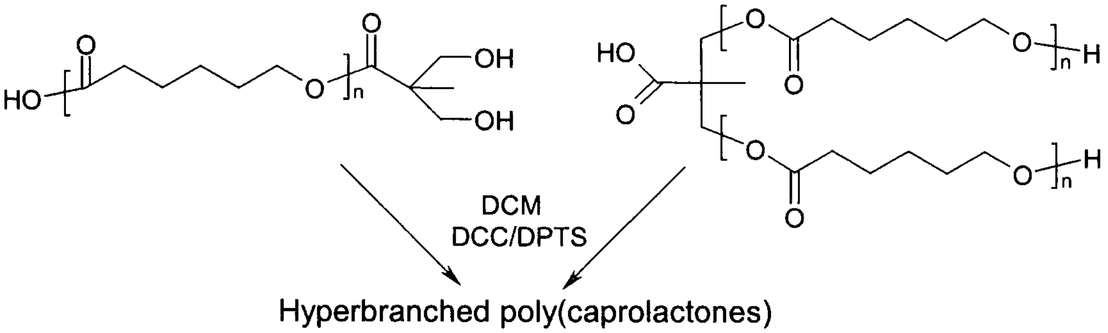


Figure 1.24. A scheme of synthesis of hyperbranched poly(ε-caprolactone)s.

This strategy allowed the preparation of hyperbranched polymers with variation in architecture by altering the degree of polymerisation or replacing ε-caprolactone with an alternative monomer. According to this method hyperbranched polymers could be produced with significant versatility, including the variation of the monomer type and the size of the macromonomer. These variations could generate hyperbranched polymers with a different degree of crystallinity as well as hyperbranched block copolymers.

Gao and Yan prepared hyperbranched polymers with alternating ureido and urethano units.[70] The strategy used was based on unequal reactivity of different functional groups. They used an A_2 monomer containing two isocyanato functional groups and DB_n monomer ($n \geq 2$) containing an amino group (D) and n hydroxyl groups (B), see Figure 1.25.

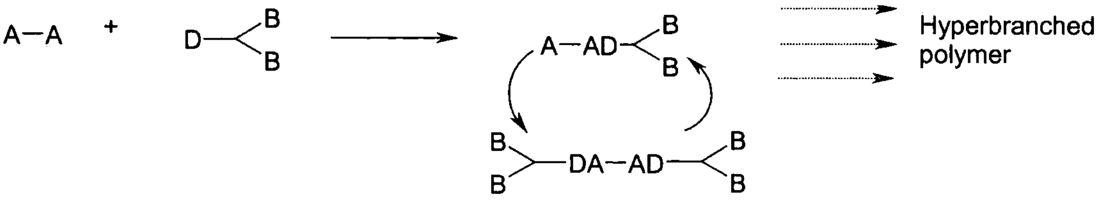


Figure 1.25. A scheme of A_2+DB_2 synthesis of hyperbranched polymers.

Both D and B groups can react with an A group, but the reaction between A and D groups is faster than that between A and B groups. In the initial step of the polymerisation an A group of A_2 monomer quickly reacts with D group of DB_n monomer generating mostly AB_n intermediate. The A group can react further with the D group of DB_n to form the B_nD-A_2-DB_n species with plenty of B groups. Further self-polycondensation of the intermediates results in hyperbranched polymers, network formation being avoided by controlling the temperature and feed ratio of the monomers.

1.2.4 Properties of hyperbranched polymers

One of the reasons for the emerging interest in hyperbranched materials and similar macromolecular architectures is their unusual properties compare to conventional, linear polymers.[1]

The most remarkable properties of the hyperbranched polymers reported to date are:

-Unusual solubility in various solvents

-Irregular globular shape that is affected both by the flexibility of components and degree of branching

-Low solution and melt viscosity

-High chemical reactivity, depending on the nature of terminal groups

-Compatibility with other polymers

-Mechanical properties that reflect their compact and highly branched structure[71]

Structurally, hyperbranched polymers are similar to dendrimers. A dendritic molecule is always wholly branched, whereas a hyperbranched polymer contains linear units with unreacted functional groups. This is the major difference between hyperbranched polymers and dendrimers. The molecular weight/intrinsic viscosity relationship for dendrimers and linear polymers is shown in Figure 1.8. The intrinsic viscosity behaviour of a hyperbranched polymer depends on its DB value, it is similar to that shown by dendrimers in cases of DB~1, in cases of DB<0.5 it is similar to that shown by linear polymers. Hobson and co-workers have prepared hyperbranched poly(amidoamine) with degree of branching > 0.9. Unsurprisingly the molecular weight/intrinsic viscosity relationship resembled a bell-shaped curve with a maximum.[27] According to Frey's simulation that neglected sterical crowding or backfolding of polymer segments, the core terminated hyperbranched polymers were found not to be sphere like structures with a hard, sterically crowded shell.[72] The maximum segment density was at the core, decreasing with the distance. For example, only 3% of the available space was occupied in the fourth pseudogeneration. Hult and coworkers studied aliphatic hyperbranched polyesters based on 2,2-bis (hydroxymethyl)propionic acid (bis-MPA) to investigate influence of the core moiety on the esterification process and properties of products as tougheners in epoxy-based composites.[1] They also have produced core-terminated polymers with DB~0.5.[73] Core terminated hyperbranched polymers were found to change volume in solution depending on their structure and nature of the solvent. This may allow trapping of guest molecules within the hyperbranched molecules and when the environment is changed it may be possible to deliver the guest.[74]

Branching and a large number of surface functional groups results in enhanced solubility of hyperbranched polymers and high surface reactivity. Hydrophobic molecules were solubilised in water by Hawker and Chu using hyperbranched poly(etherketone)s with acid end-groups.[75] In this respect hyperbranched polymers appear to function in a different manner to conventional amphiphiles and it is suggested that hyperbranched molecules act as unimolecular micelles. The number and nature of chain ends in hyperbranched structures allows their application as initiators. Brenner and Voit prepared free radical polymerisation initiators by introducing azo functionalities at the surface of modified acid and alcohol terminated hyperbranched polyesters.[76]

Usually hyperbranched polymers appear to be of broad molecular weight distribution. They possess a great number of end groups easily accessible for chemical modification, which generally makes them non-entangled and non-crystalline. The properties of hyperbranched polymers are strongly influenced by the three-dimensional globular shape and nature of end groups.[1] Modification of functional groups of hyperbranched polyglycerols resulted in fully branched "pseudo-dendrimer".[77]

Thermal properties of hyperbranched polymers are widely reported. It was proposed that their glass transition temperature (T_g) is a translation movement of the whole molecule, unlike the classical segmental movement approach.[78] Various factors influence the T_g, such as degree of branching, steric hindrance, nature of end groups, backbone rigidity and polarity.[79] Thompson synthesised hyperbranched aromatic polyetherimides with exceptional thermal stability. The polymers were stable up to 530°C, with no perceptible T_g before decomposition suggesting few intermolecular entanglements.[80]

It is possible to make hyperbranched polymers compatible or incompatible with other polymers by adjusting their polarity. This may be achieved by reaction-induced phase separation of hyperbranched aliphatic polyester in an epoxy/amine thermoset matrix.[81] Carboxylic ended aryl-alkyl hyperbranched polyester poly(5-hydroxyethoxyisophthalic acid) was employed for an electrostatic layer-by-layer self-assembly by Qiu.[82] To date, the use of hyperbranched polymers as thermosets, toughness additives, gas permeation membranes, materials for molecular imprinting and molecular recognition, luminescent materials, liquid crystalline materials, NLO materials, optical active materials, nanocomposites has been reported.[83,84, 85,86,87,88,89,90] The only factor limiting their potential use is commercial availability of AB_n monomers. Due to the lack of a well-defined structure and wide MWD the possible applications discussed for dendrimers are not suitable for hyperbranched polymers. The lower cost of these materials has led them to be considered for numerous industrial applications, as their one-step synthesis would allow mass production. They have little use as bulk materials as they tend to be very brittle (due to lack of entanglements), however there are many applications in which their viscosity and large number of functional groups would be an advantage. It seems likely that in the future these applications will increase in number and hyperbranched polymers will become an important class of industrial polymers. There is a number of reports suggesting commercial applications of hyperbranched polymers as coatings, toners, detergents, inks, degradable materials, materials for home and personal care applications and modifiers for thermoset resins.[91,92,93,94]

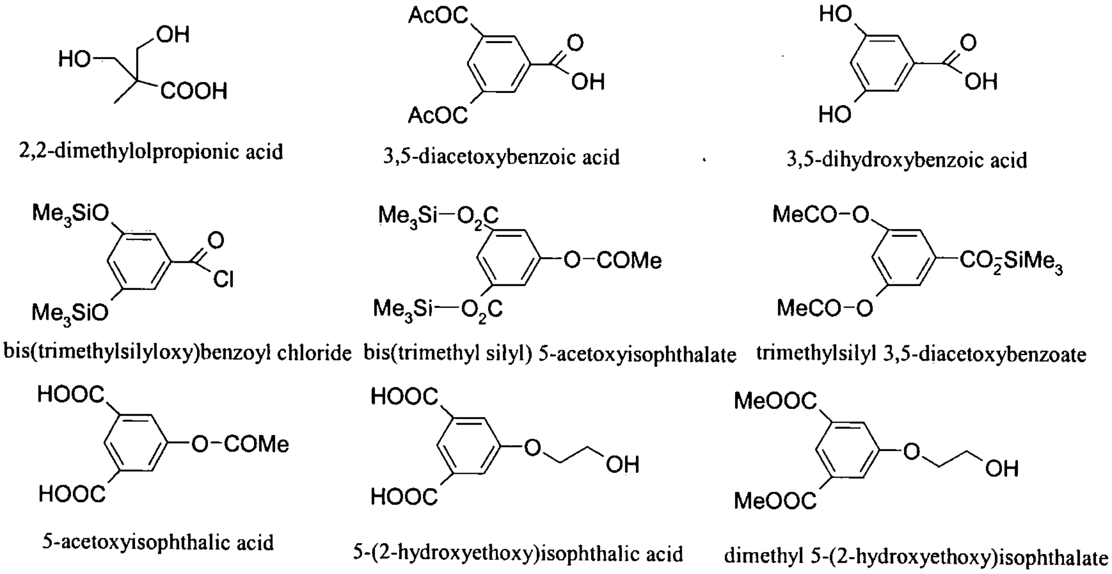
1.3 Background and aim of work

To date hyperbranched polyesters are conceived as one of the most studied types of hyperbranched polymers due to the availability of the starting materials, well-defined processes of synthesis and similarities with commercial polyesters.[1] The structures of these polymers extend from fully aliphatic to fully aromatic.

One of the first attempts to study hyperbranched polyesters was made in 1980 by Kricheldorf.[95] Polycondensation of difunctional and trifunctional trimethylsiloxybenzoylchlorides resulted in products of low DB. Turner has prepared polymers of a similar structure from 3,5-diacetoxybenzoic acid using the same synthetic approach.[96]

Hawker and coworkers reported syntheses of hyperbranched polyesters from 3,5-dihydroxybenzoic acid.[10] The chemical and physical properties of these polyesters were studied and compared with dendritic, hyperbranched and linear polymers.[97] Kumar and Hawker reported properties of polyesters based on the same monomer varying the spacer segment length between the branching points.[98,99] The T_g was found to decrease with an increasing number of methylene units in the spacer. Kricheldorf used the same monomer for copolycondensation with pentafunctional monomers.[100] 3,5-dihydroxybenzoic acid was also polymerised in the presence of carbonyl diimidazole (CDI).[101]

Recently, hyperbranched polymers prepared from 5-hydroxyisophthalic acid derivatives have been thoroughly studied. Kricheldorf *et al.* have found a strong dependence between DB and T_g of silylated poly(3,5-acetoxyisophthalic acid)s and poly(bis (trimethylsilyl) 5-acetoxyisophthalate)s.[102,103] Turner *et al.* have reported melt polymerisation of 5-(2-hydroxyethoxy)isophthalic acid resulting in hyperbranched polyesters.[104] A selection of monomers used in hyperbranched polyesters is shown in Figure 1.26.



2,2-dimethylolpropionic acid
3,5-diacetoxybenzoic acid
3,5-dihydroxybenzoic acid
bis(trimethylsilyloxy)benzoyl chloride
bis(trimethyl silyl) 5-acetoxyisophthalate
trimethylsilyl 3,5-diacetoxybenzoate
5-acetoxyisophthalic acid
5-(2-hydroxyethoxy)isophthalic acid
dimethyl 5-(2-hydroxyethoxy)isophthalate

Figure 1.26. Monomers used for the synthesis of hyperbranched polyesters.

Feast and Stainton polymerised dimethyl 5-(2-hydroxyethoxy)isophthalate with the addition of a trifunctional co-monomer (B_3 core).[105] The product showed interesting polydispersity, approaching three, contrary to wide distributions predicted by Flory's theory.[23] Feast *et al.* have also prepared hyperbranched polyesters based on dimethyl 5-(ω-hydroxyalkoxy)isophthalates varying number of methylene units in the alkylene chain from n=2 to n=6, see Figure 1.27.[25,26]

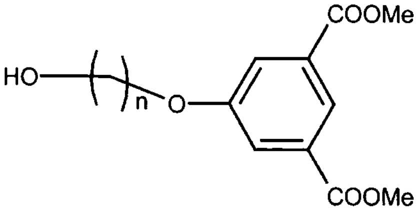


Figure 1.27. Structure of monomers used in the synthesis of hyperbranched polyesters by Feast *et al.*

Poly(dimethyl 5-(2-hydroxyethoxy)isophthalate)s showed interesting characteristics compared with other polymers. M_w value was found to increase when M_n reached a plateau. The resulting polymer was an amorphous material with T_g proportional to $1/M_w$ and no melting point.

The aim of this work was to establish the detailed mechanism by which hyperbranched polymers from poly(dimethyl 5-(2-hydroxyethoxy)isophthalate) are formed under different conditions, along with the influence of catalysts on the polymerisation reactions and side reactions such as intermolecular cyclisation, transesterification and polymer degradation.

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Chapter Two

The synthesis of monomers used in this study.

2.0 Introduction

The route used for the synthesis of the monomer dimethyl 5-(2-hydroxyethoxy)isophthalate was established by Stainton and Parker, see Figure 2.1.[1,2]

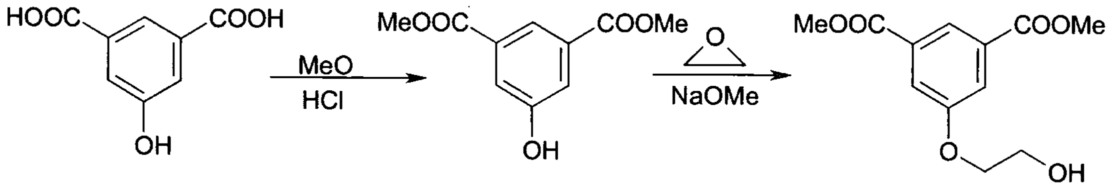

Figure 2.1. Scheme for synthesis of dimethyl 5-(2-hydroxyethoxy)isophthalate.

Dimethyl 5-(2-hydroxyethoxy)isophthalate was prepared by nucleophilic addition of ethylene oxide to dimethyl 5-hydroxyisophthalate. Dimethyl 5-hydroxyisophthalate was obtained by esterification of 5-hydroxyisophthalic acid.

Methyl 3,5-bis(2-hydroxyethoxy)benzoate was prepared by a modification of the route reported by Kumar and Gibson, see Figure 2.2.[3,4]

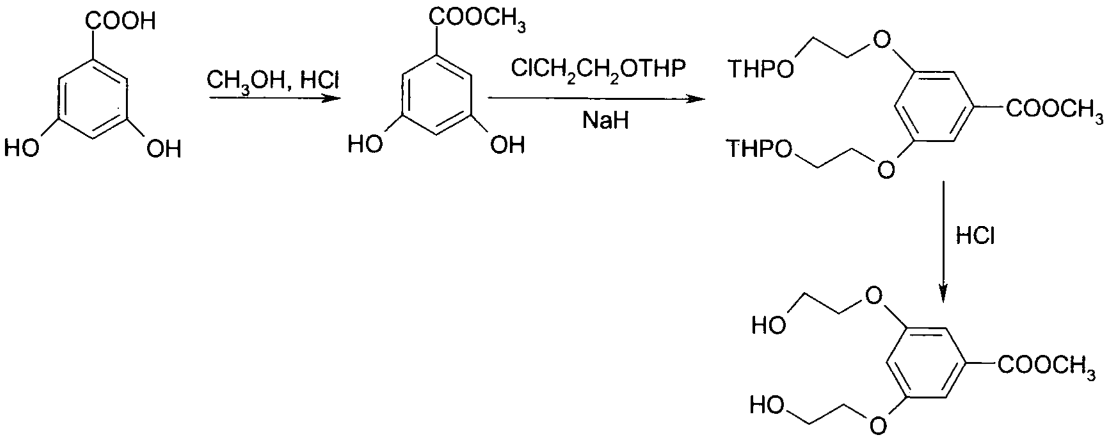

Figure 2.2. Scheme for synthesis of methyl 3,5-bis(2-hydroxyethoxy)benzoate.

Methyl 3,5-bis(2-hydroxyethoxy)benzoate was prepared by nucleophilic substitution of THP protected 2-chloroethanol by the anion derived by reaction of methyl ester of 3,5-dihydroxybenzoic acid with sodium hydride, followed by deprotection of the product. Methyl ester of 3,5-dihydroxybenzoic acid was obtained by esterification of 3,5-dihydroxybenzoic acid.

2.1 Materials and techniques

All reagents were obtained from Aldrich Chemicals and used without further purification. Elemental analyses were performed using an Exeter Analytical Elemental Analyser CE-440. Mass spectra were recorded on a Micromass AutoSpec instrument. ^{1}H and ^{13}C NMR spectra were acquired on a Varian Unity 300 spectrometer at 299.91MHz (^{1}H) and 75.41MHz (^{13}C) or Varian Inova 500 spectrometer at 499.89MHz (^{1}H) and 125.69MHz (^{13}C). Melting points were obtained using an Electrothermal digital melting point apparatus IA9200.

2.2 Synthesis of dimethyl 5-hydroxyisophthalate

5-Hydroxyisophthalic acid was esterified by refluxing for four hours in an excess of acidic methanol. The product, dimethyl 5-hydroxyisophthalate, which crystallised from the cold reaction mixture was recovered by filtration and recrystallised from methanol as a white solid (Yield 82%).

In a typical reaction, 5-hydroxyisophthalic acid (275.0g, 1.51 mol) and methanol (1300cm^{3}) were charged in 2.5-litre flask equipped with a stirrer bar, gas inlet and outlet and a reflux condenser. Anhydrous hydrogen chloride (38.5g, 1.04mol) was bubbled through the reaction mixture to form a clear solution. The reaction mixture was heated under reflux for four hours. On cooling to the room temperature crude product crystallised from the acidic methanol solution as white needles. The solid was recovered from methanol and washed with cold distilled water. The product was purified by recrystallisation from methanol to give dimethyl 5-hydroxyisophthalate as fine white needles and dried in *vacuo* (Yield 258.0g, 1.21mol, 82%). M.pt. 158.3°C, Lit.[1] 158-159°C. Analysis by thin layer chromatography (TLC) (silica gel/ethyl acetate) showed a pure compound (single spot, R_f=0.73).

Elemental analysis: calculated for $C_{10}H_{10}O_5$; C=57.14, H=4.76, found; C=56.88, H=4.71.

^{1}H NMR, Appendix 1.1 ($CDCl_3$, 300MHz): δ3.97 (s, 6H, $2OCH_3$), δ7.79 (s, 2H, 2ArH), δ8.27 (s, 1H, ArH).

^{13}C NMR, Appendix 1.2 (acetone-d_6, 125MHz): δ52.52 (OCH_3), δ120.85, 122.97 (aromatic C-H), δ131.88 (aromatic C-R), δ156.04 (aromatic C-O), δ166.21 (C=O).

MS (EI+), Appendix 1.3: 210 (M), 179 (M-OCH_3), 151 (M-CO_2CH_3), 136 (M-CH_3, M-CO_2CH_3). The spectral data is consistent with that reported.[2,5]

2.3 Synthesis of dimethyl 5-(2-hydroxyethoxy)isophthalate

The final product, dimethyl 5-(2-hydroxyethoxy)isophthalate was produced by nucleophilic addition of ethylene oxide to the dimethyl 5-hydroxyisophthalate. The process was conducted in methanol with a two-fold excess of ethylene oxide and sodium methoxide as a basic catalyst. The reaction mixture was pressurised with 100 psi of nitrogen in a Parr apparatus and heated to 95°C for six hours, see Figure 2.3.

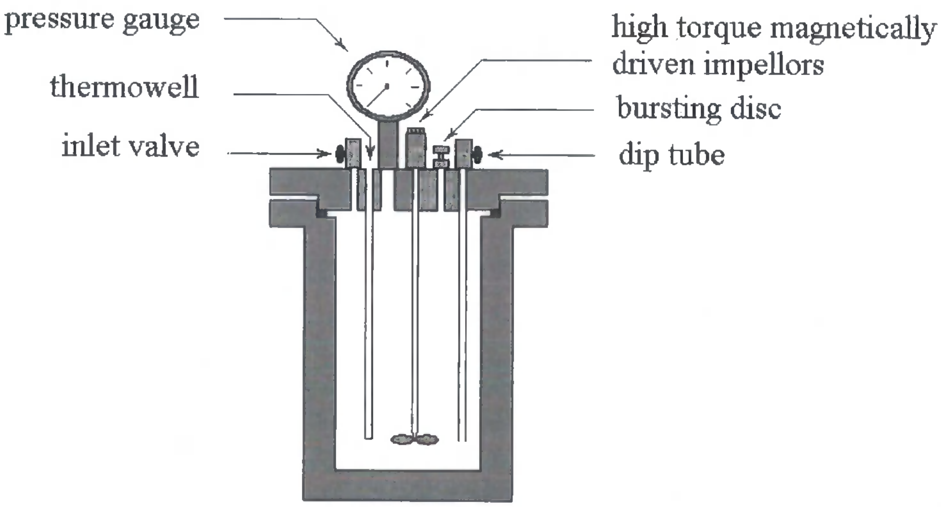

Figure 2.3. Parr apparatus.

Dimethyl 5-(2-hydroxyethoxy)isophthalate precipitated as a white solid (Yield 78%), which was recovered by filtration and then purified by recrystallisation from a 50/50 methanol/water solution.

In a typical reaction, a 2-litre Parr pressure reactor was charged with dimethyl 5-hydroxyisophthalate (100.0g, 0.48mol), sodium methoxide (6.0g, 0.17mol) and methanol (600cm^3). The reactor was purged with nitrogen gas for 10min, immersed into liquid air and evacuated. Ethylene oxide (44.0g, 1.00mol) was condensed into the reactor, which was allowed to reach room temperature overnight. The contents were pressurised with 100 psi of nitrogen gas and the solution stirred at 95°C for six hours. The product precipitated as a white solid, which was recovered by filtration and washed with cold distilled water. The product was purified by recrystallisation from a mixture of methanol and water and dried in *vacuo* (Yield 95.0g, 0.37mol, 78%). M.pt. 110.1°C, Lit.[1] 109.8-110.2°C. TLC (silica gel/ethyl acetate) showed a pure compound (single spot R_f=0.55).

Elemental analysis: calculated for $C_{12}H_{14}O_6$; C=56.69, H=5.51, found; C=56.68, H=5.55.

^1H NMR, Appendix 1.4 ($CDCl_3$, 300MHz): δ2.18 (s, 1H, OH), δ3.77 (s, 6H, 2OCH_3), δ3.81 (s, 2H, CH_2), δ3.98 (s, 2H, CH_2), δ7.74 (s, 2H, 2ArH), δ8.11 (s, 1H, ArH).

^{13}C NMR, Appendix 1.5 ($CDCl_3$, 125MHz): δ52.69 (CH_3), δ61.78 (CH_2OH), δ70.98 (CH_2O), δ120.05, 123.52 (aromatic C-H), δ132.01 (aromatic C-R), δ158.92 (aromatic C-O), δ166.25 (C=O).

MS (EI+), Appendix 1.6: 254(M), 223(M-OCH_3), 210(M-CH_2=CHOH), 179(M-CH_2=CHOH, -OCH_3), 151 (M-CH_2=CHOH, -CO_2CH_3), 136 (M- CH_2=CHOH, -CO_2CH_3, -CH_3). The spectral data is consistent with that reported.[1,2]

2.4 Synthesis of methyl ester of 3,5-dihydroxybenzoic acid

3,5-dihydroxybenzoic acid was esterified by refluxing for ten hours in an excess of acidic methanol. The reaction mixture was neutralised and methanol was evaporated. The product, methyl 3,5-dihydroxybenzoate, was dissolved in ethyl acetate washed with water and concentrated to give a white solid (Yield 90%).

In a typical reaction, 3,5-dihydroxybenzoic acid (200.0g, 1.29mol), methanol (1600cm^3) and catalytic amount of sulphuric acid (2ml) were charged into a 2-litre flask equipped with a stirrer bar and a reflux condenser. The reaction mixture was heated under reflux for ten hours. On cooling to room temperature the contents of the reaction were neutralised with 2M NaOH solution. After concentration, the residue was dissolved in 2L of ethyl acetate. The solution was washed with 2L of water and 2L of brine, dried over $MgSO_4$, filtered and concentrated to give the methyl 3,5-dihydroxybenzoate as a white solid (Yield 177.7g, 1.06mol, 82%). M.pt. 170.8°C. TLC (silica gel/ethyl acetate: hexane=3:7) showed a pure compound (single spot, R_f=0.44).

Elemental analysis: calculated for $C_8H_8O_4$; C=57.14, H=4.76, found; C=56.96, H=4.79.

^1H NMR, Appendix 1.7 (D_2O, 300MHz): δ3.72 (s, 3H, OCH_3), δ6.42 (s, 1H, ArH), δ6.79 (s, 2H, ArH).

^{13}C NMR, Appendix 1.8 (D_2O, 125MHz): δ52.78 (OCH_3), δ107.65, 108.53 (aromatic C-H), δ131.79 (aromatic C-R), δ157.01 (aromatic C-O), δ168.82 (C=O).

MS (EI+), Appendix 1.9: 168 (M), 137 (M-OCH_3), 109 (M-CO_2CH_3), 81 (M-CO_2CH_3, -C_2H_3). The spectral data is consistent with that reported.[6]

2.5 Synthesis of tetrahydropyranyl ether of 2-chloroethanol

2-chloroethanol was protected by reacting with an excess of 2,3-dihydropyran at room temperature in acidic conditions. The product, tetrahydropyranyl ether of 2-chloroethanol was dissolved in diethyl ether, washed with water and distilled to give the tetrahydropyranyl ether of 2-chloroethanol as a transparent liquid (Yield 76%).

In a typical reaction, 2-chloroethanol (5g, 4.2ml, 0.06mol), excess of freshly distilled 2,3-dihydropyran (7.88g, 8.5ml, 0.09mol) and catalytic amount of hydrochloric acid (0.3ml) were charged into 50ml flask equipped with a stirrer bar. The reaction mixture was stirred for five hours at room temperature and neutralised with 2M NaOH solution. The contents of the reaction flask were dissolved in excess of diethyl ether, washed with 100ml of water and 100ml of brine, dried over $MgSO_4$, filtered and concentrated. The product was filtered from the solid residue and distilled under reduced pressure to give the tetrahydropyranyl ether of 2-chloroethanol as a transparent liquid (Yield 7.89g, 8.13ml, d=1.03g/cm^3, 0.05mol, 76%).

Elemental analysis: calculated for $C_7H_{13}O_2$; C=51.22, H=7.93, found; C=51.46, H=8.01.

^1H NMR, Appendix 1.10 ($CDCl_3$, 500MHz): δ1.40-δ1.90 (br. m, 6H, C_3H_6), δ3.40-δ4.00 (br. t, 6H, $ClCH_2CH_2O$, CH_2 THP), δ4.66 (br. s, 1H, OCH).

^{13}C NMR, Appendix 1.11 ($CDCl_3$, 125MHz): δ19.23, 25.46, 30.44 (3CH_2), δ43.11 (CH_2Cl), δ61.85 (CH_2O), δ67.59 (CH_2O THP), δ98.78 (CHO).

MS (ES+), Appendix 1.12: 163:165=3:1 (M), 109:111=3:1 (M-C_4H_6), 85 (M-ClC_2H_4O).

2.6 Synthesis of bis-tetrahydropyranyl ether of methyl 3,5-bis(2-hydroxyethoxy)benzoate

Methyl 3,5-dihydroxybenzoate was etherified by tetrahydropyranyl ether of 2-chloroethanol refluxing for five days in the presence of NaH in dimethylformamide (DMF). The reaction mixture was distilled from the solvent under reduced pressure. The product, bis-tetrahydropyranyl ether of methyl 3,5-bis(2-hydroxyethoxy)benzoate was purified by column chromatography to give a colorless viscous liquid (Yield 26%).

In a typical reaction, methyl 3,5-dihydroxybenzoate (10.0g, 0.06mol) was dissolved in 100ml of DMF in a 250ml flask equipped with a stirrer bar and a reflux condenser. NaH (5.0g, 0.2mol, 60% in mineral oil) was added to the solution. The mixture was heated to 110°C for two hours, cooled to 50°C, tetrahydropyranyl ether of 2-chloroethanol (23.0g, 0.14mol) was added while stirring. After 5 days the mixture was cooled to room temperature the contents of the reaction were neutralised with 30% HCl solution and distilled under reduced pressure to give a brown viscous oil. The oil was dissolved in acetone and filtered from the solid residue. The obtained oil was purified by column chromatography on silica gel (Davisil, 40-63μ, 60A); eluent (3:7) ethyl acetate: hexane. Appropriate fractions, analysed by TLC, were collected, the solvent was evaporated under reduced pressure to give bis-tetrahydropyranyl ether of methyl 3,5-bis(2-hydroxyethoxy)benzoate as a viscous colorless oil and dried in *vacuo* (Yield 6.4g, 0.02mol, 26%). TLC (silica gel/ethyl acetate: hexane=3:7) showed a pure compound (single spot, R_f=0.51).

Elemental analysis: calculated for $C_{22}H_{32}O_8$; C=62.26, H=7.57, found; C=61.95, H=7.61.

^{1}H NMR, Appendix 1.13 ($CDCl_3$, 300MHz): δ1.00-δ2.00 (br. m, 12H, CH_2 THP), δ3.20-δ4.10 (br. m, 15H, CH_3O, $2CH_2$ THP, $2OCH_2CH_2O$), δ4.57 (s, 2H, 2CHO), δ6.57 (s, 1H, ArH), δ7.08 (s, 2H, ArH).

^{13}C NMR, Appendix 1.14 ($CDCl_3$, 125MHz): δ19.45, 25.52, 30.63 ($3CH_2$), δ52.31 (OCH_3), δ62.20 (CH_2O), δ65.83 (OCH_2 THP), δ67.88 (CH_2O), δ99.04 (CHO), δ107.16, 108.18 (aromatic C-H), δ131.99 (aromatic C-R), δ160.04 (aromatic C-O), δ166.85 (C=O).

MS (ES+), Appendix 1.15: 447 (2M+Na).

2.7 Synthesis of methyl 3,5-bis(2-hydroxyethoxy)benzoate

Bis-tetrahydropyranyl ether of methyl 3,5-bis(2-hydroxyethoxy)benzoate was deprotected in acidified methanol. The reaction mixture was neutralised and the solvent was evaporated. The product, methyl 3,5-bis(2-hydroxyethoxy)benzoate was recrystallised from a 50/50 ethyl acetate/hexane solution as a fine white powder (Yield 90%).

In a typical reaction, bis-tetrahydropyranyl ether of methyl 3,5-bis(2-hydroxyethoxy)benzoate (6.4g, 0.02mol) was dissolved in 50 ml of methanol and a catalytic amount of hydrochloric acid (0.3ml) was added to the solution. The reaction mixture was refluxed overnight, cooled to room temperature, neutralised with 2M NaOH solution and concentrated. The product was purified by 3 recrystallisations from a 50/50 mixture of ethyl acetate and hexane, washed with diethyl ether and dried in *vacuo* (Yield 3.5g, 0.14mol, 90%). M.pt. 100.7°C. TLC (silica gel/ethyl acetate: hexane=3:7) showed a pure compound (single spot R_f=0.06).

Elemental analysis: calculated for $C_{12}H_{16}O_6$; C=56.25, H=6.25, found; C=56.40, H=6.38.

^{1}H NMR, Appendix 1.16 ($CDCl_3$, 300MHz): δ2.03 (br. s, 2H, 2OH), δ3.90 (s, 3H, $2OCH_3$), δ3.98 (s, 4H, $2CH_2$), δ4.01 (s, 4H, $2CH_2$), δ6.67 (s, 1H, ArH), δ7.21 (s, 2H, ArH).

^{13}C NMR, Appendix 1.17 ($CDCl_3$, 125MHz): δ52.71 (OCH_3), δ61.73 (OCH_2), δ79.83 (CH_2OH), δ107.28, 109.16 (aromatic C-H), δ132.19 (aromatic C-R), δ159.88 (aromatic C-O), δ167.01 (C=O).

MS (ES+), Appendix 1.18: 279(M+Na), 535(2M+Na). The spectral data is consistent with that reported.[3]

See Appendices 1.1-1.18 for full detail of MS, ^{1}H and ^{13}C NMR spectra of dimethyl 5-hydroxyisophthalate, dimethyl 5-(2-hydroxyethoxy)isophthalate, methyl 3,5-dihydroxybenzoate, tetrahydropyranyl ether of 2-chloroethanol and tetrahydropyranyl ether of methyl 3,5-bis(2-hydroxyethoxy)benzoate.

2.8 References

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[1] (a) Parker, D., The Synthesis and Characterisation of Hyperbranched Polyesters, *Ph.D. Thesis*, Durham University (2000); (b) Parker, D., Feast, W. J., *Macromolecules*, **34(17)**, 5792 (2001); (c) Parker, D., Feast, W. J., *Macromolecules*, **34(7)**, 2048 (2001)

[2] (a) Stainton, N. M., The preparation and properties of dendritic and hyperbranched polyesters and their blends with PET, *Ph.D. Thesis*, Durham University (1994); (b) Feast, W. J., Stainton, N. M., *J. Mater. Chem.*, **5(3)**, 405 (1995)

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Chapter Two

The synthesis of monomers used in this study.

2.0 Introduction

The route used for the synthesis of the monomer dimethyl 5-(2-hydroxyethoxy)isophthalate was established by Stainton and Parker, see Figure 2.1.[1,2]

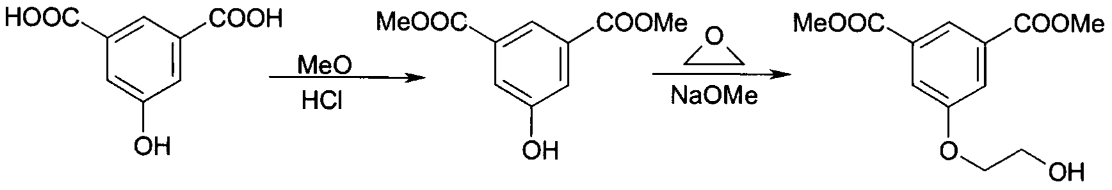

Figure 2.1. Scheme for synthesis of dimethyl 5-(2-hydroxyethoxy)isophthalate.

Dimethyl 5-(2-hydroxyethoxy)isophthalate was prepared by nucleophilic addition of ethylene oxide to dimethyl 5-hydroxyisophthalate. Dimethyl 5-hydroxyisophthalate was obtained by esterification of 5-hydroxyisophthalic acid.

Methyl 3,5-bis(2-hydroxyethoxy)benzoate was prepared by a modification of the route reported by Kumar and Gibson, see Figure 2.2.[3,4]

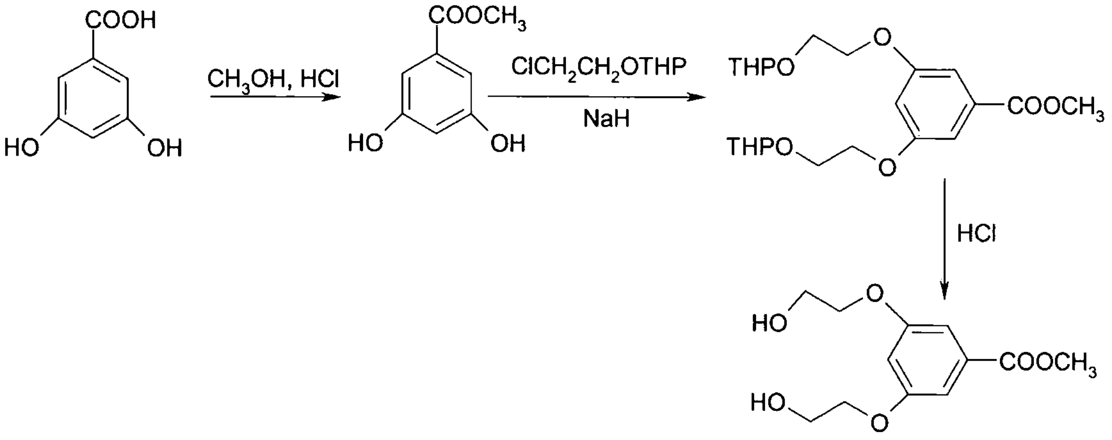

Figure 2.2. Scheme for synthesis of methyl 3,5-bis(2-hydroxyethoxy)benzoate.

Methyl 3,5-bis(2-hydroxyethoxy)benzoate was prepared by nucleophilic substitution of THP protected 2-chloroethanol by the anion derived by reaction of methyl ester of 3,5-dihydroxybenzoic acid with sodium hydride, followed by deprotection of the product. Methyl ester of 3,5-dihydroxybenzoic acid was obtained by esterification of 3,5-dihydroxybenzoic acid.

2.1 Materials and techniques

All reagents were obtained from Aldrich Chemicals and used without further purification. Elemental analyses were performed using an Exeter Analytical Elemental Analyser CE-440. Mass spectra were recorded on a Micromass AutoSpec instrument. ^{1}H and ^{13}C NMR spectra were acquired on a Varian Unity 300 spectrometer at 299.91MHz (^{1}H) and 75.41MHz (^{13}C) or Varian Inova 500 spectrometer at 499.89MHz (^{1}H) and 125.69MHz (^{13}C). Melting points were obtained using an Electrothermal digital melting point apparatus IA9200.

2.2 Synthesis of dimethyl 5-hydroxyisophthalate

5-Hydroxyisophthalic acid was esterified by refluxing for four hours in an excess of acidic methanol. The product, dimethyl 5-hydroxyisophthalate, which crystallised from the cold reaction mixture was recovered by filtration and recrystallised from methanol as a white solid (Yield 82%).

In a typical reaction, 5-hydroxyisophthalic acid (275.0g, 1.51 mol) and methanol (1300cm^{3}) were charged in 2.5-litre flask equipped with a stirrer bar, gas inlet and outlet and a reflux condenser. Anhydrous hydrogen chloride (38.5g, 1.04mol) was bubbled through the reaction mixture to form a clear solution. The reaction mixture was heated under reflux for four hours. On cooling to the room temperature crude product crystallised from the acidic methanol solution as white needles. The solid was recovered from methanol and washed with cold distilled water. The product was purified by recrystallisation from methanol to give dimethyl 5-hydroxyisophthalate as fine white needles and dried in *vacuo* (Yield 258.0g, 1.21mol, 82%). M.pt. 158.3°C, Lit.[1] 158-159°C. Analysis by thin layer chromatography (TLC) (silica gel/ethyl acetate) showed a pure compound (single spot, R_f=0.73).

Elemental analysis: calculated for $C_{10}H_{10}O_5$; C=57.14, H=4.76, found; C=56.88, H=4.71.

^{1}H NMR, Appendix 1.1 ($CDCl_3$, 300MHz): δ3.97 (s, 6H, $2OCH_3$), δ7.79 (s, 2H, 2ArH), δ8.27 (s, 1H, ArH).

^{13}C NMR, Appendix 1.2 (acetone-d_6, 125MHz): δ52.52 (OCH_3), δ120.85, 122.97 (aromatic C-H), δ131.88 (aromatic C-R), δ156.04 (aromatic C-O), δ166.21 (C=O).

MS (EI+), Appendix 1.3: 210 (M), 179 (M-OCH_3), 151 (M-CO_2CH_3), 136 (M-CH_3, M-CO_2CH_3). The spectral data is consistent with that reported.[2,5]

2.3 Synthesis of dimethyl 5-(2-hydroxyethoxy)isophthalate

The final product, dimethyl 5-(2-hydroxyethoxy)isophthalate was produced by nucleophilic addition of ethylene oxide to the dimethyl 5-hydroxyisophthalate. The process was conducted in methanol with a two-fold excess of ethylene oxide and sodium methoxide as a basic catalyst. The reaction mixture was pressurised with 100 psi of nitrogen in a Parr apparatus and heated to 95°C for six hours, see Figure 2.3.

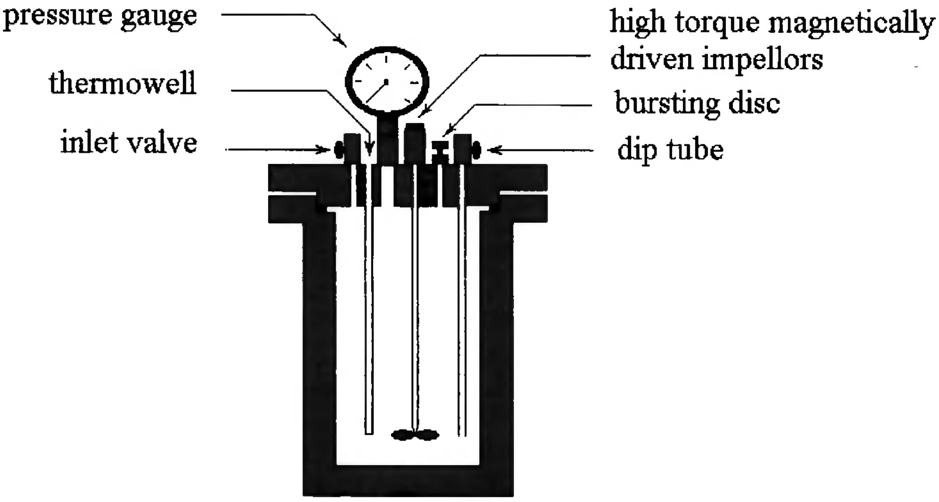

Figure 2.3. Parr apparatus.

Dimethyl 5-(2-hydroxyethoxy)isophthalate precipitated as a white solid (Yield 78%), which was recovered by filtration and then purified by recrystallisation from a 50/50 methanol/water solution.

In a typical reaction, a 2-litre Parr pressure reactor was charged with dimethyl 5-hydroxyisophthalate (100.0g, 0.48mol), sodium methoxide (6.0g, 0.17mol) and methanol (600cm^3). The reactor was purged with nitrogen gas for 10min, immersed into liquid air and evacuated. Ethylene oxide (44.0g, 1.00mol) was condensed into the reactor, which was allowed to reach room temperature overnight. The contents were pressurised with 100 psi of nitrogen gas and the solution stirred at 95°C for six hours. The product precipitated as a white solid, which was recovered by filtration and washed with cold distilled water. The product was purified by recrystallisation from a mixture of methanol and water and dried in *vacuo* (Yield 95.0g, 0.37mol, 78%). M.pt. 110.1°C, Lit.[1] 109.8-110.2°C. TLC (silica gel/ethyl acetate) showed a pure compound (single spot R_f=0.55).

Elemental analysis: calculated for $C_{12}H_{14}O_6$; C=56.69, H=5.51, found; C=56.68, H=5.55.

^{1}H NMR, Appendix 1.4 ($CDCl_3$, 300MHz): δ2.18 (s, 1H, OH), δ3.77 (s, 6H, 2OCH_3), δ3.81 (s, 2H, CH_2), δ3.98 (s, 2H, CH_2), δ7.74 (s, 2H, 2ArH), δ8.11 (s, 1H, ArH).

^{13}C NMR, Appendix 1.5 ($CDCl_3$,, 125MHz): δ52.69 (CH_3), δ61.78 (CH_2OH), δ70.98 (CH_2O), δ120.05, 123.52 (aromatic C-H), δ132.01 (aromatic C-R), δ158.92 (aromatic C-O), δ166.25 (C=O).

MS (EI+), Appendix 1.6: 254(M), 223(M-OCH_3), 210(M-CH_2=CHOH), 179(M-CH_2=CHOH, -OCH_3), 151 (M-CH_2=CHOH, -CO_2CH_3), 136 (M- CH_2=CHOH, -CO_2CH_3, -CH_3). The spectral data is consistent with that reported.[1,2]

2.4 Synthesis of methyl ester of 3,5-dihydroxybenzoic acid

3,5-dihydroxybenzoic acid was esterified by refluxing for ten hours in an excess of acidic methanol. The reaction mixture was neutralised and methanol was evaporated. The product, methyl 3,5-dihydroxybenzoate, was dissolved in ethyl acetate washed with water and concentrated to give a white solid (Yield 90%).

In a typical reaction, 3,5-dihydroxybenzoic acid (200.0g, 1.29mol), methanol (1600cm^3) and catalytic amount of sulphuric acid (2ml) were charged into a 2-litre flask equipped with a stirrer bar and a reflux condenser. The reaction mixture was heated under reflux for ten hours. On cooling to room temperature the contents of the reaction were neutralised with 2M NaOH solution. After concentration, the residue was dissolved in 2L of ethyl acetate. The solution was washed with 2L of water and 2L of brine, dried over $MgSO_4$, filtered and concentrated to give the methyl 3,5-dihydroxybenzoate as a white solid (Yield 177.7g, 1.06mol, 82%). M.pt. 170.8°C. TLC (silica gel/ethyl acetate: hexane=3:7) showed a pure compound (single spot, R_f=0.44).

Elemental analysis: calculated for $C_8H_8O_4$; C=57.14, H=4.76, found; C=56.96, H=4.79.

^{1}H NMR, Appendix 1.7 (D_2O, 300MHz): δ3.72 (s, 3H, OCH_3), δ6.42 (s, 1H, ArH), δ6.79 (s, 2H, ArH).

^{13}C NMR, Appendix 1.8 (D_2O, 125MHz): δ52.78 (OCH_3), δ107.65, 108.53 (aromatic C-H), δ131.79 (aromatic C-R), δ157.01 (aromatic C-O), δ168.82 (C=O).

MS (EI+), Appendix 1.9: 168 (M), 137 (M-OCH_3), 109 (M-CO_2CH_3), 81 (M-CO_2CH_3, -C_2H_3). The spectral data is consistent with that reported.[6]

2.5 Synthesis of tetrahydropyranyl ether of 2-chloroethanol

2-chloroethanol was protected by reacting with an excess of 2,3-dihydropyran at room temperature in acidic conditions. The product, tetrahydropyranyl ether of 2-chloroethanol was dissolved in diethyl ether, washed with water and distilled to give the tetrahydropyranyl ether of 2-chloroethanol as a transparent liquid (Yield 76%).

In a typical reaction, 2-chloroethanol (5g, 4.2ml, 0.06mol), excess of freshly distilled 2,3-dihydropyran (7.88g, 8.5ml, 0.09mol) and catalytic amount of hydrochloric acid (0.3ml) were charged into 50ml flask equipped with a stirrer bar. The reaction mixture was stirred for five hours at room temperature and neutralised with 2M NaOH solution. The contents of the reaction flask were dissolved in excess of diethyl ether, washed with 100ml of water and 100ml of brine, dried over $MgSO_4$, filtered and concentrated. The product was filtered from the solid residue and distilled under reduced pressure to give the tetrahydropyranyl ether of 2-chloroethanol as a transparent liquid (Yield 7.89g, 8.13ml, d=1.03g/cm^3, 0.05mol, 76%).

Elemental analysis: calculated for $C_7H_{13}O_2$; C=51.22, H=7.93, found; C=51.46, H=8.01.

^1H NMR, Appendix 1.10 ($CDCl_3$, 500MHz): δ1.40-δ1.90 (br. m, 6H, C_3H_6), δ3.40-δ4.00 (br. t, 6H, $ClCH_2CH_2O$, CH_2 THP), δ4.66 (br. s, 1H, OCH).

^{13}C NMR, Appendix 1.11 ($CDCl_3$, 125MHz): δ19.23, 25.46, 30.44 ($3CH_2$), δ43.11 (CH_2Cl), δ61.85 (CH_2O), δ67.59 (CH_2O THP), δ98.78 (CHO).

MS (ES+), Appendix 1.12: 163:165=3:1 (M), 109:111=3:1 (M-C_4H_6), 85 (M-ClC_2H_4O).

2.6 Synthesis of bis-tetrahydropyranyl ether of methyl 3,5-bis(2-hydroxyethoxy)benzoate

Methyl 3,5-dihydroxybenzoate was etherified by tetrahydropyranyl ether of 2-chloroethanol refluxing for five days in the presence of NaH in dimethylformamide (DMF). The reaction mixture was distilled from the solvent under reduced pressure. The product, bis-tetrahydropyranyl ether of methyl 3,5-bis(2-hydroxyethoxy)benzoate was purified by column chromatography to give a colorless viscous liquid (Yield 26%).

In a typical reaction, methyl 3,5-dihydroxybenzoate (10.0g, 0.06mol) was dissolved in 100ml of DMF in a 250ml flask equipped with a stirrer bar and a reflux condenser. NaH (5.0g, 0.2mol, 60% in mineral oil) was added to the solution. The mixture was heated to 110°C for two hours, cooled to 50°C, tetrahydropyranyl ether of 2-chloroethanol (23.0g, 0.14mol) was added while stirring. After 5 days the mixture was cooled to room temperature the contents of the reaction were neutralised with 30% HCl solution and distilled under reduced pressure to give a brown viscous oil. The oil was dissolved in acetone and filtered from the solid residue. The obtained oil was purified by column chromatography on silica gel (Davisil, 40-63μ, 60A); eluent (3:7) ethyl acetate: hexane. Appropriate fractions, analysed by TLC, were collected, the solvent was evaporated under reduced pressure to give bis-tetrahydropyranyl ether of methyl 3,5-bis(2-hydroxyethoxy)benzoate as a viscous colorless oil and dried in *vacuo* (Yield 6.4g, 0.02mol, 26%). TLC (silica gel/ethyl acetate: hexane=3:7) showed a pure compound (single spot, R_f=0.51).

Elemental analysis: calculated for $C_{22}H_{32}O_8$; C=62.26, H=7.57, found; C=61.95, H=7.61.

^{1}H NMR, Appendix 1.13 ($CDCl_3$, 300MHz): δ1.00-δ2.00 (br. m, 12H, CH_2 THP), δ3.20-δ4.10 (br. m, 15H, CH_3O, $2CH_2$ THP, $2OCH_2CH_2O$), δ4.57 (s, 2H, 2CHO), δ6.57 (s, 1H, ArH), δ7.08 (s, 2H, ArH).

^{13}C NMR, Appendix 1.14 ($CDCl_3$, 125MHz): δ19.45, 25.52, 30.63 ($3CH_2$), δ52.31 (OCH_3), δ62.20 (CH_2O), δ65.83 (OCH_2 THP), δ67.88 (CH_2O), δ99.04 (CHO), δ107.16, 108.18 (aromatic C-H), δ131.99 (aromatic C-R), δ160.04 (aromatic C-O), δ166.85 (C=O).

MS (ES+), Appendix 1.15: 447 (2M+Na).

2.7 Synthesis of methyl 3,5-bis(2-hydroxyethoxy)benzoate

Bis-tetrahydropyranyl ether of methyl 3,5-bis(2-hydroxyethoxy)benzoate was deprotected in acidified methanol. The reaction mixture was neutralised and the solvent was evaporated. The product, methyl 3,5-bis(2-hydroxyethoxy)benzoate was recrystallised from a 50/50 ethyl acetate/hexane solution as a fine white powder (Yield 90%).

In a typical reaction, bis-tetrahydropyranyl ether of methyl 3,5-bis(2-hydroxyethoxy)benzoate (6.4g, 0.02mol) was dissolved in 50 ml of methanol and a catalytic amount of hydrochloric acid (0.3ml) was added to the solution. The reaction mixture was refluxed overnight, cooled to room temperature, neutralised with 2M NaOH solution and concentrated. The product was purified by 3 recrystallisations from a 50/50 mixture of ethyl acetate and hexane, washed with diethyl ether and dried in *vacuo* (Yield 3.5g, 0.14mol, 90%). M.pt. 100.7°C. TLC (silica gel/ethyl acetate: hexane=3:7) showed a pure compound (single spot R_f=0.06).

Elemental analysis: calculated for $C_{12}H_{16}O_6$; C=56.25, H=6.25, found; C=56.40, H=6.38.

^{1}H NMR, Appendix 1.16 ($CDCl_3$, 300MHz): δ2.03 (br. s, 2H, 2OH), δ3.90 (s, 3H, $2OCH_3$), δ3.98 (s, 4H, $2CH_2$), δ4.01 (s, 4H, $2CH_2$), δ6.67 (s, 1H, ArH), δ7.21 (s, 2H, ArH).

^{13}C NMR, Appendix 1.17 ($CDCl_3$, 125MHz): δ52.71 (OCH_3), δ61.73 (OCH_2), δ79.83 (CH_2OH), δ107.28, 109.16 (aromatic C-H), δ132.19 (aromatic C-R), δ159.88 (aromatic C-O), δ167.01 (C=O).

MS (ES+), Appendix 1.18: 279(M+Na), 535(2M+Na). The spectral data is consistent with that reported.[3]

See Appendices 1.1-1.18 for full detail of MS, ^{1}H and ^{13}C NMR spectra of dimethyl 5-hydroxyisophthalate, dimethyl 5-(2-hydroxyethoxy)isophthalate, methyl 3,5-dihydroxybenzoate, tetrahydropyranyl ether of 2-chloroethanol and tetrahydropyranyl ether of methyl 3,5-bis(2-hydroxyethoxy)benzoate.

2.8 References

[1] (a) Parker, D., The Synthesis and Characterisation of Hyperbranched Polyesters, *Ph.D. Thesis*, Durham University (2000); (b) Parker, D., Feast, W. J., *Macromolecules*, **34(17)**, 5792 (2001); (c) Parker, D., Feast, W. J., *Macromolecules*, **34(7)**, 2048 (2001)

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[6] Brouwer, A. J., Mulders, S. J. E., Liskamp, R. M. J., *Eur. J. Org. Chem.*, **10**, 1903 (2001)

Chapter Three

The synthesis of poly (dimethyl 5-(2-hydroxyethoxy) isophthalate) and poly(methyl 3,5-bis(2-hydroxyethoxy)benzoate).

3.0 Introduction

In this chapter the synthesis of poly (dimethyl 5-(2-hydroxyethoxy) isophthalate) and poly(methyl 3,5-bis(2-hydroxyethoxy)benzoate) will be described. Studies of the polymerisation reaction of dimethyl 5-(2-hydroxyethoxy) isophthalate have been reported by Stainton, Keeney and Parker previously.[1,2,3] The reaction apparatus used in previous studies has been modified to achieve better control over the reaction. The influence of temperature, stirring rate, monomer amount and nitrogen flow speed was studied on uncatalysed polymerisations of dimethyl 5-(2-hydroxyethoxy) isophthalate. Optimal reaction conditions were established and various catalysts were applied to the polymerisation of dimethyl 5-(2-hydroxyethoxy) isophthalate. The methyl 3,5-bis(2-hydroxyethoxy)benzoate was polymerised without presence of a catalyst.

3.1 Materials and techniques

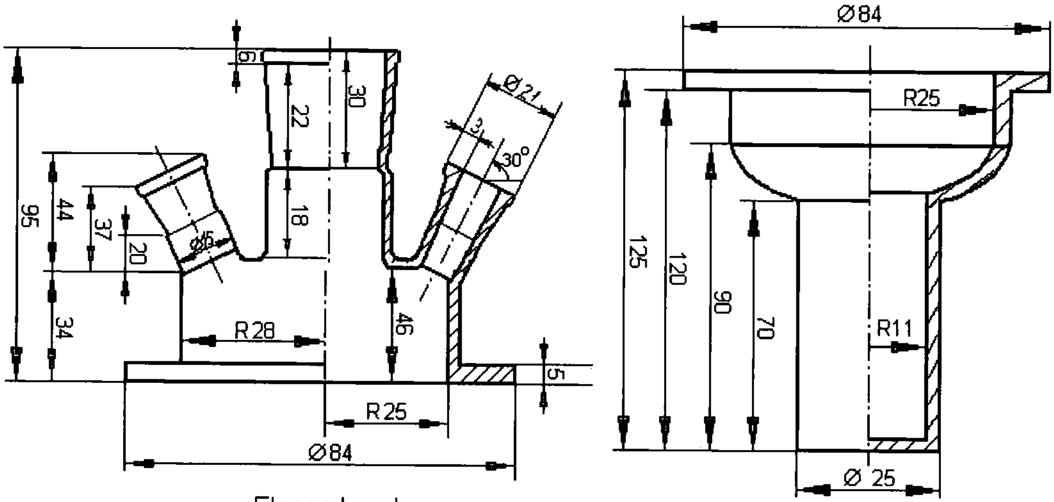
All reagents were obtained from Aldrich Chemicals and used without further purification. Catalyst Vertec 400AC was supplied by Johnson Matthey Synetix and used without further purification. The synthesis and purification of monomers was described in the previous chapter. ^{1}H NMR spectra were acquired on a Varian Unity 300 spectrometer at 299.91MHz (^{1}H).

3.2 Polymerisation of dimethyl 5-(2-hydroxyethoxy) isophthalate and methyl 3,5-bis(2-hydroxyethoxy)benzoate

Both poly(dimethyl 5-(2-hydroxyethoxy) isophthalate)s and poly(methyl 3,5-bis(2-hydroxyethoxy)benzoate)s are formed in bulk condensation polymerisations. The classical definition of the bulk polymerisation is the formation of polymer from pure, undiluted monomers. Small amounts of catalysts, promoters and chain-transfer agents may also be present.[4] Examples of polymers synthesised by bulk condensation polymerisation include polysulfones, polycarbonates and poly(ethylene terephthalate)s. Polycondensation reactions generate a low molecular weight by-product. The condensate has to be removed to shift the equilibrium in favour of polymer production, which can be difficult to achieve efficiently. This becomes increasingly problematic at the final stages of the reaction when the viscosities are high and molecular diffusivities are low, therefore effective polycondensation syntheses demand specially designed apparatus. Reaction exotherms are moderate, with most of the heat being liberated when the viscosities are low and heat loss is easily managed.

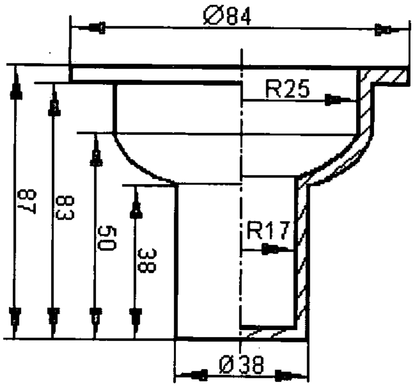
The monomers, dimethyl 5-(2-hydroxyethoxy) isophthalate and methyl 3,5-bis(2-hydroxyethoxy)benzoate are polymerised at high temperatures forming a polymer and a condensate, methanol.

Two cylindrical flasks with flat bases and flange heads were used as polymerisation reactors 1 and 2, see Figure 3.1.



Flange head

Polymerisation reactor 1



Polymerisation reactor 2

Figure 3.1. Technical drawings of polymerisation reactors 1 and 2, dimensions in mm, Ø is diameter, R is radius.

Polymerisation reactor 2 equipped with a 'Jiffy' stirrer was used in previous studies, see Figure 3.2.[1,2,3] Stirring with the 'Jiffy' mixer was problematic due to sticking of viscous polymer to the mixer blades. It was decided to replace the existing polymerisation reactor 2 with polymerisation reactor 1 equipped with a helical stirrer. The helical stirrer has a larger stirring surface compare to the 'Jiffy' stirrer, which may result in more efficient agitation, see Figure 3.2. The clearance between the blades of the stirrer and the walls of the polymerisation vessel was ~1-2mm.

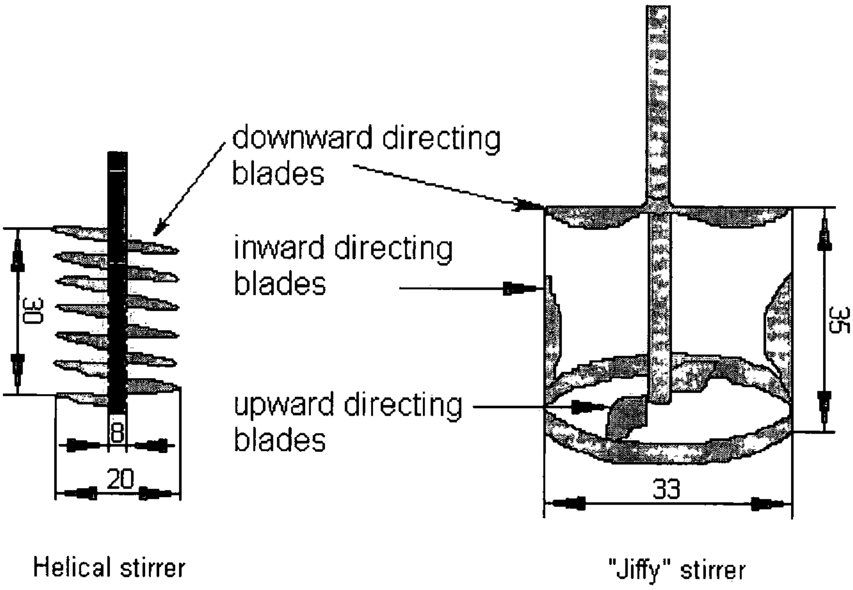


Figure 3.2. The helical stirring rod and the conventional Jiffy mixer, dimensions in mm.

To facilitate methanol removal, the helical stirrer had a nitrogen inlet at the top and exit holes between the blades at the bottom. In the first stage of developing the reaction methodology, nitrogen gas was flushed through the holes in the stirring rod. After 4-5 hours the nitrogen could not penetrate through the polymer because of the increased viscosity. It was not possible to keep the same conditions over a long period of time. At this stage it was decided to deliver the nitrogen through a metal tube, 3mm in diameter, which ended a few mm above the polymer mixture, see Figure 3.3 following page.

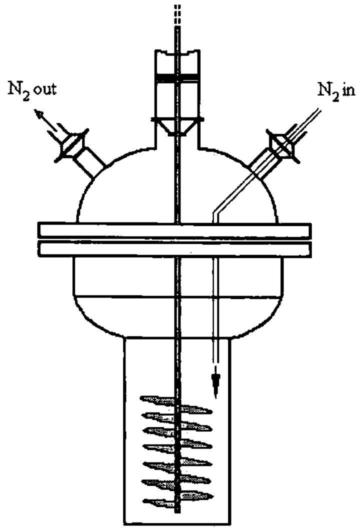


Figure 3.3. A scheme of nitrogen gas delivery to polymerisation reactor 1.

The stirring rod was fitted with a rubber seal inserted into a metal gland. The mechanical stirrer rotated in a clockwise direction in the reaction vessel. The stirrer and the reaction vessel were clamped onto a heavy-duty metal stand to prevent misalignment of the stirrer in the vessel. The stainless steel helical mixer was driven by an IKA RW 20.n overhead mechanical stirrer. The stirring rate was measured in revolutions per minute. The reaction vessel had a flange head and two inlets to allow sampling and easy removal of the product. The reaction vessel was immersed in a high temperature silicone oil bath surrounded by a 1kW heating jacket, which was connected to a Eurotherm temperature controller 808 with two thermocouples, see Figure 3.4. The oil was stirred by a teflon-coated rod driven by an IKA RCT basic magnetic stirrer.

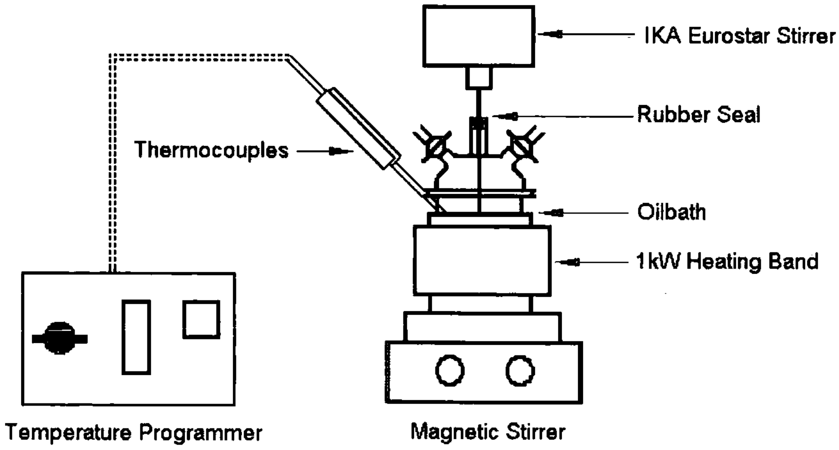


Figure 3.4. Polymerisation kit.

A monomer was placed into the reaction flask and compressed down into the base of the reaction vessel. The oil in the oil bath was heated from room temperature to 200°C at a temperature rise rate of 10°C/min. During the reaction the temperature of the oil in the oil bath was constant within a maximum variation of 2°C. The temperature of the polymer, assessed by a direct thermocouple was constant at 199°C. The monomer was stirred under a flow of nitrogen. The nitrogen was delivered through a metal tube, which ended a few mm above the polymer mixture, see Figure 3.3. The nitrogen flow rate was measured using an oil filled Dreschel bottle at the entrance to the reactor in units of "bubbles of nitrogen" per minute. The reaction mixture was sampled using a stainless steel spatula to remove *ca.* 100mg of the product every 5 hours.

All experiments were run until it was not possible to stir the polymer mixture any longer due to the increase in viscosity. At the end of the polymerisation, the vessel was removed from the oil bath and the stirrer removed from the reaction vessel. The polymer on the sides of the vessel and stirrer blades was chipped off and removed from the flask. The polymerisation procedure was repeated twice for each set of reaction conditions, see Table 3.1, and experimental errors were estimated, see Chapter 4.

Reaction	Temperature, °C	Stirring, r/min	Monomer Amount, g	N_2, b/min	Polym. Reactor
1	200	100	20	--	1
2	200	100	20	160	1
3	200	50	20	--	1
4	240	100	5	--	1
5	240	100	20	--	1

Table 3.1. Reaction conditions for the polymerisation of dimethyl 5-(2-hydroxyethoxy) isophthalate.

The influence of reaction conditions on the polymerisation was determined. At this stage it was decided to use a bigger oil bath, which allowed two polymerisation vessels to be used at the same time, see Figure 3.5 following page. In this set up we attempted to improve the control of heating by increasing the volume of oil used and by having two reactors in the same heating oil. The oil was stirred by a propeller stirrer driven by an IKA RW 20.n overhead stirrer at a rate of 80r/min.

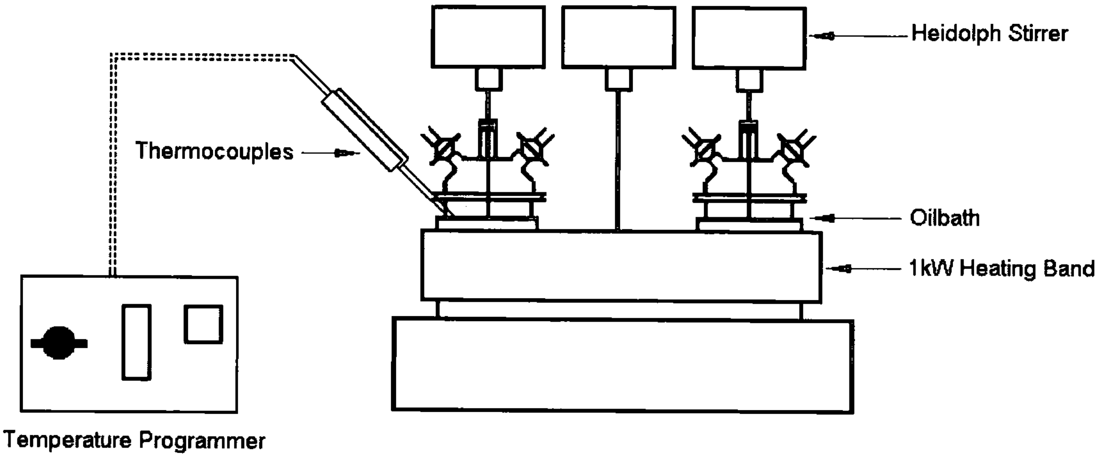


Figure 3.5. Improved polymerisation apparatus.

This modification allowed quicker accumulation of sample data and a better control over the temperature of the reaction. Commercially available catalysts: $Mn(OAc)_2$, Sb_2O_3, $Mn(OAc)_2/Sb_2O_3$, $Co(OAc)_2$, $Bu_2Sn(OAc)_2$, Vertec 400AC and $Ti(OBu)_4$ were applied to the polymerisation of dimethyl 5-(2-hydroxyethoxy) isophthalate, see Table 3.2.

Reaction	Catalyst	Catalyst Amount, molar %
6	--	--
7	$Mn(OAc)_2$	1
8	Sb_2O_3	1
9	$Mn(OAc)_2/Sb_2O_3$	1
10	$Co(OAc)_2$	1
11	$Bu_2Sn(OAc)_2$	1
12	Vertec AC400	0.1
13	$Ti(OBu)_4$	1

Table 3.2. Amounts of catalysts used in the polymerisations.

All reactions were run in polymerisation reactor 1 at a temperature of 200°C. Dimethyl 5-(2-hydroxyethoxy) isophthalate was polymerised on a 20g scale, at a stirring rate of 100r/min. The nitrogen flow rate was 160b/min. The reactions were sampled every hour.

Methyl 3,5-bis(2-hydroxyethoxy)benzoate was polymerised on a 5g scale in polymerisation reactor 1, at the stirring rate of 100r/min at the temperature of 200°C. The nitrogen flow rate was 160b/min. The reaction was sampled every hour.

Poly(methyl 3,5-bis(2-hydroxyethoxy)benzoate) was not soluble in organic solvents similar to poly(ethyl 3,5-bis(2-hydroxyethoxy)benzoate).[5] Such behaviour was attributed to presence of strong intermolecular hydrogen bonding interactions between large number of terminal hydroxyl groups and/or to high molecular weights observed in poly(dimethyl 5-(2-hydroxyethoxy)isophthalate) of similar structure. Hydroxyl groups of poly(methyl 3,5-bis(2-hydroxyethoxy)benzoate) were converted to acetoxy groups by a reaction with acetic anhydride.

The as-obtained products were examined without further purification by size exclusion chromatography (SEC) and matrix assisted laser desorption time of flight mass spectrometry (MALDI-TOF MS).

3.3 Experimental

3.3.1 Polymerisation of dimethyl 5-(2-hydroxyethoxy) isophthalate

In a typical reaction, dimethyl 5-(2-hydroxyethoxy) isophthalate (20g, 0.079mol) was placed into the lower section of the polymerisation reactor and compressed into the base of the vessel. The catalyst components were added to the monomer in a ratio of 1% or 0.1% molar ($Mn(OAc)_2$: 0.13615g, 0.00079mol, Sb_2O_3: 0.22823g, 0.00079mol, $Mn(OAc)_2/Sb_2O_3$: 0.06808g, 0.00039mol of $Mn(OAc)_2$ and 0.11412g, 0.00039mol of Sb_2O_3, $Co(OAc)_2$: 0.13929g, 0.00079mol, $Bu_2Sn(OAc)_2$: 0.27702g, 0.00079mol, Vertec 400AC: 0.19583g, 0.000079mol, $Ti(OBu)_4$: 0.26853g, 0.00079mol). The reactor was immersed in the oil bath and heated by a 1kW heating jacket, connected to a Eurotherm temperature controller 808 with two thermocouples. The oil bath was heated to a temperature of 200°C. The oil in the oil bath was stirred by an overhead stirrer at the speed of 80r/min. The polymer mixture was stirred continuously in clockwise direction by a stainless helical steel stirrer driven by an IKA RW 20.n overhead mechanical stirrer at a rate of 100r/min. The nitrogen flow rate was 160b/min. After cooling the resulting polymer was obtained as brown brittle glass, chipped off the sides of the vessel and stirrer blades and removed from the flask (Yield 13.3g, 0.06mol, 76%). The product was analysed without further purification. ^{1}H NMR, Appendix 1.19 ($CDCl_3$, 300MHz): δ3.83 (br. s, OCH_3), δ4.02, δ4.12 (br. s, CH_2CH_2OH), δ4.42, δ4.66 (br. s, CH_2CH_2O), δ7.81 (br. s, ArH), δ8.13 (br. s, ArH). The spectral data are consistent with that reported.[3]

3.3.2 Polymerisation of methyl 3,5-bis(2-hydroxyethoxy)benzoate

In a typical reaction, methyl 3,5-bis(2-hydroxyethoxy)benzoate (5g, 0.020mol) was placed into the lower section of the polymerisation reactor and compressed into the base of the vessel. The reactor was immersed in the oil bath and heated by a 1kW heating jacket, connected to a Eurotherm temperature controller 808 with two thermocouples. The oil bath was heated to a temperature of 200°C. The oil in the oil bath was stirred by an overhead stirrer at the speed of 80r/min. The polymer mixture was stirred continuously in clockwise direction by a stainless steel helical stirrer driven by an IKA RW 20.n overhead mechanical stirrer at a rate of 100r/min. The nitrogen flow rate was 160b/min. After cooling the resulting polymer was obtained as brown brittle glass, chipped off the sides of the vessel and stirrer blades and removed from the flask (Yield 2.3g, 0.01mol, 53%).

3.3.3 Functionalisation of poly(methyl 3,5-bis(2-hydroxyethoxy)benzoate)

In a typical reaction, poly(methyl 3,5-bis(2-hydroxyethoxy)benzoate) (0.05g) was dissolved in 50 ml of acetic anhydride and refluxed for several days until clear solution was obtained. The reaction mixture was cooled to room temperature, filtered and acetic anhydride was distilled under reduced pressure. The product, poly(methyl 3,5-bis(2-acetoxyethoxy)benzoate) was obtained as transparent oil and dried in *vacuo* (Yield 0.05g). The procedure was repeated for all poly(methyl 3,5-bis(2-hydroxyethoxy)benzoate) samples. TLC (silica gel/ethyl acetate: hexane=3:7) showed a pure compound (single spot R_f=0.06).

^{1}H NMR, Appendix 1.20 ($CDCl_3$, 500MHz): δ2.02 (s, CH_3), δ3.84 (s, $COOCH_3$), δ4.11 (s, CH_2O), δ4.23 (s, CH_2OCO), δ4.35 (s, CH_2O), δ4.48 (s, CH_2OCO), δ6.62 (s, 1H, ArH), δ7.13 (s, 2H, ArH).

^{13}C NMR, Appendix 1.21 ($CDCl_3$, 125MHz): δ21.10 (OCH_3), δ52.46 (OCH_3, mon.), δ62.82 (OCH_3), δ63.62 (CH_2OH), δ66.47 (CH_2), δ107.27, 108.58 (aromatic C-H), δ132.01 (aromatic C-R), δ159.79 (aromatic C-O), δ166.19 (C=O), δ171.20 (C=O).

See Appendices 1.19-1.21 for full detail of ^{1}H and ^{13}C NMR spectra of poly(dimethyl 5-hydroxyisophthalate) and poly(methyl 3,5-bis(2-acetoxyethoxy)benzoate.

3.4 Conclusions

The synthesis of poly(dimethyl 5-(2-hydroxyethoxy)isophthalate) and poly(methyl 3,5-bis(2-hydroxyethoxy)benzoate) have been achieved successfully. Poly(dimethyl 5-(2-hydroxyethoxy)isophthalate) was prepared on a 13g scale and fully characterised. The influence of reaction conditions and catalysts on the polymerisation of dimethyl 5-(2-hydroxyethoxy)isophthalate was studied. Poly(methyl 3,5-bis(2-hydroxyethoxy)benzoate) was prepared on a 2.3g scale, functionalised with acetoxy groups and fully characterised. The analysis and properties of the materials synthesised are presented in Chapter 4.

3.5 References

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Chapter Four

Physical analysis of hyperbranched polymers.

4.0 Introduction

In this chapter the characterisation of the hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalate)s and poly(methyl 3,5-bis(2-acetoxyethoxy)benzoate)s is reported. All poly(dimethyl 5-(2-hydroxyethoxy)isophthalate) samples were soluble in common organic solvents, such as chloroform, dimethylformamide (DMF), and tetrahydrofuran (THF). This allowed a range of analytical techniques to be used for their characterisation. The molecular weight distributions (MWD) were obtained by size exclusion chromatography (SEC) and structural information was provided by matrix assisted laser desorption/ionisation time of flight mass spectrometry (MALDI-TOF MS).

4.1 Size exclusion chromatography

A polymer is usually characterised by its molecular weight distribution and associated molecular weight averages, rather than by a single molecular weight.[1] The MWD is a consequence of the statistics of the polymerisation process, see Figure 4.1.[2]

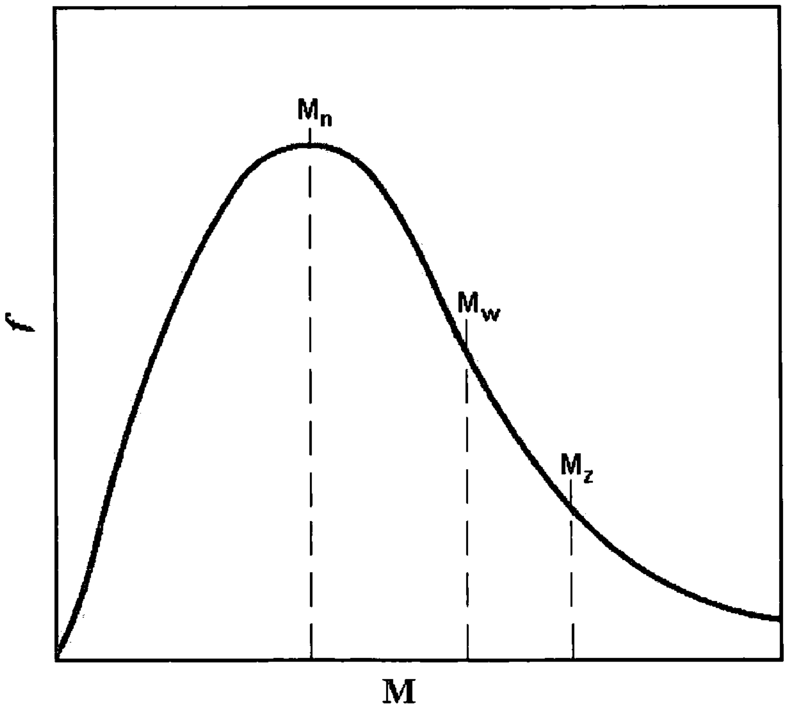


Figure 4.1. A typical molecular weight distribution for a synthetic polymer sample, where f is the fraction of polymer in each interval of absolute molecular weight (M). M_n, M_w and M_z are the commonly used molecular weight averages.

Molecular weight averages are calculated on the basis of the molecular weight (M_i) and the number of moles (N_i) or the weight (w_i) of molecules in a sample. Osmometry and SEC methods are based on counting the number of molecules; they provide values for the number average molecular weight (M_n). It is defined as the total weight of all molecules present in a sample divided by the total number of the molecules, see Equation 4.1.

$$\overline{M}_n = \frac{\sum N_i M_i}{\sum N_i}$$

Equation 4.1. The number average molecular weight, where N_i is the number of molecules of species i with molecular weight M_i.

Molecular weight determining methods that depend on the size of molecules such as light scattering provide values for the weight average molecular weight, M_w, see Equation 4.2.

$$\overline{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

Equation 4.2. The weight average molecular weight, where N_i is the number of molecules of species i with molecular weight M_i.

There are other average molecular weights, for example M_z and M_{z+1}, which are required for description of mechanical properties of a polymer. The width of the MWD can be estimated by the heterogeneity or polydispersity index, see Equation 4.3.

$$P_d = \frac{M_w}{M_n}$$

Equation 4.3. Polydispersity index, where M_n is the number average molecular weight, M_w is the weight average molecular weight and P_d is the polydispersity index.

The most probable value of the P_d for many linear polymers is 2, but larger and smaller values can be obtained. For a perfectly branched dendrimer P_d is one. Flory showed that as the polymerisation of an AB_2 monomer progresses, the polydispersity of the resulting branched molecules tends towards infinity, see Chapter 1 pages 14-18.[3]

SEC or gel permeation chromatography, GPC, is well recognised for determination of both number and weight average molecular weights. This is a chromatographic separation method, which uses a liquid mobile phase for the separation of the solute molecules in solution according to their size. In SEC, a sample is dissolved at very low concentration (0.1 to 0.2%) so that the polymer molecules exist as individual random conformation species with no entanglements, injected in a stream of the same solvent and carried through a chromatographic column at a constant flow rate, see Figure 4.2.

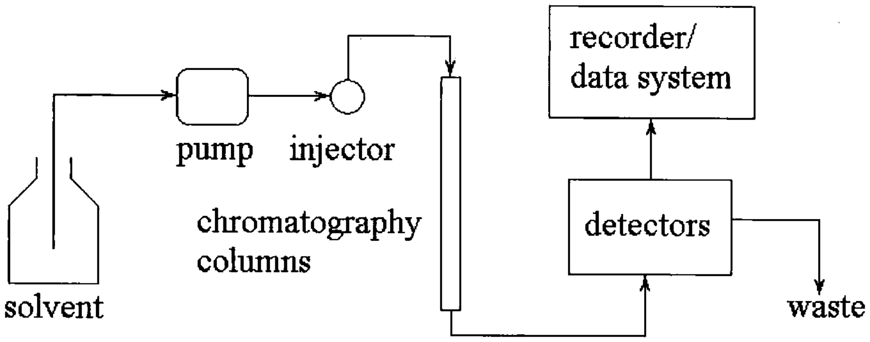


Figure 4.2. A basic scheme of SEC.

Chromatographic columns are usually packed with a porous cross-linked gel, several columns with different pore size material are usually used. The smaller molecules can diffuse into more pores and hence exit from the column at longer elution times than the larger ones. Thus, larger polymer molecules leave the column before smaller molecules and monomer; that is, the column separates the polymer molecules on the basis of their hydrodynamic volumes. After leaving the column a sample passes one or several detectors. Different kinds of detectors are in common use, including those based on detection by changes in refractive index (RI), ultraviolet absorption (UV), viscosity and light scattering (LS); there are several configurations for light scattering detectors.

A typical SEC trace consists of a plot of logM vs. V (elution volume), where M is the relative molar mass, see Figure 4.3 following page. During the elution, molecules that are too large to penetrate the pores are excluded and remain in the interparticle volume (V_0) (known as void or interstitial volume). This also may be interpreted as the minimum amount of solvent sufficient to move the material from the top of the column to the bottom without entering the pores. The molecules larger than the biggest pores are eluted first and cannot be separated on the basis of size.

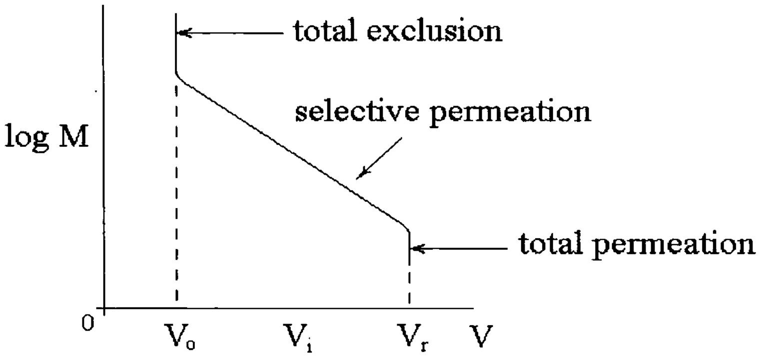


Figure 4.3. A typical size exclusion chromatography curve.

The remaining molecules spend a fraction of time inside the pores and elute in a region of selective permeation (V_i), which represents the pore volume of the packing medium. Smaller molecules, which can permeate all pores, elute at the total solvent volume (V_r). Values for the interparticle volume, region of selective permeation and total solvent volume are obtained from a SEC calibration curve and related by Equation 4.4:

$$V_r = V_i + V_o$$

Equation 4.4. Total solvent volume formula.

The SEC calibration curve is built by measuring the peak elution volumes ($\overline{V}_r$) of monodisperse polymer standards with known molecular masses. The elution volume is the volume of a mobile phase entering the column between the start of the elution and the emergence of the peak maximum. It depends on the logM of the sample. Calibration relates elution volume of a polymer to the molecular weight.

There are a number of calibration methods for the calculation of the molecular weight. They are based on semi-empirical equations, which have to be established for every polymer/solvent/temperature system by analysis of samples with known molecular weights. The estimates of molecular weight provided by these methods are not absolute.

According to a conventional calibration, the system is calibrated with narrow polydispersity polymer standards, usually with linear polystyrene. The molecular weight values obtained by this method correspond to a linear polystyrene standard of an equivalent size in solution as a given polymer sample. This calibration method is frequently used when only comparison of MWD is required. Polymers of different structures will have a different coil volume in solution thus producing inaccurate results.

An improved calibration method known as 'universal' calibration was suggested to avoid this problem. It is supposed that polymers with the same extended chain length are eluted at the same time. The hydrodynamic volume, defined as log[η]xM, where [η] is the intrinsic viscosity and M is the average molecular weight, has been used by Benoit to relate the elution behaviour of polymers with different structures.[4] The SEC system used in their studies was equipped with an in-line viscometer and a concentration detector. The plot of the hydrodynamic volume against the elution volume produced a single universal curve for linear and branched homopolymers and copolymers.

Although reliable M_w values were obtained using a viscosity detector and universal calibration, it was recently suggested that the conventional GPC technique is not appropriate for the determination of the real molecular weights of novel topology materials due to the lack of suitable polymer samples for calibration.[5] Some dendrimers exhibit a non-linear relationship between intrinsic viscosity and the molecular weight and the universal calibration method may or may not be applicable.[6, 7] The universal calibration relates hydrodynamic volume of the polymer, proportional to its molecular weight, to the retention volume. However, the presence of a maximum in the plot of log[η] vs. logM proves that the relationship between hydrodynamic volume and molecular weight for dendritic materials is different from linear polymers. In such cases, absolute calibration methods are required.

Light scattering (LS) is a well-established technique for determining weight average molecular weights of polymers in solution.[8] In LS, a polymer solution is irradiated with an intense monochromatic light source, usually a laser. The electric vector of the electromagnetic radiation induces dipole moments in the molecules. The magnitude of the induced dipole is proportional to the intensity of the electric field and the proportionality constant is called polarisability.[9] The molecule scatters light in all directions. The ratio of the scattered light intensity at a scattering angle θ (corrected for the distance of the observation point from the scattering centre), to the incident light intensity is known as Rayleigh scattering ratio, R_θ.

The information about the size and molecular weight of a polymer is derived from the excess light scattering intensity above the solvent background. This intensity is proportional to the polymer M_w and sample concentration, see Equation 4.5.

$$Kc / R_\theta = 1/(M_w(P(\theta)) + 2A_2c$$

Equation 4.5. The light scattering equation, where, R_θ is the Rayleigh scattering ratio at an angle θ, c is the sample concentration, M_w is the weight average molecular weight, A_2 is the second virial coefficient, $P(\theta)$ is the particle scattering function at angle θ, K is the optical constant.

Significant attempts have been made to develop an in-line light scattering detector for SEC to achieve determination of absolute molecular weights. Three types of LS detectors are used in SEC: low angle (LALLS), multi angle (MALLS) and right angle (RALLS) laser light scattering detectors. Low angle light scattering (LALLS) detector collects information at low angles (5-7°), which is then extrapolated to zero concentration at each retention volume. Molecular weights for hyperbranched polyesters based on 3,5-diacetoxybenzoic acid obtained from LALLS and universal calibration were in a good agreement.[10] Frechét showed that the values obtained from LALLS were 3-5 times higher than those determined using polystyrene standards.[11] This technique has not found widespread use due to problems with calibration, output data and overall expense. It was proposed that the problems encountered could be overcome by use of intrinsic viscometry measurements. According to this method, concentration and viscosity detectors are used to determine intrinsic viscosities. All the solution viscosities are then extrapolated to zero concentration as in the LALLS method. Absolute molecular masses were calculated by the ‘universal’ calibration method based on the Mark-Houwink equation.[12]

A similar instrument known as multi-angle laser light scattering (MALLS) detector directly measures M_w and radius of gyration (R_g) by extrapolation to zero angle to exclude effects of intramolecular interference.[13] Reliable values of molecular parameters are obtainable only for M_w>200,000 or more by this technique.

The right angle laser light scattering (RALLS) detector provides optimal signal-to-noise performance in SEC LS detection. In the LALLS or MALLS methods bending of the scattered beam through the liquid glass interface occurs, therefore an angular correction factor is needed to compensate for this refraction effect. At the 90° angle the scattered beam exits at a normal angle to the liquid glass interface, consequently no detector angle correction is needed.

The Viscotek TriSEC instrument used in this study uses refractive index (RI), viscometer and light scattering detectors in series. SEC using a LS detector coupled with an in-line viscometer provides additional precision in determining molecular sizes and produces useful information about polymer branching. The results are insensitive to typical variations of SEC experimental conditions, such as flowrate inconsistency, band broadening, column deterioration and others. The TriSEC system determines accurate MWD for polymer samples over a wide range of molecular weights. The technique provides extra sensitivity even at low molecular weights. The triple detector combination eliminates the need for SEC column calibration and instrumental band broadening correction. To date, this technique provides the most accurate values for M_w, $[\eta]$ and branching factors.

Twyman reported that SEC failed to provide reasonable relative mass measurements for dendritic molecules based on 1,3-diaminopropan-2-ol, especially in the case of high molecular weight examples.[14] According to Moore, the elution profiles of hyperbranched polyetherimides were sensitive to the mobile phase used, which resulted in different molecular weights determined for each polymer/solvent system.[15] This difference was attributed to aggregation and adsorption on the column. Frey reported higher molecular weights compared to those determined from ^{1}H NMR spectra for multi-arm star block copolymers and hyperbranched aliphatic polyesters.[16] Different hydrodynamic behaviours of a sample and a reference might lead to underestimated molecular weights. Conversely, interaction of the large number of polar end groups with the solvent and SEC columns can lead to strong overestimation of molecular weights.[17,6] Both effects undoubtedly would lead to incorrect molecular weight values.

To conclude, SEC is a quite straightforward technique experimentally and is applicable for a wide range of potential uses. It is still being extended to more complex applications. However, care should be taken of possible limitations with respect to calibration and the complications inherent in data handling.

4.2 Matrix assisted laser desorption/ionisation–time of flight mass spectrometry

Molecular weight measurements by mass spectrometry are based on the production, separation and detection of molecular ions. Matrix assisted laser desorption mass spectrometry (MALDI MS) used in combination with time of flight analysis (TOF) is a powerful method for the determination of molecular weights for large molecules.[18] In MALDI MS non-volatile samples are vaporised and ionised from a solid-state phase directly into the gas phase.[19] The ions are accelerated with the same potential from a fixed point, at a fixed initial time and are allowed to drift towards a detector. The ions are separated from matrix ions, individually detected based on their mass-to-charge ratios, m/z, and analysed. Abundances of ions are calculated from the time of flight required for ions to reach the detector.

A conventional MALDI-TOF MS consists of an ion source, analyser, detector and a data system, see Figure 4.4.

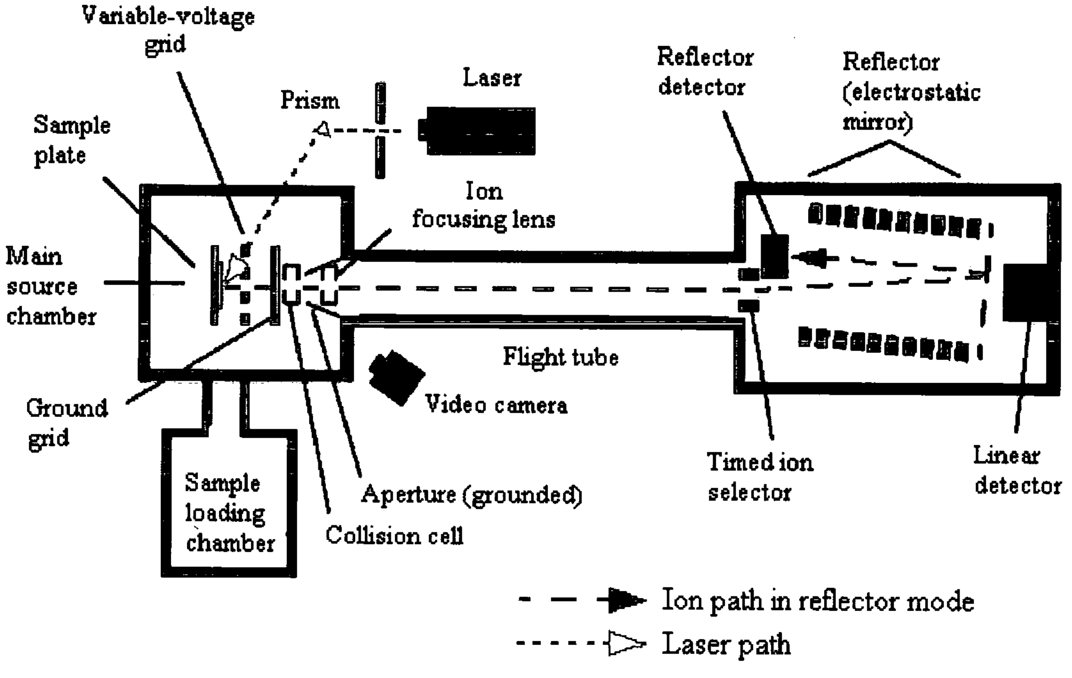


Figure 4.4. Basic scheme of MALDI-TOF MS.

In MALDI-TOF MS samples are embedded in a matrix that enhances desorption and ionisation of a sample. The matrix is present in great excess and isolates individual sample molecules. Most of the matrices in common use are organic substances with low molecular weights. The laser light is condensed by an optical lens and directed onto a target area where the sample is deposited. The sample is very rapidly heated, vapourised and ionised. Ions in MALDI-TOF MS are usually detected as: $[M+H]^+$ and $[M+\text{cation}]^+$, where M is a sample molecule, cations are usually K^+ and Na^+ ions generated by K and Na present in the sample or environment.

Linear and reflector methods of acquisition can be used for the sample analysis. According to the first method ions are generated by the laser pulse and drift into a field free region towards linear detector. Their m/z ratio is determined by the time during which they reach the detector. M/z ratio is calculated on the basis of Equation 4.6:

$$E = \frac{1}{2}\frac{m}{z}v^2$$

Equation 4.6. Formula of kinetic energy of an ion, where *E* is the energy imparted on charged ions as a result of the voltage applied by the instrument, m is the ion mass, z is the ion charge and *v* is the velocity of the ions drifting along the flight tube.

All similarly charged ions have similar energies, because all ions are exposed to the same electric field. Therefore, ions that have larger masses have lower velocities and hence require longer times to reach the detector. Time of flight and number of ions that have reached the detector are measured and the data obtained is converted into readable or graphic display. The m/z ratio of an ion is related to its time of flight by the Equation 4.7:

$$\frac{m}{z} = \frac{2V_0t^2}{L^2}$$

Equation 4.7. Relation between *m/z* ratio and time of flight of an ion, where *m* is the ion mass, *z* is the ion charge, V_0 is potential difference between the sample probe and the extraction grid, *L* is the length of the flight tube and *t* is the time taken by an ion to reach the detector.

The reflector method is used to compensate for the differences in flight times of ions with the same m/z ratio of slightly different kinetic energies by means of an ion reflector. Ions extracted from an ion source move towards the ion mirror, reflector. Voltage applied to the reflector directs ions towards the reflector detector. Ions with higher energy penetrate deeper into the reflector, whereas ions with lower energy have a longer time of flight before they reach the detector. Thus all ions with equivalent m/z ratios are focused in space and time at the reflector detector. Hence, ions with same m/z ratio are detected together, irrespective of their initial energy, which enhances mass resolution.

In a traditional MALDI-TOF MS, ions exhibit a broad energy distribution. If desorption occurs in a strong electrical field, energy is lost by collisions with the ion plume, which results in further energy dispersion. Broad energy distributions of ions result in poor resolution of a spectrum. The dependence of ion time of flight can be determined more accurately by delaying the extraction of ions from the source. The Voyager MALDI-TOF MS, used in this study, works in a delayed extraction mode, when TOF of an ion is independent of the initial velocity. According to this mode position of ions released from the sample surface, is correlated with their initial velocity. After ions are formed in a field-free region they are extracted by applying a high extraction voltage pulse to the accelerating voltage after predetermined time of delay. This makes initially slower ions acquire slightly higher energy from accelerating field than initially faster ions. By tuning variable-voltage grid in the source of and the delay time applied to acceleration, slow and fast ions of the same mass reach the detector plane at the same time. This mode also allows to produce a less dense ion plume, which minimises ion collisions and improves the resolution and mass accuracy.

MALDI-TOF MS is a relatively new technique developed in the 1980s, and it was extensively used in the analysis of biopolymers such as proteins. It can analyse a theoretically unlimited mass range. The only limitation is the ionisation ability, not the analyser physics. A mass spectrum can be obtained from a single ionisation event. Different classes of biopolymers, peptides and synthetic polymers were analysed by MALDI-TOF MS.

Only recently this technique has been extensively applied to synthetic polymers, such as polystyrene, poly(methyl methacrylate) and polyethylene glycol.[20] It is utilised in novel dendrimer structure analysis such as molecular weight determination, presence of defects or impurities.[21,22,23] The MALDI technique appears to give reliable results for polymers with low polydispersity, analyses comparable with other conventional methods are obtained. In some cases it fails to provide correct molecular weight distributions for materials with high polydispersity.[24,25]

This technique has been used to identify side reactions, intramolecular cyclisation and functional group exchange reactions between catalyst and a hyperbranched polymer.[26,27,28] It was also used in analysis of poly(dimethyl 5-(2-

hydroxyethoxy)isophthalate)s for determination of intermolecular cyclisation and ester-ester interchange reactions.[29,30]

4.3 Previous studies of poly(dimethyl 5-(2-hydroxyethoxy) isophthalate)

Hyperbranched polyesters based on dimethyl 5-(ω-hydroxyalkoxy)isophthalates with different number of methylene units in the alkylene chain from n=2 to n=6 have been extensively studied previously, see Figure 4.5.[29,30]

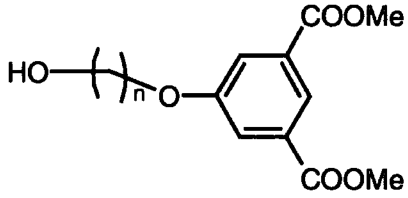


Figure 4.5. Structure of monomers used in the synthesis of hyperbranched polyesters based on dimethyl 5-(ω-hydroxyalkoxy)isophthalates.

The polymers prepared showed interesting characteristics compared with other polymers. In the case of poly(dimethyl 5-(2-hydroxyethoxy)isophthalate) a general trend in increase of the weight average molecular weight (M_w) with increasing polymerisation time was observed. The number average molecular weight (M_n) reached a plateau after relatively short reaction times leading to broad MWD, see Figure 4.6.

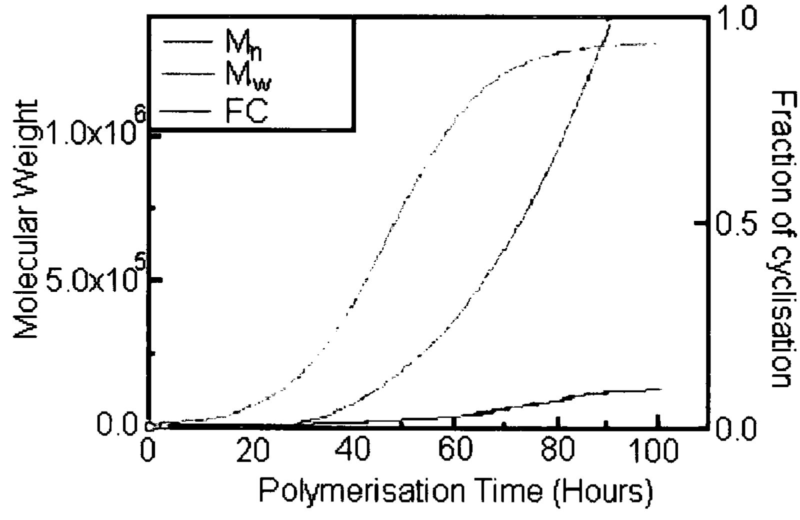


Figure 4.6. Schematic growth of molecular weight and cyclised species content vs. time of the polymerisation of dimethyl 5-(2-hydroxyethoxy)isophthalate.

The plateau in M_n, also observed in other hyperbranched polymers was attributed to an intramolecular cyclisation reaction, see Figure 4.7. The relative amounts of cyclised material were determined by MALDI-TOF MS, the procedure will be explained in detail in section 4.4.1.

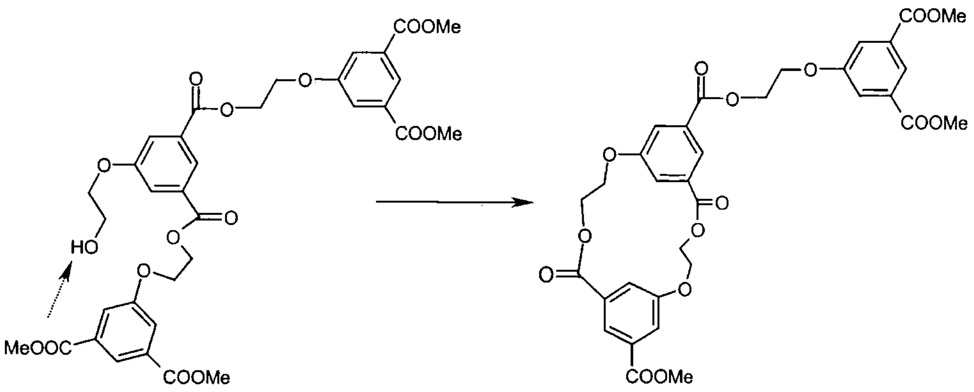


Figure 4.7. A proposed cyclisation route for a trimer.

Theoretically, the polymerisation of an AB_2 monomer should proceed until functional group A becomes sterically inaccessible, or consumed in cyclisation reactions.[31] The occurrence of such phenomena would lead to a maximum achievable molecular weight that would vary with different types of monomers and polymers. In systems with intramolecular cyclisation as soon as all the A groups are used, the polymerisation will stop even in the absence of steric factors. This "self-limiting" growth constrains the molecular weights achievable. Increase in polymerisation time or reaction scale will not affect molecular weight, polydispersity or yield of the reaction. Frechét suggested that incorporation of fresh monomer into large polymer molecules might be slower than intramolecular cyclisation or reaction of monomer with other monomer or oligomer molecules.[32] He proposed that the fresh monomer would tend to be transformed into new oligomeric species rather than build up larger pre-existing polymer molecules. It is unlikely that substantial molecular weights may be achieved by a simple batch addition of monomer and catalyst as long as large quantities of cyclised oligomers are present or formed in the reaction mixture. In an AB_n polymerisation, intramolecular and intermolecular BA bonds are chemically identical, which resulted in overestimation of molecular weight for hyperbranched aliphatic polyesters when end-group counting analyses are used.[16] The cyclisation has a strong impact on MWD and polydispersity. However, computer simulation of DB by Frey showed that cyclisation introduces only minor changes in the internal structure of the molecule and even at late stages of the reaction relatively high DB values may be obtained.[33]

Intramolecular cyclisation was not a favourable process for hyperbranched poly(amidoamine)s.[25] The negligible extent of cyclisation observed in this case was probably due to the conformationally rigid nature of the polymers obtained. Hawker observed the loss of 5% or fewer of the focal A groups in hyperbranched polymers based on 4,4-bis(4'-hydroxyphenyl)pentanoate, see Figure 4.8.[34(a)]

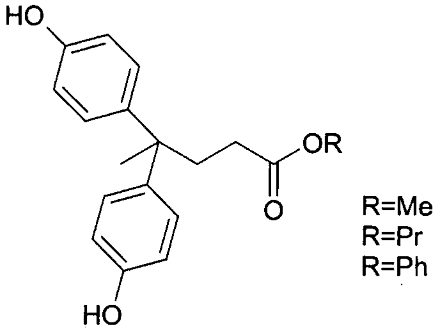


Figure 4.8. Structure of monomers used in the synthesis of hyperbranched polyesters by Hawker.[34(a)]

Perčec *et al.* have determined by NMR that hyperbranched allyl-terminated poly(13-bromo-1-(4-hydroxyphenyl)-2-(4-hydroxy-4'-p-terphenylyl)tridecane)s (TPT-b-All) lost 56% of their focal A groups due to cyclisation, see Figure 4.9.[34(b)]

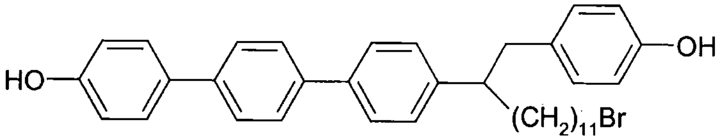


Figure 4.9. Structure of monomer used in the synthesis of hyperbranched polyethers by Perčec.[34(b)]

It can be concluded that the presence of cyclisation in hyperbranched polymers is system specific, it is likely to be related to the conformational mobility of both monomer and oligomer units. The cyclisation is a well-known fact and it is widely observed in various hyperbranched systems.[11,16,29,30,32,34]

The extent of cyclisation for poly(dimethyl 5-(2-hydroxyethoxy)isophthalate)s reaches a level of 100%. The point at which all polymer species are cyclised corresponds to the plateau in M_n. Fully cyclised polymer cannot take part in polycondensation reactions due to absence of A groups. Poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s with three to six methylene units in the alkylene chain showed plateaus in both M_n and M_w growth curves. By contrast, the M_w value of poly(dimethyl 5-(2-hydroxyethoxy)isophthalate)s continues to increase after complete cyclisation and total consumption of A groups, see Figure 4.10.

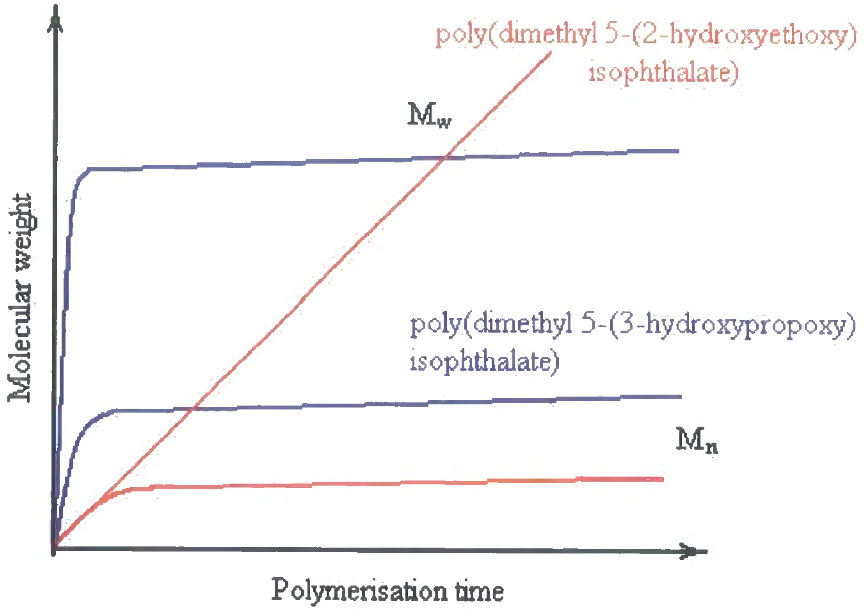


Figure 4.10. Schematic molecular weight growth of poly(dimethyl 5-(ω-hydroxyalkoxy)isophthalate)s.

It has been shown that for linear polyesters transesterifications or ester-ester interchange reactions occur in the melt as their chains undergo scission and recombination processes, resulting in rapid randomisation of mixtures of polymers.[35] Three types of interchange reactions, namely alcoholysis, acidolysis and esterolysis are distinguished.

Most polyesters can be prepared by an exchange reaction between ester and hydroxyl group, alcoholysis.[36] Polyesters in industry are manufactured in large part via such reactions, see Figure 4.11.

$$nR_1OOCRCOOR_1 + (n+1)HOR_2OH \rightleftharpoons H(OR_2OOCRCO)nOR_2OH + 2nR_1OH$$

$$nHORCOOR_1 \rightleftharpoons H(ORCO)nOR_1 + (n-1)\ R_1OH$$

Figure 4.11. A scheme of an alcoholysis process for AA/BB- and AB monomers respectively.

The exchange reaction between carboxyl and ester groups is known as acidolysis, see Figure 4.12 following page.

$$nR_1COOROOCR_1 + nHOOCR_2COOH \rightleftharpoons R_1COO(ROOCR_2COO)nH + (n\text{-}1)R_1COOH$$

Figure 4.12. A scheme of an acidolysis reaction.

The number of studies of this type of reaction is less abundant than those for the alcoholysis reaction. Last type of ester exchange reaction is a reaction between two ester groups, known as ester-ester interchange or esterolysis reaction, see Figure 4.13:

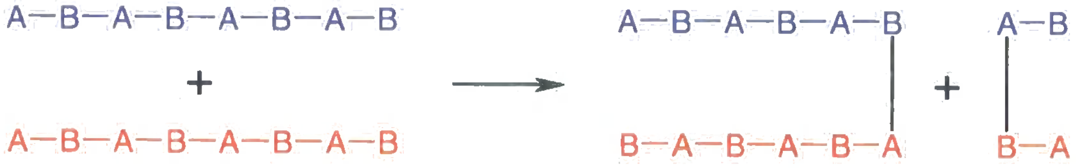
$$RCOOR_1 + R_2COOR_3 \rightleftharpoons R_2COOR_1 + RCOOR_3$$

Figure 4.13. A scheme of an esterolysis reaction.

This type of reaction is even less studied than acidolysis and has not found any practical application in the preparation of polyesters. Esterolysis, although a less frequent reaction, may play an important role in determining the chemical structure of polyesters. Redistribution of chain lengths and randomisation of chemical units are the consequences of all three kinds of intra- and intermolecular ester-ester exchange reactions, although alcoholysis is generally believed to be the dominant type of reaction. The control of these reactions may provide a new method for the preparation of copolymers with a wide variation in microstructure. Esterolysis is believed to be the slowest of these three interchange reactions and alcoholysis is the fastest. However, in contrast to direct esterification, alcoholysis proceeds very slowly in the absence of catalysts even at high temperatures.

Polycondensation of dimethyl 5-(2-hydroxyethoxy)isophthalate proceeds via the alcoholysis reaction. It stops when focal A groups, hydroxyl groups in this case, become inaccessible. The main reasons for this are cyclisation reactions and steric hindrance of the focal groups. Plateaus both in the degree of cyclisation and in the M_n are observed at this moment. Acidolysis reactions are not possible in this system, due to absence of acid groups. Ester groups are present in the resulting polymer, hence esterolysis reactions may occur, leading to changes in MWD.

In linear polyesters an interchange reaction does not lead to a net change in the number of linkages between repeat units.[3] The number of molecules before and after the reaction is not changed, hence the value of M_w will be affected and the value of M_n will not be affected. Such processes may change MWD, e.g. two molecules of equal size can produce one shorter and one longer molecule in comparison with the initial molecules. For example, two polymer chains having four repeat units with molecular weight of each unit equal to one will have M_n=4 and M_w=4. If they redistribute their units forming a bigger and a smaller molecule, with six and two units, the M_w value will increase to five, while the M_n value will remain unaltered, see Figure 4.14:



$$\overline{M}_n = \frac{1x4+1x4}{1+1} = 4 \qquad \overline{M}_n = \frac{1x6+1x2}{1+1} = 4$$

$$\overline{M}_w = \frac{1x4^2+1x4^2}{1x4+1x4} = 4 \qquad \overline{M}_w = \frac{1x6^2+1x2^2}{1x6+1x2} = 5$$

Figure 4.14. Evaluations of M_n and M_w for an interchange reaction.

Similarly, a large and a small molecule may react to form two molecules of equal size. In this case, the M_w value will decrease to four, leaving the M_n value unaltered. Flory postulated that interchange reactions lead to a state of equilibrium in which the concentration of each species remains constant. These concentrations define the equilibrium MWD for a given extent of polymerisation. The equilibrium MWD will be identical to that from random intermolecular condensation without occurrence of interchange reactions. This hypothesis was proved by studies of the behaviour of mixtures of decamethylene adipate polyesters.[3]

The polydispersity index of a linear polymer tends to two as the extent of the reaction approaches one, see Chapter 1 for detailed description. An AB_2 hyperbranched polymer would have a polydispersity approaching infinity, theoretically, this is the most probable MWD for hyperbranched polyesters due to redistribution of polymer chains by interchange reactions. However, it should be mentioned that Flory's statistical approach to AB_2 step growth polymerisation did not take into account cyclisation reactions.

As was shown originally by Parker, the M_w value of poly(dimethyl 5-(2-hydroxyethoxy)isophthalate) increases continuously, hence the number of molecules of different sizes must outweigh the number of molecules of equal size.[30] At present it is unclear why this is the case for the hyperbranched polyesters. Probably, interchange reactions are occurring at the more accessible chain ends of polymer molecules. Richards *et al.* have found that the rate of transesterification in poly(ethylene terephthalate)s is highly dependent on the concentration of hydroxyl end groups.[37] In the present system, there are numerous end groups, but no hydroxyl groups and although the rate of increase in the M_w value resulting from the postulated ester-ester exchange is slow it might be expected to increase as the number of end groups increases, because such exchange is only possible where end groups of different molecules interpenetrate.[30]

Esterolysis reaction between B groups, methyl ester groups, of different hyperbranched molecules does not change the size of the molecules. However, the reaction between a methyl ester end group in one polyester molecule with a main chain ester linkage in another molecule would lead to formation of a bigger and a smaller molecule. The molecule initially bearing the methyl ester increases in mass as the end group converts into a main chain ester, see Figure 4.15:

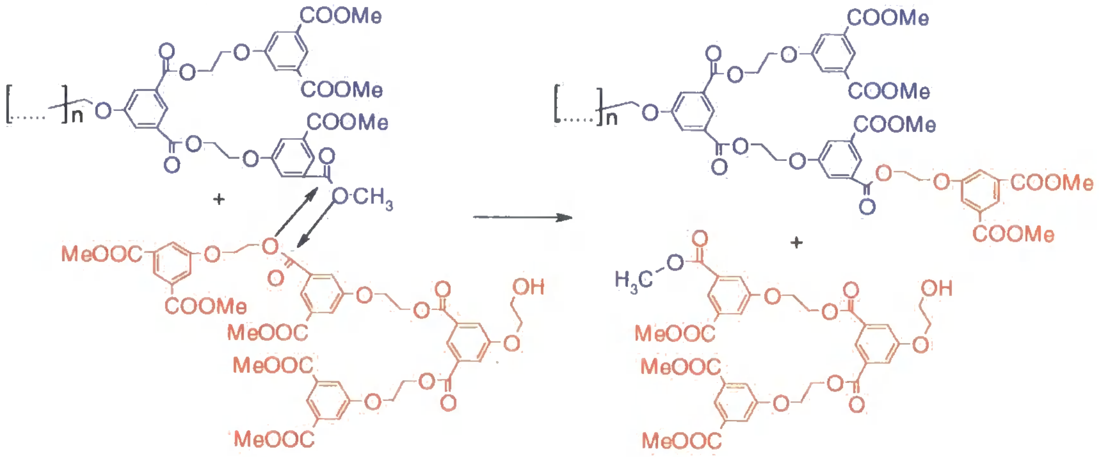


Figure 4.15. A scheme of esterolysis reaction between a polymer (shown in blue) and oligomer (shown in red) molecules of poly(dimethyl 5-(2-hydroxyethoxy)isophthalate).

Increase in the M_w value due to a reaction between a large and a small macromolecule is possible if the large molecule increases in size. Generally, larger molecules have more methyl ester end groups therefore this type of esterolysis reaction will favour the growth of the larger molecules.

Intramolecular and intermolecular reactions that may involve the cyclised and/or branched part of molecules are possible for hyperbranched polymers, see Figure 4.16:

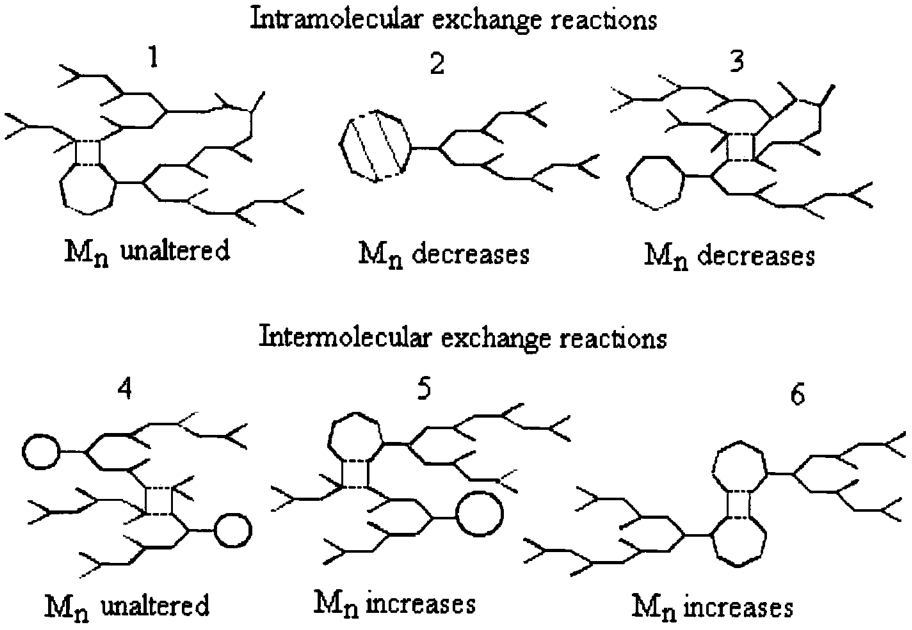


Figure 4.16. Influence of the ester-ester interchange reactions on the M_n value in a fully cyclised hyperbranched polyester (original bonds are dotted lines, new bonds are red).

An intramolecular interchange reaction between a branched and a cyclic part of a hyperbranched macromolecule does not change the number of molecules, therefore the M_n value remains unaltered, see Figure 4.16, case 1. Only an intramolecular interchange reaction between branched parts or between cyclic parts of the same molecule increases the number of molecules present and decreases the M_n value, see Figure 4.16, cases 2 and 3. If the intermolecular exchange reaction occurs between the branched parts of both molecules the number of molecules remains unaltered and the M_n value is not affected, see Figure 4.16, case 4. An intermolecular exchange reaction between the cyclic parts of one or two molecules reduces the number of molecules and increases the M_n value, see Figure 4.16, cases 5 and 6. If these reactions took place with an equal probability they would not affect the M_n value, as there is an equal number of ways to increase it as to decrease it. Obviously, interchange reactions involving a cyclic part of a molecule would be less favourable due to steric hindrances. The interchange reactions do not produce uncyclised material but they may result in the formation of new cyclic species.

Heating a mixture of the fully cyclised polyester with a core molecule, a di- or trifunctional ester, resulted in complete incorporation of the core molecule into the polyester. The M_w value in the fully cyclised system with no A groups available grew steadily, in a similar manner to the polycondensation of the pure AB_2 monomer, dimethyl 5-(2-hydroxyethoxy)isophthalate. The evidence supporting these assertions was provided by the MALDI-TOF MS.[30]

4.4 Results and Discussion

4.4.1 SEC and MALDI-TOF analysis of poly(dimethyl 5-(2-hydroxyethoxy)isophthalate) for noncatalysed polymerisations, experimental protocol and errors

In this section the author discusses the choice of the experimental protocol adopted and reviews attempts to optimise the reproducibility of the noncatalysed polymerisation.

The hyperbranched poly(dimethyl 5-(2-hydroxyethoxy)isophthalate)s produced in this study have been analysed using a Viscotek triple detection system (RI-DV-RALLS) using tetrahydrofuran (THF), dimethylformamide (DMF) and chloroform as solvents. The refractive index increment, dn/dc, was determined previously for a series of hyperbranched polyester solutions of different concentrations at a variety of wavelengths.[30] This is an important characteristic of a particular polymer-solvent system at a given temperature and is assumed to be independent of molecular weight. The refractive index values of the of poly(dimethyl 5-(2-hydroxyethoxy)isophthalate) in tetrahydrofuran and chloroform are 0.141 cm^3g^{-1} and 0.123 cm^3g^{-1}, respectively.

In the previous studies it was established that as the reaction progresses, the number average molecular weight, M_n, reaches a limit.[30] At the same time, the weight average molecular weight, M_w, continues to increase. A steady increase in M_w with constant M_n value leads to increase in polydispersity, P_d.

The P_d values of poly(dimethyl 5-(2-hydroxyethoxy)isophthalate)s are about two at the beginning of the polymerisation and increase with increasing reaction time. This observation is similar to that of Turner in relation to hyperbranched polyesters based on 3,5-diacetoxybenzoic acid.[7] In the current work, negative peaks were often observed in DMF and THF chromatograms, but this phenomenon was not understood and since it could lead to incorrect results these solvents were discarded for this study.

Chloroform appeared to be a better solvent for SEC analysis of the poly(dimethyl 5-(2-hydroxyethoxy)isophthalate)s studied here, especially for samples of higher molecular weight, since conventional detector responses were invariably observed.

MALDI-TOF MS was used for the determination of relative amounts of cyclised material in all samples. The analyses were performed on an Applied Biosystems Voyager-DE Biospectrometer Workstation. All samples were dissolved in $CHCl_3$ and analysed the following day. A 1% solution of 2-(4-hydroxyphenylazo)-benzoic acid in THF was used to deposit the matrix. For all samples data were collected from about 4000 laser shots. The instrument was calibrated using a commercial sample of poly(ethylene) oxide (Polymer Labs PEO 1080). The spectra were resolved up to a DP of about 30, however the calibration was adequate only in the low molecular weight region.

Belu has reported that for linear polymers of different molecular weight, the spectrum obtained at the threshold power was the most representative of the polymer composition.[38] However, the intensity of the high molecular weight part of the spectrum was too low to be useful. Wooley showed that additional power allowed heavier oligomers to be seen.[39] The laser power required for ionisation of higher molecular weight species was greater than that for lower molecular weight oligomers, which made the low mass part of the spectra complex due to fragmentation and matrix ions.

A typical MALDI-TOF spectrum is composed of peaks attributed to oligomers of different DP, see Figure 4.17; see Appendix 1.25 for the whole spectrum.

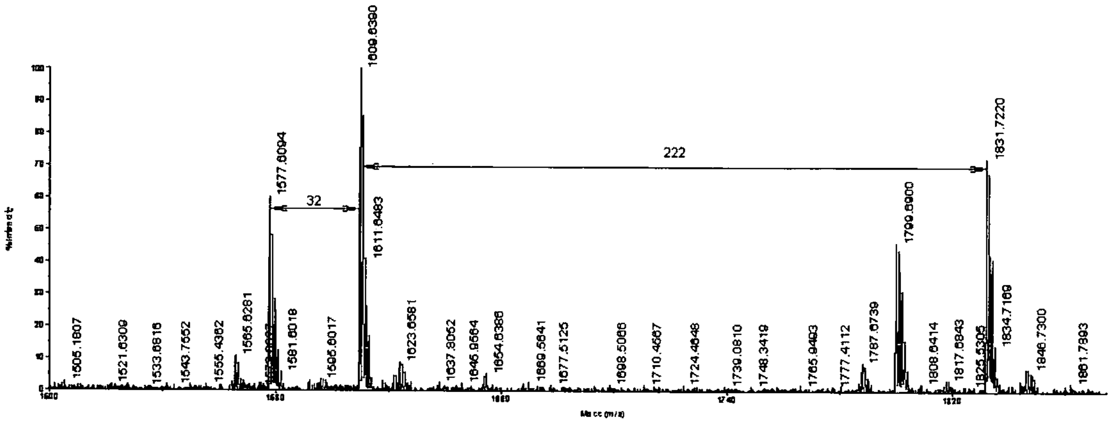


Figure 4.17. An expansion of a representative MALDI-TOF spectrum.

In MALDI-TOF MS cyclised and uncyclised oligomer molecules are detected as series of peaks as a consequence of the instrument's capability to effect isotopic resolution. The number of peaks for each cyclised oligomer was equal to the number of peaks in the corresponding uncyclised oligomer. The intensity of peaks decreased with the molecular weight of the oligomers. In MALDI-TOF MS molecular ions were observed with attached proton $[M+H]^+$ or cation $[M+cation]^+$. The most intense ions in the spectra were observed in the form of $[M+Na]^+$.

In the system under study, the synthesis of n-mer requires n-1 steps, during which n-1 methanol molecules are lost. Hence, masses of the oligomers can be calculated by the formula: $M_N=222xN + 32$, where N is the N-mer number and M_N is the N-mer molecular weight. The observed differences between oligomer peaks were, as expected, 222m/z. In each oligomer region 2 ion series were observed. The difference between the peaks in these two series was 32m/z, which is accounted for by the loss of an extra methanol molecule leading to formation of a cyclised oligomer, for example see Figure 4.7, p. 69. No further methanol molecule losses from oligomer and polymer were observed proving that the M-32 ions are a consequence of cyclisation and not methyl ester hydrolysis.

Analysis of the MS data does not allow the determination of the number of repeat units in a cycle. It was supposed that the oligomers of DP<4 and DP>30, which were not detected, contain proportions of cyclic material similar to those identified in the detected oligomer range. It has been reported that the polydispersities measured by MALDI-TOF MS are usually lower than those derived by SEC.[6,13] Also, the MALDI-TOF technique does not sample the full range of species in a polymer sample, because the higher oligomers are less easily vapourised than the lower ones. For these reasons MALDI-TOF MS was primarily used as a structure probe rather than for measurement of molecular weights.

The difference in mass between peaks corresponding to cyclised and uncyclised material is not large. It was assumed, that all mass fragments had the same response from the mass detector. Only peaks for oligomers of the expected molecular weights were detected in the spectra. Cyclised and uncyclised species had similar chemical structures and molecular weights. Based on these assumptions, the relative amounts of cyclised and uncyclised material were calculated using Equation 4.8 following page:

$$C = A_C/(A_C + A_U) \qquad U = A_U/(A_C + A_U)$$

Equation 4.8. Relative fractions of cyclised and uncyclised material, where C and U are relative fractions of cyclised and uncyclised material respectively, A_C and A_U are areas under peaks corresponding to cyclised and uncyclised material respectively.

In the current work, sets of samples produced under the same conditions of temperature, stirring rate, nitrogen flow and time were analysed by SEC and MALDI-TOF MS to test the reproducibility of the polymerisation and analysis protocol. The average experimental errors (Er.) in M_n, M_w and the fraction of cyclisation (FC) values were calculated as standard deviations, S.D., divided by arithmetic mean, M, see Equation 4.9:

$$Er. = \frac{S.D.}{M} \times 100\% \qquad S.D. = \sqrt{\frac{n\sum_{i=1}^{n} y_i^2 - (\sum_{i=1}^{n} y_i)^2}{n(n-1)}},$$

Equation 4.9. Average experimental error formula, where *Er.* is the average experimental error, *S.D.* is the standard deviation, *n* is the number of points in each series, *i* is the point number in series, y_i is the data value of *i*th point, M is the arithmetic mean.

The amount of cyclised material measured by MALDI-TOF MS was not affected by the measurement conditions, suggesting that cyclisation occurs during polymerisation, not during sample preparation or in the mass spectrometer. Sample fractionation or fragmentation was not significant during the analysis. The FC values determined by this approach varied only by about 5% across the oligomer mass range studied for all samples produced under a variety of conditions, see Figure 4.18 following page.

Each of the uncatalysed reactions 1 to 5, carried out under the conditions defined in Chapter 3, p. 51, was repeated once to study possible sources of error. While the number of repetitions is too low for a proper statistical errors analysis to be valid, the author hoped that this procedure would at least identify the key sources of error. The limited number of repetitions resulted from the restricted quantity of monomer available. In this study a total of two kilograms has been used, which took six to seven months to make and purify, the limiting step being the ethylene oxide addition reaction, carried out under pressure, which is difficult to scale up for safety reasons. Another constraint is the length of time required for these reference uncatalysed reactions; namely two to seven days for each reaction.

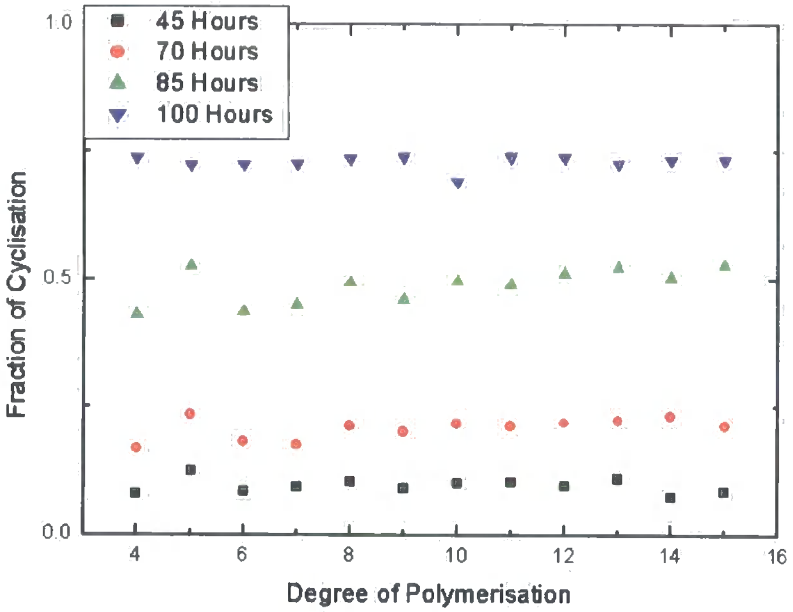


Figure 4.18. Proportion of cyclised oligomer as a function of oligomer mass derived by MALDI-TOF MS analysis.

After a sufficiently good reproducibility was achieved it was intended that the effects of catalysts could be studied with a greater degree of confidence. The M_n and M_w values obtained from the Viscotek TriSEC data system are summarised in Tables 4.1-4.3, p. 81-82, the tables record values of M_n and M_w for samples removed from the polymerising melt as a function of time. The FC values were calculated by Equation 4.8, based on data from MALDI-TOF MS. All data were calculated using the pentamer to pentadecamer oligomers (m/z ratio 1100-3600). Tables 4.4 and 4.5, p. 82-83, record FC values for samples removed from the polymerising melt as a function of time. The samples were quenched by cooling and the whole sample was analysed, blanks in the table correspond to points where samples were not taken, e.g. during the night. The errors between duplicate measurements of M_n, M_w and FC, recorded in Table 4.6, p. 83, as a function of reaction conditions.

Time, Hours	Reaction 1(a)		Reaction 1(b)		Reaction 2(a)		Reaction 2(b)	
	M_n	M_w	M_n	M_w	M_n	M_w	M_n	M_w
0	0	0	0	0	0	0	0	0
5	3930	4410						
10	5680	7360						
15			2200	4210	15600	18800	5600	8830
20			4700	5700	11300	16000	10600	16300
25			3270	4920	12000	19200	12300	23200
30	11700	18100						
35	9110	14800						
40			18600	19500	25900	64200	31500	120600
45			9990	12200	22400	114800	25200	300500
50	15600	26500	8200	11900	34600	178400	38600	506700
55	13700	27600						
60	21200	37000						
65			19200	21600	28600	220300		
70	24000	44900	3570	16800	32400	492300	91700	907400
75	22500	45600	14700	23000	40400	559900	90000	1405000
80	18100	51700						
85	25900	66500						
90			1910	28900	59700	1.319E6	105400	3593000
95	45400	195300	13500	27400				
100	57600	421300						
115	110600	353800	20300	52400				
120	113400	302200	23100	57600				

Table 4.1. M_n and M_w values for reactions 1 and 2, where a and b represent duplicate reactions.

Time, Hours	Reaction 3(a)		Reaction 3(b)	
	M_n	M_w	M_n	M_w
0	0	0	0	0
20	4390	5620	4980	8230
30	6100	7680	5390	10600
40	6030	8220	3590	13300
50	7770	10300	6630	19000
65	8700	12100	5420	34200
70	8230	12700	10100	44800
75	8220	13000	8060	54100
90	10300	16100	10600	93900
95	13100	17700	12800	104200
100	12400	18300	16400	120200
115	13100	22700	36600	319100
120	13800	23800		
125			33900	372300
135	17200	30600	38300	564400
140			36400	665000
145	21100	34300		
160	18000	38700	37900	1692000
165	21600	41000	41500	2034000
170	20800	42800	52400	1834000

Table 4.2. M_n and M_w values for reaction 3, where a and b represent duplicate reactions.

Time, Hours	Reaction 4(a)		Reaction 4(b)		Reaction 5(a)		Reaction 5(b)	
	M_n	M_w	M_n	M_w	M_n	M_w	M_n	M_w
0	0	0	0	0	0	0	0	0
4	6760	11600	13300	31800	7140	12500	8340	13600
8	18400	29100	26900	96700	11500	17400	11100	19700
12					13000	25400	15400	33700
16	31600	111900	72500	123400				
20	40500	553100	65700	78000	24900	59100	30000	107600
24					35600	113500	41100	474300
28					49500	470100	80100	1019000
32					69500	3448000	50600	96900

Table 4.3. M_n and M_w values for reactions 4 and 5, where a and b represent duplicate reactions.

Time, Hours	Reaction 1(a)	Reaction 1(b)	Reaction 2(a)	Reaction 2(b)	Reaction 3(a)	Reaction 3(b)
0	0	0	0	0	0	0
15	0.09		0.22	0.18	0.15	
20	0.13		0.22	0.18	0.22	0.28
25	0.16		0.30	0.22	0.23	0.28
30					0.24	0.35
40	0.21	0.28	0.36	0.26	0.31	0.40
45	0.21		0.65	0.46	0.37	0.41
50	0.25	0.36	0.76	0.55	0.37	0.44
55		0.38	0.82	0.63		
65	0.28				0.53	0.53
70	0.29	0.43	0.92	0.68	0.61	0.55
75	0.31	0.45	0.90	0.78	0.67	0.58
80		0.49	0.93	0.78		
85		0.49				
90	0.37				0.79	0.63
95	0.40	0.66	0.96	0.93	0.89	
100		0.72	0.96	0.92	0.85	0.69
110			0.97			
115	0.47	0.85	0.96	0.94	0.91	0.79
120	0.49	0.88	0.91	0.92	0.94	0.81
125	0.51		0.97	0.93	0.91	
135			0.98		0.95	0.85
140	0.61		0.98	0.90	0.91	
145	0.61		0.96	0.95	0.91	0.87
160	0.75		0.93		0.93	0.87
165	0.79				0.93	0.89
170					0.93	0.87
185						0.86
190						0.87
195						0.87

Table 4.4. FC values as a function of time for reactions 1-3, where a and b represent duplicate reactions.

Time, Hours	Reaction 4(a)	Reaction 4(b)	Reaction 5(a)	Reaction 5(b)
0	0	0	0	0
4	0.61	0.42	0.35	0.37
8	0.91	0.83	0.42	0.45
12			0.53	0.51
16	0.97	0.95		
20	0.91	0.90	0.69	0.65
24		0.91	0.87	0.79
28			0.97	0.85
32			0.91	0.88
36				0.91

Table 4.5. FC values as a function of time for reactions 4 and 5, where a and b represent duplicate reactions.

Reaction	Temperature, °C	Stirring, r/min	Monomer Amount, g	N_2, b/min	Er. M_n, %	Er. M_w, %	Er. FC, %
1	200	100	20	--	80.4	78.7	31.1
2	200	100	20	160	29.3	45.3	17.4
3	200	50	20	--	27.6	87.3	12.2
4	240	100	5	--	40.4	63.8	11.5
5	240	100	20	--	14.9	36.7	4.5

Table 4.6. Reaction conditions and average experimental error values for M_n, M_w and FC determined by SEC and MALDI-TOF MS for reactions 1-5.

It follows from the data presented in Table 4.6, that introducing a nitrogen gas flow improves the reproducibility of the reaction (*cf.* Reactions 1 and 2), possibly as a result of efficient venting of methanol. It appears that, high temperature is not sufficient to drive the methanol out of the reaction vessel and consequently the nitrogen sweep is necessary because methanol may promote the reverse reaction and shift the equilibrium of the process in favour of starting materials. The reaction is endothermic, it was observed that high temperatures (*cf.* Reactions 1 and 4,5) increase the reaction rate and the reproducibility of the polymerisation. A lower stirring rate (*cf.* Reactions 1 and 3) appeared to lower the average experimental error values, possibly the mixture was stirred more thoroughly, although the effect on M_w is not consistent with the effects on M_n and FC. Increased monomer batch size (*cf.* Reactions 4 and 5) appeared to improve the reproducibility, the smaller monomer batch engages only half of the surface area of the helical stirrer and when the full area is employed the stirring may be more efficient and temperature distribution in the polymer mixture may be more even. All the variable reaction conditions appear to have an influence on the reproducibility of the reaction but, from this brief survey, higher temperature appears to be the most important parameter. At higher temperatures it was anticipated that the viscosity of a catalysed reaction would increase rapidly during a short period of time, and that there would be insufficient time to collect samples so as to make an objective comparison between reactions. Probably by gaining a better control over the temperature of the reaction, a better reproducibility would be achieved.

Generally high average experimental errors for both M_n and M_w values, reported in Table 4.6, may be attributed to poor control over the reaction conditions, temperature in particular, and to limitations in the analysis technique, see section 4.1, p.64.

The number average and the weight average molecular weight values obtained from experiments 1 to 5 are plotted against the polymerisation time in Figures 4.19 to 4.22. Generally, M_n and M_w values increase with the polymerisation time. The former increases more slowly than the latter and eventually reaches a plateau, leading to broad MWD, $P_d>10$, at later stages of the polymerisation, which is consistent with previous studies and predictions of Flory.[3,30] The degree of cyclisation values for all reactions increase steadily until all polymer species are fully cyclised. This trend in the average cyclic content in a polymer sample is consistent with previous studies. Parker achieved full cyclisation after 40 hours of uncatalysed polymerisation at the temperature of 240°C.[30] Dušek showed that theoretically at high conversions, the fraction of cyclic molecules converges to 100%.[40]

It was found that nitrogen gas flow increases the rate of growth in molecular weights and in FC, see Figure 4.19 following page. It is probable that venting the by-product of the reaction, methanol, promotes polymer formation and side reactions such as cyclisation, because elimination of one of the products of a reaction shifts the equilibrium of the process in favour of products, according to Le Chatelier's principle.

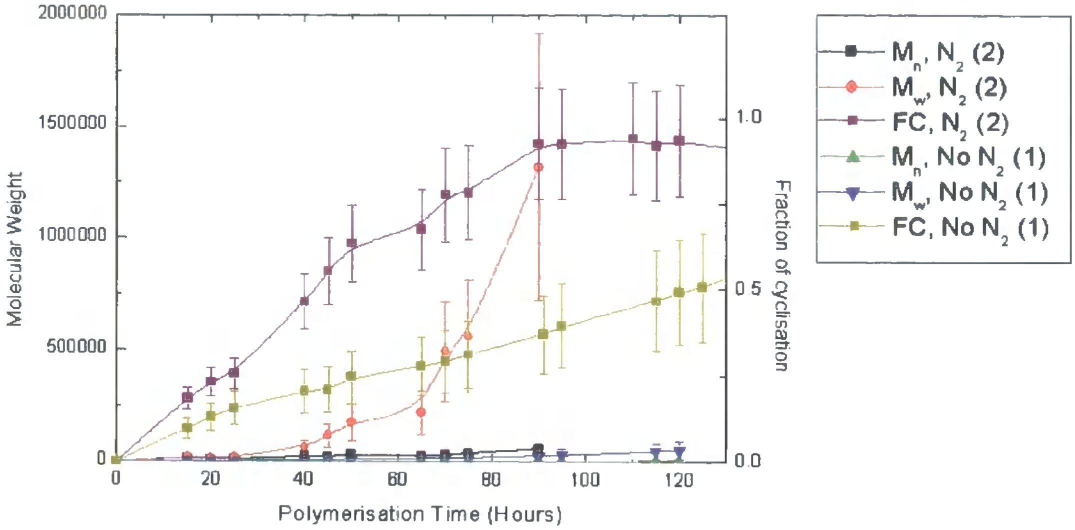


Figure 4.19. Influence of nitrogen gas flow rate on the rate of increase in molecular weight and in FC, comparison of reactions 2 and 1.

Higher stirring rate increases the rate of growth in molecular weight, probably because stirring facilitates the polymerisation by increasing efficiency of mixing, see Figure 4.20. The behaviour in the detected FC was unexpected, since the fraction of cyclisation was anticipated to develop slowly under low stirring rate similarly to molecular weights. Possibly the lower stirring rate decreases the probability of interaction between reacting species and favours the intramolecular cyclisation reaction, the differences are small but consistent in relative magnitude.

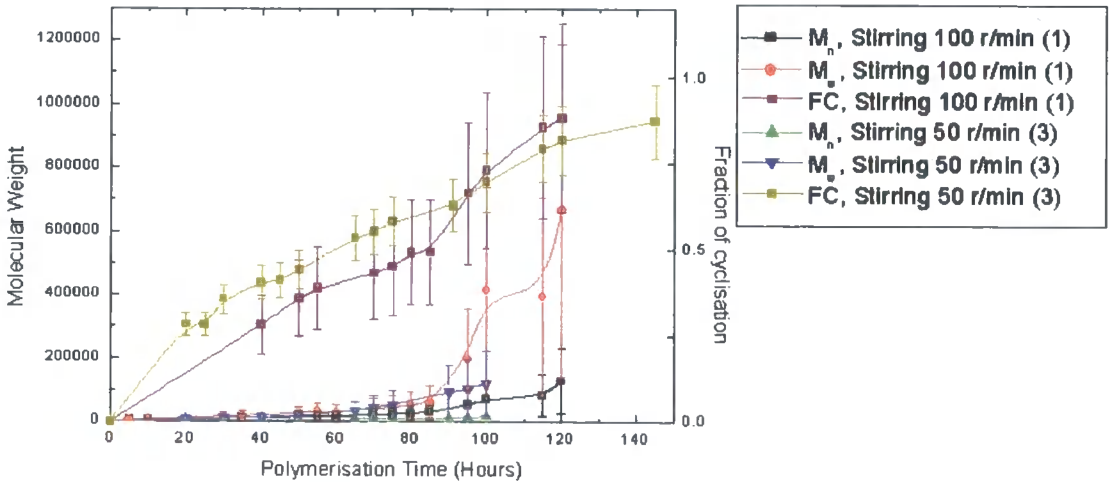


Figure 4.20. Influence of stirring rate on the rate of increase in molecular weight and in FC, comparison of reactions 1 and 3.

It is observed that higher temperature increases the rate of increase in molecular weight and in cyclisation, which is consistent with the polymerisation being an endothermic process, higher temperatures increasing both the rate of polymerisation and of side reactions such as cyclisation, see Figure 4.21:

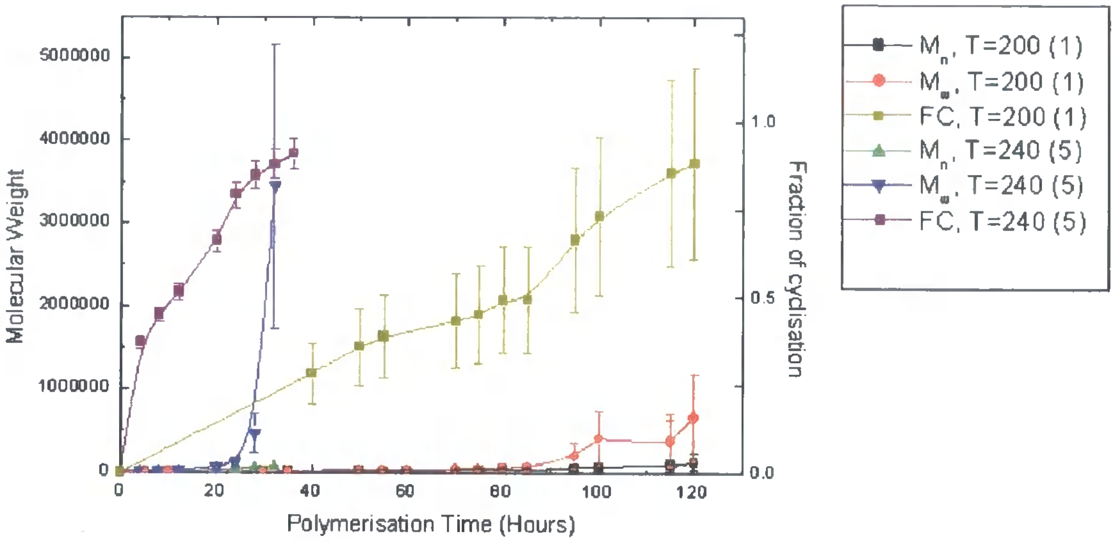


Figure 4.21. Influence of temperature on the rate of increase in molecular weight and in FC, comparison of reactions 1 and 5.

The reaction at 240°C stopped after 35 hours when the stirrer was blocked; at this stage the M_W value had reached 3.5×10^6, whereas for a reaction at 200°C an M_W value of about 4×10^5 was observed.

Polymerisation batch size effects suggest that a smaller batch resulted in a more rapid increase in molecular weight, this is possibly due to a different distribution of temperatures in different sized batches, see Figure 4.22:

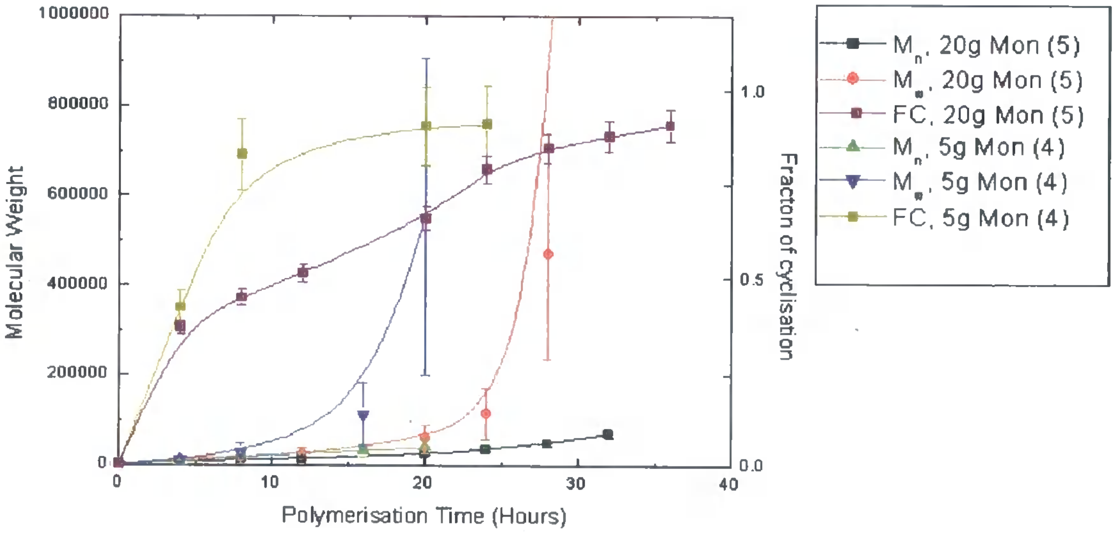


Figure 4.22. Influence of monomer batch size on the rate of increase in molecular weight and in FC, comparison of reactions 5 and 4.

Probably, the temperature of the polymer mixture during reaction 4, when 5g of monomer was used, was higher compared to the reaction 5, when 20g of monomer was used.

At this stage of the optimisation process the following polymerisation conditions were chosen, based on observations of behaviour of the molecular weight growth and average experimental errors. Nitrogen gas flow, 160b/min, and higher monomer amount, 20g, were chosen because these parameters decrease average experimental errors. A higher stirring rate was chosen, because at low stirring rate the M_n and M_w values grow very slowly, the M_w values for the reaction 3 with the stirring rate of 50r/min are several times lower than those for the reaction 1 with the stirring rate of 100r/min. Average experimental error was quite low for reaction 5 with the temperature of the reaction 240°C, but in this case molecular weights and viscosity of the reaction increased quickly and the reaction could be run only for 35 hours. A catalyst would increase the speed of the polymerisation and low viscosities will be maintained only during a short period of time insufficient for an objective study of the catalysis. It was decided to attempt to gain a better control over the temperature of the reaction by increasing the thermal mass of the oil bath, which also allowed the insertion of two polymerisation reactors into the same oil bath. By changing the stirring of the oil bath from a magnetic stirrer to a more efficient overhead paddle stirrer, it was hoped that any deviations from the set temperature would be smoothed and that both polymerisation reactors would always be at the same temperature.

In the next set of experiments, the monomer was polymerised on a 20g scale, at the stirring rate of 100r/min in the polymerisation reactor of type 1 at a temperature of 200°C. The nitrogen flow rate, sweeping over the top of the polymer melt was 160b/min. Two polymerisation reactors of the same design were used in the same oil bath at the same time. The oil in the oil bath was stirred by an overhead stirrer at a constant speed of 80r/min. Table 4.7 records the M_n, M_w and FC values of polymers produced in reactions 6(a) and 6(b).

Time,	Reaction 6(a) Uncatalysed		Reaction 6(b) Uncatalysed		Reaction 6(a) Uncatalysed	Reaction 6(b) Uncatalysed
Hours	M_n	M_w	M_n	M_w	FC	FC
0	0	0	0	0	0	
20	4050	6540	4050	5510	0.17	0.11
25	5350	8630	4370	5440	0.2	0.09
30	5870	10700	4810	6710	0.24	0.14
45	10300	29500	8240	17600	0.48	0.35
50	13300	33500	8410	21200	0.54	0.39
55	12600	42600	8860	21100	0.61	0.39
70	19300	184900	8500	21500	0.85	0.42
75	22100	215900	10500	26500	0.88	0.44
80	25300	268500	16800	81800	0.84	0.63
95	27200	407600	8880	121400	0.88	0.91
100	30600	375000	24100	267100	0.92	0.91
105	36700	567300	22400	314500	0.92	0.89
120	53400	628600	26200	379300	0.95	0.88
125	54300	1035000	28600	321200	0.95	0.87
140	73700	1127000	42500	692600	0.96	0.87
145	79500	1660000	48000	694200	0.95	0.93
150	63900	4244000	45300	1039000		0.93
165	55800	3809000	31200	1224000		0.93
170			71500	1531000		

Table 4.7. M_n, M_w and FC values for reaction 6, where a and b represent duplicate reactions, see script for comments.

The bigger oil bath and choice of reaction conditions resulted in a decrease in the average experimental errors from 80.4% for M_n, 78.7% for M_w and 31.1% for the proportion of cyclic species, see Table 4.7, to 31.8% for M_n, 55.0% for M_w and to 21.1% for the proportion of cyclic species, respectively. This effect is probably due to better control over the temperature of reaction and stirring and to selection of a defined reaction protocol. The reproducibility, although not good enough for meaningful kinetic investigations, was considered sufficiently good at this stage for a qualitative study and therefore it was decided to use this reaction protocol to study the effect of catalysts. It was thought that the conditions defined above would provide optimal time to perform the polymerisation, both without and with a catalyst, and that the viscosities of the reaction mixture would be low enough for long enough to allow collection of a sufficient number of samples to construct a reaction profile.

4.4.2 SEC and MALDI-TOF analysis of poly(dimethyl 5-(2-hydroxyethoxy)isophthalate) for catalysed polymerisations

In this section the author discusses and compares effects of various catalysts on the polymerisation.

Commercially available catalysts, namely $Mn(OAc)_2$, Sb_2O_3, $Mn(OAc)_2/Sb_2O_3$, $Co(OAc)_2$, $Bu_2Sn(OAc)_2$, and $Ti(OBu)_4$ were applied to the polymerisation in concentrations of 1% molar with respect to monomer, this being selected for simplification of calculations, weighing and ease of comparison between catalysts. Catalyst Vertec 400AC was applied to the polymerisation in a concentration of 0.1% molar due to its high activity. All reactions were run until significant increases in viscosity were observed visually. It was supposed that this amount of time would allow collection of a sufficient number of samples to construct reaction profiles and to study the effects of catalysis. Tables 4.8-4.11, p. 89-91, record the M_n, M_w and FC values for samples removed from the polymerising melts as a function of time.

Time, Hours	Reaction 7 $Mn(OAc)_2$ 1%		Reaction 8 Sb_2O_3 1%		Reaction 9 $Mn(OAc)_2$:Sb_2O_3 0.5%:0.5%	
	M_n	M_w	M_n	M_w	M_n	M_w
0	0	0	0	0	0	0
1					9040	12100
2	7030	12700	1770	1940	13000	16700
3					10200	17700
4	5730	45500	5240	8490	8900	12100
5					11300	19300
6	6690	236200	6750	11700		
8	11100	372000	6990	14800		
10	14200	500300	8220	28700	14900	29200
12	10300	467900	12200	72700		
14			12700	121100		
15					26800	76800
24			30000	192000		
25					23400	132500
26			24700	209900		
28			23400	249500		
30			29500	283900	40100	197100
32			14200	307100		
34			19800	335400		
36			31500	387400		
45					108100	755600
50					72400	1887000
55					108100	2499000
70					56100	4378000

Table 4.8. M_n and M_w values for reactions 7-9, see script for comments.

Time, Hours	Reaction 10 $Co(OAc)_2$ 1%		Reaction 11 $Bu_2Sn(OAc)_2$ 1%		Reaction 12 Vertec400AC 0.1%		Reaction 13 $Ti(OBu)_4$ 1%	
	M_n	M_w	M_n	M_w	M_n	M_w	M_n	M_w
0	0	0	0	0	0	0	0	0
1	4920	6610	7660	13600	4300	6550	6460	10400
2	6260	9470	7180	13700	5660	21100	7400	12000
3	7590	12900	9420	19000	6700	26400	7000	13700
4	8650	17800	12400	32900	8570	32900	11000	20700
5	12300	33700	16500	69200	5550	69600	10200	35200
6	12600	56000	23800	138600			12500	61200
7	16000	91400	34800	180600			14700	93600
8	21800	159200	33900	214900			14900	109200
9	33000	162100	40300	212000			12400	113200
10	78900	264300	28000	228000			12500	120200
11	135500	354800	26500	152000			10600	127700
12			35000	251300				
13			40800	256800				
14			40100	260700				

Table 4.9. M_n and M_w values for reactions 10-13, see script for comments.

Time, Hours	Reaction 7 $Mn(OAc)_2$ 1%	Reaction 8 Sb_2O_3 1%	Reaction 9 $Mn(OAc)_2$: Sb_2O_3 0.5%:0.5%	Reaction 10 $Co(OAc)_2$ 1%
0	0	0	0	0
1			0.22	0.16
2	0.25	0.03	0.22	0.22
3			0.23	0.27
4	0.58	0.17	0.25	0.32
5			0.25	0.47
6	0.85	0.22		0.55
7				0.60
8	0.92	0.27		0.65
9				0.66
10	0.97	0.45	0.41	0.68
11				0.72
12	0.95	0.69		
14		0.87		
20			0.72	
25		0.92	0.83	
30			0.81	
45			0.93	
50			0.95	

Table 4.10. FC values for reactions 7-10, see script for comments.

Time, Hours	Reaction 11 $Bu_2Sn(OAc)_2$ 1%	Reaction 12 Vertec 400AC 0.1%	Reaction 13 $Ti(OBu)_4$ 1%
0	0	0	0
1	0.24	0.09	0.18
2	0.26	0.21	0.23
3	0.31	0.21	0.23
4	0.45	0.24	0.31
5	0.69	0.30	0.45
6	0.89		0.62
7	0.97		0.75
8	0.99		0.77
9	0.95		0.79
10			0.80
11			0.81

Table 4.11. FC values for reactions 10-13, see script for comments.

The M_n, M_w and FC values for the reactions 7 to 13 are plotted against time of polymerisation in Figures 4.23, 4.24 and 4.26 to 4.29. The M_n and FC values steadily increase reaching a limit at approximately the same time, whereas M_w values continue to increase as was seen for the uncatalysed reactions 1 to 5.

In this study catalysts showed significant influence on the rate of increase in molecular weights. Higher molecular weights and FC values obtained using the least effective catalyst, namely an equimolar mixture of $Mn(OAc)_2$ and Sb_2O_3, were achieved significantly faster than in uncatalysed reactions, see Figure 4.23:

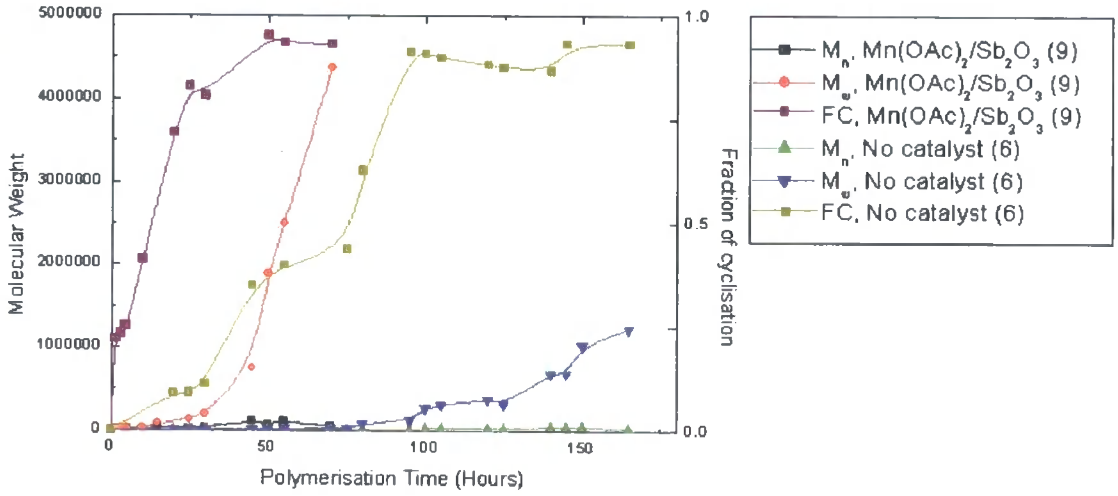


Figure 4.23. Influence of the catalyst $Mn(OAc)_2/Sb_2O_3$ on the rate of increase in molecular weight and in FC, comparison of reactions 9 and 6(a).

M_n values for polymers produced in reaction 6(a) slowly increase and reach a limit at M_n~60,000 after 120 hours of polymerisation, due to complete cyclisation, which is shown by a plateau in the FC achieved at approximately the same time, see Table 4.7, p.89, for M_n, M_w and FC values for reaction 6(a). This means that all A groups, hydroxyls in this case, are consumed at this point and the number of polymer molecules remains unaltered until completion of reaction, see section 4.3, p.69, for a more detailed explanation. After 120 hours of polymerisation M_w values for polymers produced in reaction 6(a) continue to increase steadily, due to ester-ester interchange reactions, with the maximum of M_w~3.9×10^6, which results in a broadening of MWD, P_d increases from 12 to 68 in the period between 120 and 165 hours of polymerisation. The high molecular weights obtained with these polymers, and the consequent increase in viscosity of the molten polymer mixture resulted in blocking of the stirrer. Molecular weight and FC values for polymers produced in reaction 9 catalysed by an equimolar mixture of $Mn(OAc)_2$ and Sb_2O_3, increase faster than in uncatalysed reaction 6(a). M_n values for polymers produced in reaction 9 reach a plateau at a higher value than in reaction 6(a), namely at M_n~90,000 after 45 hours of polymerisation, see Tables 4.8 and 4.10, for M_n, M_w and FC values. M_w values for polymers produced in reaction 9 continue to increase reaching a maximum at M_w~4.4×10^6, leading to an increase in P_d from 7 to 78 in the period between 45 and 70 hours of polymerisation.

The molecular weights and the FC values for polymers produced in reaction 8, catalysed by Sb_2O_3 increased with a similar but slightly higher rate than in reaction 9, catalysed by an equimolar mixture of $Mn(OAc)_2$ and Sb_2O_3, see Figure 4.24 following page. The molecular weights and the FC values for polymers produced in reactions 8 and 9, catalysed by Sb_2O_3 and by an equimolar mixture of $Mn(OAc)_2$ and Sb_2O_3 respectively, steadily increase with similar rates. Generally, both molecular weights and FC values increase quite slowly compared to other catalysts used in this study, which may be a result of a low catalytic activity of Sb_2O_3. In reaction 8, catalysed by Sb_2O_3 alone, complete cyclisation was achieved after 24 hours of polymerisation, which resulted in a plateau in M_n at ca. 25,000, whereas in reaction 9, the complete cyclisation and a plateau in M_n were achieved after 45 hours of polymerisation. P_d values for polymers produced in reaction 8, increased from 6 to 21 in the period between 24 and 36 hours of polymerisation, see Tables 4.8 and 4.10, for M_n, M_w and FC values.

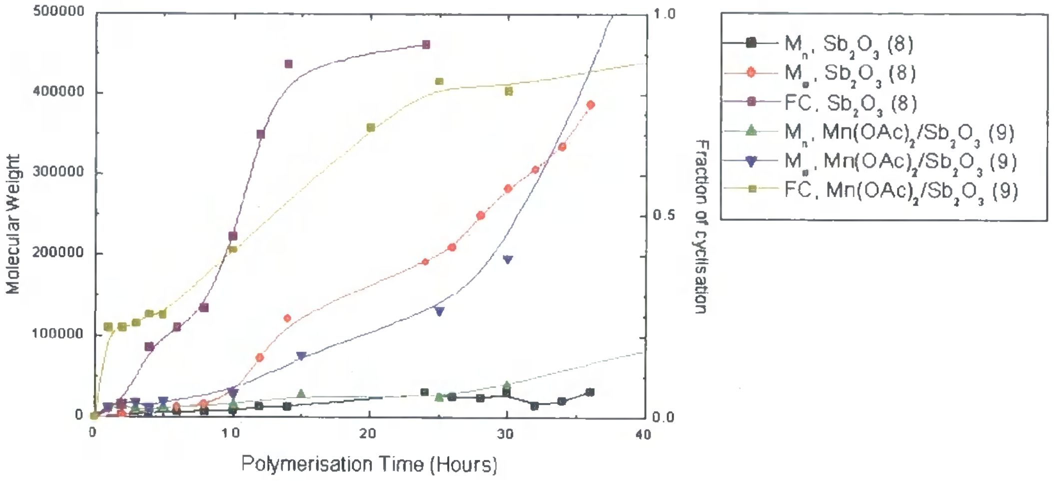


Figure 4.24. Influence of the catalysts Sb_2O_3 and $Mn(OAc)_2/Sb_2O_3$ on the rate of increase in molecular weight and in FC, comparison of reactions 8 and 9.

Sb_2O_3 is a common component of catalysts used in the synthesis of polyesters, poly(ethylene terephthalate) (PET) for example.[36] In industry PET is usually prepared from dimethyl terephthalate and ethylene glycol. The reaction proceeds in two steps, first step being the reaction between dimethyl terephthalate and ethylene glycol, eliminating methanol to give mainly bis-hydroxyethyl terephthalate and higher oligomers, see Figure 4.25, Reaction 1:

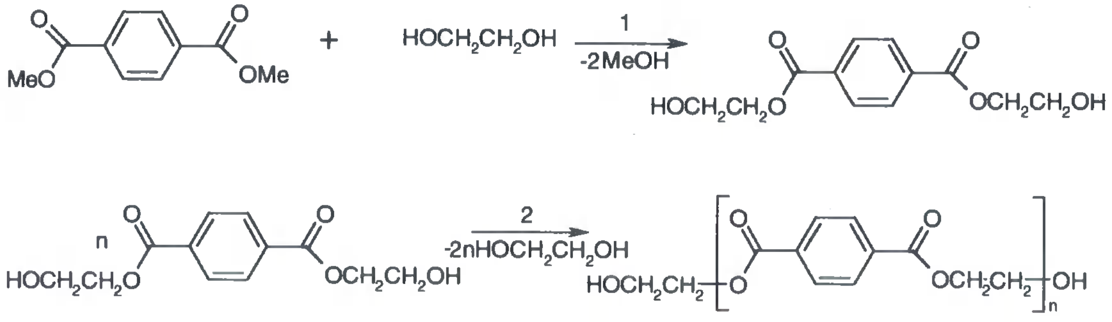


Figure 4.25. Scheme of synthesis of poly(ethylene terephthalate) from dimethyl terephthalate and ethylene glycol.

During the second step glycolic esters are polymerised via a condensation reaction with elimination of ethylene glycol, forming the resulting PET, see Figure 4.25, Reaction 2. Typical examples of catalysts for the first step of the reaction are zinc, calcium, magnesium, manganese and cobalt acetates. The second step is usually catalysed by antimony and germanium oxides. The activity of antimony oxide is reported to be dependent on the concentration of hydroxyl groups, the efficiency of the catalyst increasing with decrease in the concentration of hydroxyl groups. Ethylene glycol formed during the polymerisation of glycolic esters is eliminated from the reaction medium due to the high temperature and reduced pressure used for the reaction and hence as the degree of polymerisation increases, so does the activity of antimony oxide. The results reported on the previous page are consistent with this view.

By contrast, in polyesterifications titanium alkoxides and alkanoates are found to be very effective for both stages of the reaction, but are not widely used due to the yellow colour of the resulting polymers. The polycondensation of dimethyl 5-(2-hydroxyethoxy)isophthalate can be regarded as analogous to the first stage of the synthesis of PET. If this is true, catalysts such as manganese, cobalt acetates and titanium tetrabutoxide would be expected to be superior to antimony oxides in the polycondensation reaction, since they promote the methanol elimination reaction. In this study $Ti(OBu)_4$ appeared to be a more active catalyst than Sb_2O_3, during first 11 hours of polymerisation, which appears to be consistent with the view of its influence on PET synthesis, see Figure 4.26.

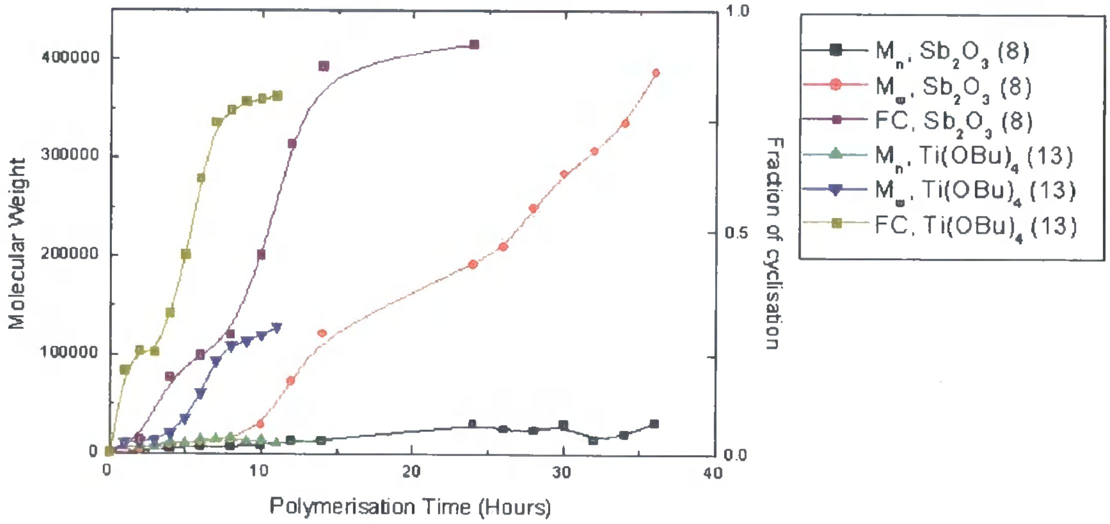


Figure 4.26. Influence of the catalysts Sb_2O_3 and $Ti(OBu)_4$ on the rate of increase in molecular weight and in FC, comparison of reactions 8 and 13.

In reaction 13, catalysed by $Ti(OBu)_4$, the maximum value of M_w was 130,000, which occurred after 11 hours (reactions continued past this time gave insoluble products). In contrast the M_w values obtained from reaction 8 continued to increase steadily, finally reaching M_w~390,000, see Table 4.9, for M_n and M_w values. Complete cyclisation in reaction 13 was achieved after 6 hours of polymerisation, see Table 4.11, and resulted in a plateau in M_n at about M_n~15,000 and in a broadening of the MWD, P_d values increased from 3.5 to 12 in the period from 6 to 11 hours.

In the present study $Bu_2Sn(OAc)_2$ was found to be slightly more active than $Ti(OBu)_4$, resulting in faster cyclisation and build up in molecular weights, see Figure 4.27:

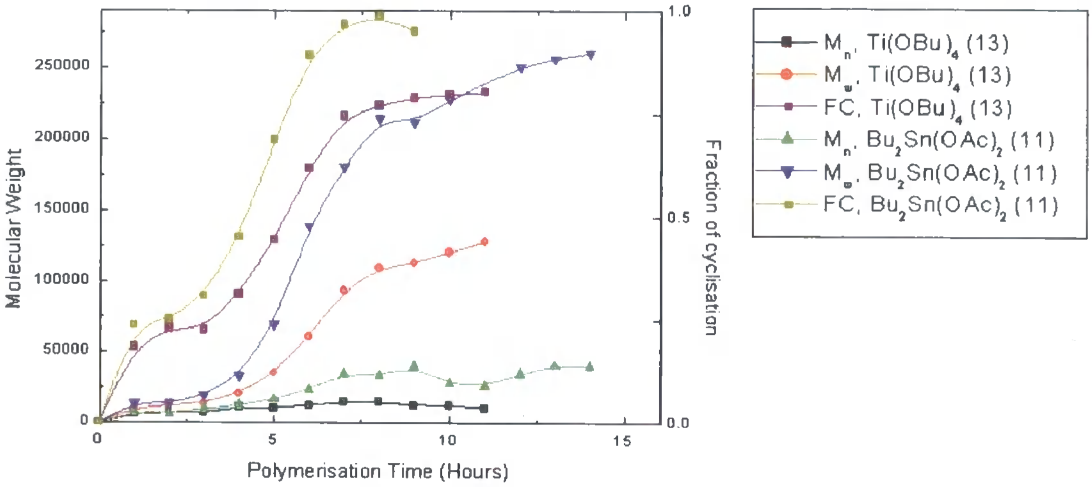


Figure 4.27. Influence of the catalysts $Ti(OBu)_4$ and $Bu_2Sn(OAc)_2$ on the rate of increase in molecular weight and in FC, comparison of reactions 13 and 11.

Although at first sight this was regarded as surprising, similar results have been reported by Hawker *et al.* They observed higher molecular weights for poly(methyl 4,4-bis(4'-hydroxyphenyl)pentanoate)s obtained in reactions catalysed by $Bu_2Sn(OAc)_2$ than in reaction catalysed by $Ti(OBu)_4$.[34(a)] Molecular weights for polymers produced in reaction 11, catalysed by $Bu_2Sn(OAc)_2$, increased faster than in reaction 13, catalysed by $Ti(OBu)_4$.

Thus, the plateau in M_n values in reaction 11 was reached at M_n~35,000 after 7 hours of polymerisation, whereas in the $Ti(OBu)_4$ catalysed reaction, the M_n plateau occurred at 6 hours at ca. 15,000. M_w values for polymers produced in reaction 13, catalysed by $Ti(OBu)_4$, continued to increase after 7 hours of polymerisation but at a slower rate than at the beginning of the reaction suggesting that this catalyst was less effective in transesterification. Consistent with this hypothesis, broadening in the MWD was not observed and P_d values remained around 6 to 7, until the end of the reaction, see Table 4.9, for M_n and M_w values.

It was observed that initially molecular weights for polymers produced in reaction 11, catalysed by $Bu_2Sn(OAc)_2$, increased faster than those in reaction 10, catalysed by $Co(OAc)_2$, but eventually after 11 hours of polymerisation higher M_w values were achieved in reaction 10, see Figure 4.28:

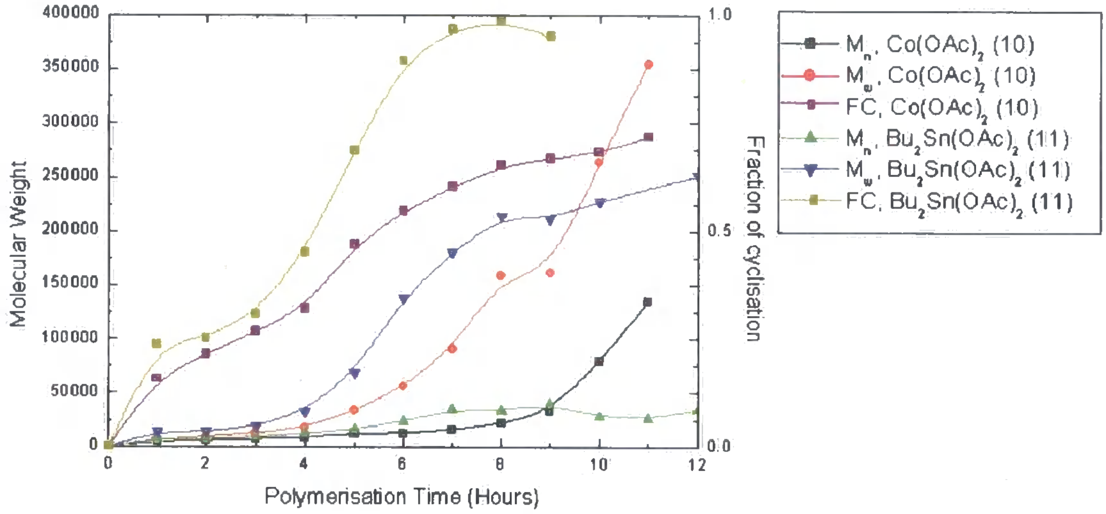


Figure 4.28. Influence of the catalysts $Co(OAc)_2$ and $Bu_2Sn(OAc)_2$ on the rate of increase in molecular weight and in FC, comparison of reactions 10 and 11.

Similarly in agreement with the current observation, Hawker *et al.* showed that molecular weights of poly(methyl 4,4-bis(4'-hydroxyphenyl)pentanoate)s, poly(propyl 4,4-bis(4'-hydroxyphenyl) pentanoate)s and poly(phenyl 4,4-bis(4'-hydroxyphenyl)pentanoate)s produced in reactions catalysed by $Co(OAc)_2$ were a factor of two higher than those produced in reactions catalysed by $Bu_2Sn(OAc)_2$.[34(a)] Complete cyclisation in reaction 10, catalysed by $Co(OAc)_2$, was not achieved and therefore a plateau value for M_n was not reached, consequently broad MWD were not observed, P_d values remained in the range of P_d=2-8 during the whole reaction, see Tables 4.9 and 4.10, for M_n, M_w and FC values.

Slow development in M_w values for polymers produced in reaction 11, catalysed by $Bu_2Sn(OAc)_2$, may be due to the fact that the rate of the ester-ester interchange reaction under these conditions, was much lower than in reaction 10, catalysed by $Co(OAc)_2$. The low P_d values for polymers produced in reaction 11 are consistent with a low rate of ester-ester interchange, whereas low P_d values for polymers produced in reaction 10, may be consequent upon a high rate of polycondensation coupled with incomplete cyclisation.

In the comparison of the effects of the cobalt and manganese acetates, it was found that the M_w values for polymers produced in reaction 7, catalysed by $Mn(OAc)_2$, increased faster than in reaction 10, catalysed by $Co(OAc)_2$, see Figure 4.29:

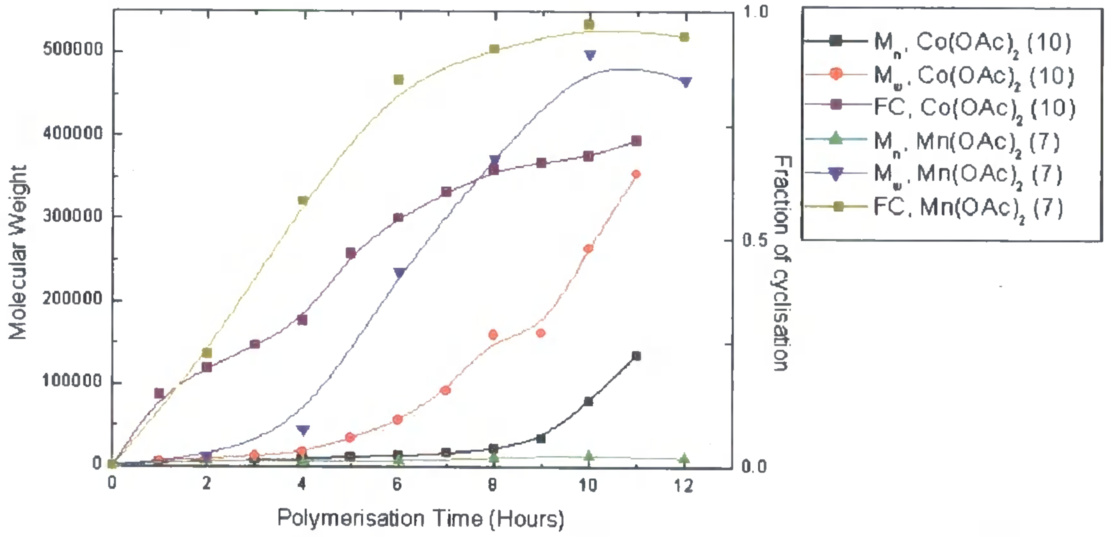


Figure 4.29. Influence of the catalysts $Co(OAc)_2$ and $Mn(OAc)_2$ on the rate of increase in molecular weight and in FC, comparison of reactions 10 and 7.

The M_n and FC values for polymers produced in reaction 7 reached a plateau after 6 hours of polymerisation at a value of M_n~10,000, the P_d in this reaction reached 45 in the period between 6 and 12 hours; whereas in reaction 10 a plateau in M_n was not reached after 11 hours when the value of M_n had reached 136,000, see Tables 4.8 to 4.11 for M_n, M_w and FC values. The M_w values for polymers produced in both reactions increase in a similar manner, with no retardations, possibly these catalysts have similar influences on rates of polycondensation and ester-ester interchange reactions.

In a study of the highly reactive polyesterification catalyst, Vertec 400AC, it was established that at a 1% molar loading the polymerisation was too fast to collect samples, so studies of that catalyst were conducted at a concentration of 0.1% molar. The catalyst Vertec 400AC at 0.1% molar loading was found to have a similar influence on the increase in weight average molecular weight as that found for $Bu_2Sn(OAc)_2$ at 1% molar loading, see Figure 4.30:

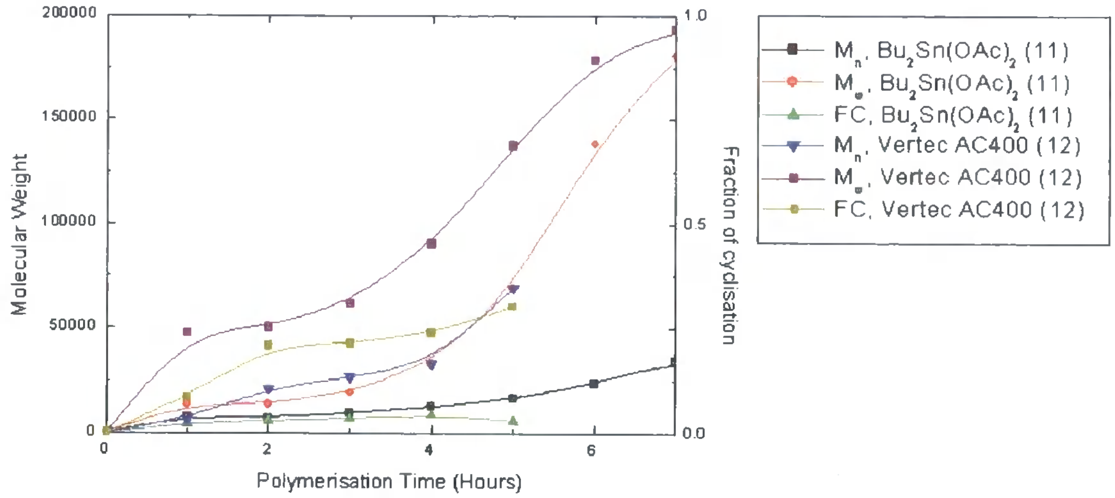


Figure 4.30. Influence of the catalysts $Bu_2Sn(OAc)_2$ and Vertec 400AC on the rate of increase in molecular weight and in FC, comparison of reactions 11 and 12.

The FC values for polymers produced in reaction 11, catalysed by $Bu_2Sn(OAc)_2$, increased faster than in reaction 12, catalysed by Vertec 400AC, whereas molecular weight values of polymers produced in both reactions increased with very similar rates, see Table 4.9, for M_n and M_w values. Curiously the reaction catalysed by the Vertec 400AC appears to be reaching a plateau value in FC at ca. 0.25 to 0.30, at the 5-hour stage when M_w had reached ca. 70,000 and by 6 hours of reaction the product had become insoluble, whereas the material produced using $Bu_2Sn(OAc)_2$ continued to increase in molecular weight and remained soluble up to M_w of ca. 250,000 obtained after 14 hours of reaction. Reaction 12 was stopped after 6 hours due to formation of powder in the reactor. The product was not soluble in any of several common organic solvents, which made it impossible to analyse, but this observation suggests that Vertec 400AC is very different in its action to any of the other catalysts examined and has to be excluded from this set of comparisons.

In summary, the rate of increase in weight average molecular weight is dependent on the catalyst used in the qualitative order shown below:

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

The rate of the cyclisation reaction is dependent on the catalyst used in the qualitative order shown below:

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

The influence of catalysts on weight average molecular weight increase and cyclisation were more or less in the same order, apart from the observation that $Co(OAc)_2$ appears to be marginally worse at cyclisation than at weight average molecular weight increase. However, it has to be noted that the effects are relatively small and the errors in measurement relatively large so we have to be cautious about drawing conclusions from these observations.

It was expected that catalysts would influence both rate of increase in weight average molecular weight and the FC in a similar manner and this appears to be justified in a qualitative sense by the data recorded above. The small deviation from this expectation observed in this study, may be because different catalysts have marginally different influences on the rates of polycondensation via alcoholysis and growth in M_W via ester-ester interchange reactions. Some of the catalysts used in this study are known to be more effective for the esterolysis reactions, e.g. $Co(OAc)_2$ and $Ti(OBu)_4$ than others, e.g. Sb_2O_3 and $Bu_2Sn(OAc)_2$.[36] In this study, the highest molecular weights were achieved in reactions catalysed by $Mn(OAc)_2$ and $Co(OAc)_2$, which is consistent with established knowledge since they are reported to be good promoters for ester-ester interchange reactions in the synthesis of PET.[36]

Unfortunately the number of publications regarding the study of catalysis in the synthesis of hyperbranched polymers is very limited. It appears that the influence of catalysts is very system specific and catalysts effective for one system may not be as effective for another.[41] For example Ti based catalysts are known for their high activity in synthesis of polyesters, but this study shows that they are less effective in polymerisation of dimethyl 5-(2-hydroxyethoxy)isophthalate leading to hyperbranched polyesters than $Mn(OAc)_2$, $Co(OAc)_2$ and $Bu_2Sn(OAc)_2$. Hawker observed different orders of activities for $Ti(OBu)_4$, $Co(OAc)_2$ and $Bu_2Sn(OAc)_2$ as indicated by molecular weights achieved in polymerisations for each of the three different monomers, methyl 4,4-bis(4'-hydroxyphenyl)pentanoate, propyl 4,4-bis(4'-

hydroxyphenyl)pentanoate and phenyl 4,4-bis(4'-hydroxyphenyl)pentanoate.[34(a)] According to Keeney *et al.* the catalysts used in this study show a different order of reactivity in the polymerisation of a monomer of a similar structure, dimethyl 5-(4-hydroxybutoxy)isophthalate, in which the only difference with respect to the monomer used in this study was an extra two methylene units.[29] During polymerisation of this monomer they found that no ester-ester interchange reactions were observed, since in catalysed and uncatalysed reactions both the M_n and M_w values of the polymers reached plateaux.

In the current work all catalysts investigated showed different activities with respect to alcoholysis and ester-ester interchange reactions. Similarly to the findings of this study on hyperbranched polymer synthesis, Sb_2O_3 was found to be an efficient catalyst but with lower activity than the acetates of Mn and Co by various research groups.[36,42] Presumably the mechanism of catalysis involves the formation of an unstable complex between a polymerising molecule and the catalyst. It was found that the catalytic activity of Sb^{3+} ions in polycondensation of bis(2-hydroxyethyl)terephthalate decreases with increasing concentration of hydroxyl groups.[43] This observation was explained by a formation of stable complexes of Sb^{3+} ions with hydroxyl ligands, although no structural evidence was provided to support this hypothesis and no proposed structure was drawn. Lower activity of an equimolar mixture of $Mn_2(OAc)_2$ and Sb_2O_3 in the polymerisation of dimethyl 5-(2-hydroxyethoxy)isophthalate may be a result of the formation of a similar antimony complex and maybe the catalytic activity of the Mn^{2+} ions is insufficient for the dissociation of the antimony complex so that polymerisation is inhibited. However, this is pure speculation without evidence.

The increased activity of $Ti(OBu)_4$ was consistent with previous studies.[44] Keeney *et al.* observed a faster increase in molecular weights for polymerisations of dimethyl 5-(4-hydroxybutoxy)isophthalate catalysed by $Ti(OBu)_4$ than by Sb_2O_3.[29]

According to Apicella *et al.*, tri- and tetravalent catalysts have different mechanisms from divalent catalysts for esterification reactions.[45] They assert that catalysts based on tri- and tetravalent metals take part in the reaction without dissociation of their ligands; whereas catalysts based on divalent metals, like $Mn(OAc)_2$ and $Co(OAc)_2$ require the dissociation of the ligands for initiation of the catalysis. In the present case, it may be more difficult for large polymer molecules to coordinate around tetravalent metal atoms with bulky ligands, which results in the relatively lower activity of these catalysts in relation to ester-ester interchange reactions, compared to catalysts based on divalent metals. This may result in higher molecular weights of hyperbranched polyesters obtained in reactions catalysed by divalent metals than by tetravalent metals, due to higher rates of ester-ester interchange reactions coupled with the polycondensation reaction. Tomita and Ida have measured initial rates of transesterification in PET synthesis as a function of metal acetate catalysis and their results are summarised in the Figure 4.31.[46]

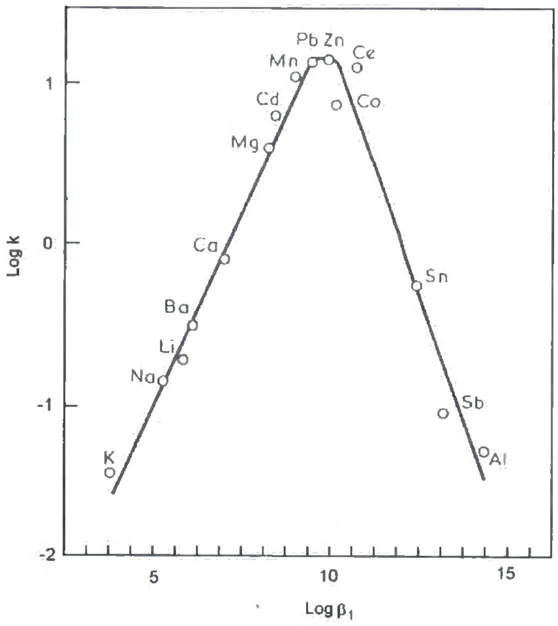


Figure 4.31. Rate constants (Log k) for transesterification in PET synthesis against stability constants (Log β_1) of complexes between polymers and corresponding metal species.

Unfortunately, this comparison did not include a titanium reference but it confirms that divalent acetates have significantly greater activity than either mono, tri- or tetravalent acetates, an observation, which is in agreement with the qualitative data recorded in this work.

To conclude, the observations reported here allow a comparison of the influences of different catalysts on the rate of polycondensation, cyclisation and ester-ester interchange reactions. Unfortunately the speed of the polycondensations, cyclisations and ester-ester interchange reactions could not be measured with any precision because of the problems associated with analysis of melt processes, e.g. mixing efficiency, uniform sampling and uniform temperature control. To control these parameters would require work on a much larger scale than was possible in this study. Thus, these observations possess qualitative rather than quantitative character. Polymerisation of dimethyl 5-(2-hydroxyethoxy)isophthalate is a complex process due to several detected reactions, polycondensation, cyclisation and esterolysis occurring at the same time and a detailed understanding of the process demands an extensive additional study.

4.4.3 SEC, MALDI-TOF and NMR analysis of poly(methyl 3,5-bis(2-acetoxyethoxy)benzoate)

This investigation also included a brief examination of the polymerisation of an esterdiol, namely methyl 3,5-bis(2-acetoxyethoxy)benzoate), as shown below and described in Chapter 3, p. 54.

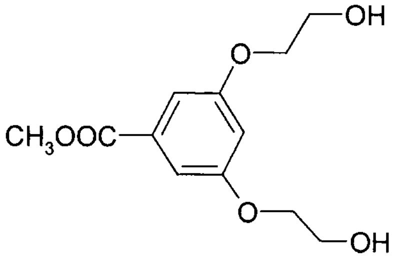


Figure 4.32. Structure of methyl 3,5-bis(2-acetoxyethoxy)benzoate).

Here the author reports characterisation carried out on the resultant polymers, which had been acetylated at every hydroxyl group in order to yield soluble materials, see Chapter 3, p. 54.

Hyperbranched poly(methyl 3,5-bis(2-acetoxyethoxy)benzoate)s have been analysed using a Viscotek triple detection system (RI-DV-RALLS) using chloroform as the solvent. The dn/dc value was measured using the Viscotek TriSEC data system on a solution of poly(methyl 3,5-bis(2-acetoxyethoxy)benzoate) with a known concentration. The dn/dc value for poly(methyl 3,5-bis(2-acetoxyethoxy)benzoate) in chloroform was 0.111 cm^3g^{-1}.

Relative amounts of cyclised material in hyperbranched poly(methyl 3,5-bis(2-acetoxyethoxy)benzoate)s were determined using an Applied Biosystems Voyager-DE Biospectrometer Workstation. All samples were dissolved in $CHCl_3$ and analysed the following day. A 1% of solution 2-(4-hydroxyphenylazo)-benzoic acid in THF was used to deposit the matrix. The data for all samples were collected from about 4000 laser shots. The instrument was calibrated using commercial sample of poly(ethylene) oxide (Polymer Labs PEO 1080). The spectra were resolved up to about DP of 30, however the calibration was adequate only in the low molecular weight region. The intensity of the high molecular weight part of the spectrum was too low to be useful. The laser power required for ionisation of high molecular weight species was greater than that for low molecular weight oligomers, which made the low mass region of the spectra complex due to fragmentation and the presence matrix ions.

The synthesis of an n-mer of poly(methyl 3,5-bis(2-hydroxyethoxy)benzoate) requires n-1 steps, where n-1 methanol molecules are eliminated. Hence, masses of the oligomers can be calculated by the formula: M_N=224xN + 32, where N is N-mer number and M_N is N-mer molecular weight. The masses of poly(methyl 3,5-bis(2-acetoxyethoxy) benzoate)s can be calculated by the formula: M_N=266xN + 74. The difference between oligomers observed in the MALDI spectra was 266m/z. The loss of an extra methanol molecule and absence of a terminal acetoxy group would lead to a formation of a cyclised polymer molecule 74 m/z units lighter than uncyclised molecule, see Figure 4.33:

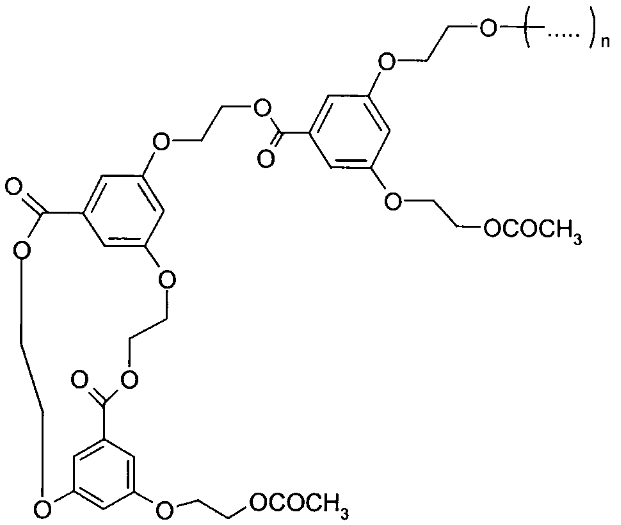


Figure 4.33. A proposed cyclised oligomer in the for poly(methyl 3,5-bis(2-acetoxyethoxy)benzoate) series.

Poly(methyl 3,5-bis(2-hydoxyethoxy)benzoate)s were produced in reaction 14 under the reaction conditions established for the polymerisation of dimethyl 5-(2-hydroxyethoxy)isophthalate, namely the monomer was polymerised on a 5g scale, at the stirring rate of 100r/min in the polymerisation reactor of type 1 at a temperature of 200°C. The nitrogen flow rate, sweeping over the top of the polymer melt was 160b/min. The oil in the oil bath was stirred by an overhead stirrer at a constant speed of 80r/min. Insoluble products were functionalised with acetoxy groups to give poly(methyl 3,5-bis(2-acetoxyethoxy) benzoate)s.

In previous studies of poly(dimethyl 5-(2-hydroxyethoxy)isophthalate)s it was established that as the reaction progresses, the M_n and FC values of polymers reach a limit.[30] At the same time, the M_w value continues to increase, which leads to increase in polydispersity (P_d).

The MWD of poly(methyl 3,5-bis(2-acetoxyethoxy)benzoate)s are broadened with increasing conversion in a similar manner to that observed in the case of poly(dimethyl 5-(2-hydroxyethoxy)isophthalate)s. M_n and M_w values for poly(methyl 3,5-bis(2-acetoxyethoxy)benzoate)s produced in reaction 14 and for poly(dimethyl 5-(2-hydroxyethoxy)isophthalate)s produced in reaction 6(a) are compared in Table 4.12.

Time	Reaction 14		Reaction 6(a)	
	M_n	M_w	M_n	M_w
0	0	0	0	0
5	3630	4010		
10	6220	7070		
20			4050	6540
25	24000	282900	5350	8630
30	76700	536000	5870	10700
35	30400	323700		

Table 4.12. M_n and M_w values for poly(methyl 3,5-bis(2-acetoxyethoxy)benzoate)s and poly(dimethyl 5-(2-hydroxyethoxy)isophthalate)s.

Both M_n and M_w values of poly(methyl 3,5-bis(2-acetoxyethoxy)benzoate)s increase much faster than those of poly(dimethyl 5-(2-hydroxyethoxy)isophthalate)s. This can be explained by the more flexible and less hindered architecture of poly(methyl 3,5-bis(2-acetoxyethoxy)benzoate)s that favours molecular weight growth. Functionalised samples obtained after 30 hours of polymerisation were not completely soluble in chloroform, which probably resulted in an underestimation in the determination of molecular weight values by SEC. The M_w values of poly(methyl 3,5-bis(2-acetoxyethoxy)benzoate)s increased faster than the M_n values, leading to a broad MWD, the P_d of the polymers increases from the beginning of the reaction to exceed 10 after 35 hours of polymerisation. According to information provided by MALDI-TOF MS all poly(methyl 3,5-bis(2-acetoxyethoxy)benzoate)s obtained after 25 hours of polymerisation were completely cyclised. This is in agreement with ^1H NMR analysis of poly(methyl 3,5-bis(2-acetoxyethoxy)benzoate)s. Unreacted terminal $COOCH_3$ groups, easily identified at δ3.84 ppm, see section 3.3.3, p. 55 for full details of the spectrum and Appendix 1.20, p. 124 for the whole spectrum, disappeared after 25 hours or reaction. This suggests absence of terminal B groups and full conversion of the monomer.

To conclude, the uncatalysed thermal polymerisation of the esterdiol, methyl 3,5-bis(2-acetoxyethoxy)benzoate, was a fast process significantly faster than that of the diesterol. The presence of polycondensation, cyclisation and ester-ester interchange reactions was clearly demonstrated. The higher reactivity of the esterdiol compared to that of the diesterol monomer is interesting and merits further investigation but this was not possible with the time constraints of this work.

4.5 Overall conclusions

Poly(dimethyl 5-(2-hydroxyethoxy)isophthalate)s were characterised by SEC and MALDI-TOF MS. Different solvents were compared for SEC analysis and chloroform appeared to be the most suitable solvent. M_n and M_w values of obtained polymers were found to increase with the polymerisation time. Plateaux in M_n and continuous growth of M_w were observed as expected on the basis of previous studies. The influence of reaction conditions on polymerisation was studied. Reaction conditions such as the presence of a nitrogen gas flow, higher stirring rate and higher temperature resulted in polymers with higher molecular weights. The presence of a nitrogen gas flow, lower stirring rate and higher temperature led to faster cyclisation within the polymer samples. Temperature was thought to be the most crucial parameter. The thermal mass of the oil bath was increased and the magnetic stirrer of the oil in the oil bath was replaced for an overhead stirrer. A better control over the temperature of the reaction resulted in an improved reproducibility of the reaction, although the reproducibility remained modest probably as a consequence of relatively poor temperature control in the bulk polymerising melt. Catalysts have been applied to the polymerisation and their influence studied. Catalyst showed significant influence on rates of increase in molecular weights and in cyclisation values compared to uncatalysed reactions. Trends of increase in molecular weights and in cyclisation were similar to those observed in uncatalysed reactions. The lowest rate of increase in molecular weights and in degree of cyclisation was observed with an equimolar mixture of $Mn(OAc)_2$ and Sb_2O_3. The highest rate in increase in molecular weights and in cyclisation values was observed with $Mn(OAc)_2$. In the mixed catalyst there was 0.5 molar % of $Mn(OAc)_2$ and with the pure $Mn(OAc)_2$ 1.0 molar % of catalysts, which may account for the differences but also demonstrates that in this case the equimolar mixture of $Mn(OAc)_2$ and Sb_2O_3 the catalysts are not acting collaboratively. Indeed the author proposes that Sb_2O_3 may inhibit the polycondensation via complexation of ester and hydroxyl groups. Generally, catalysts based on divalent metals showed higher activity than those based on tri- and tetravalent metals, an observation attributed to the different mechanisms of catalysis operating. Hyperbranched poly(methyl 3,5-bis(2-acetoxyethoxy)benzoate)s were characterised by SEC and MALDI-TOF MS. Evidence for the presence of polycondensation, cyclisation and ester-ester interchange reactions was demonstrated. Rates of increase in both molecular weights and in cyclisation for the uncatalysed thermal polymerisation of methyl 3,5-bis(2-hydroxyethoxy)benzoate were higher than those observed for uncatalysed polymerisation dimethyl 5-(2-hydroxyethoxy) isophthalate, the reason for this is not clear but may possibly be due to more flexible and less hindered architecture of the former polymer and/or differences in reactivity of the esterdiol monomer as compared to the diesterol monomer.

4.6 Experimental

Size exclusion chromatography was performed in THF, DMF and chloroform. The SEC in chloroform utilised three 5ηm PL gel packed columns, pore sizes 10, 100 and 10^4ηm at a temperature of 30°C. The system was calibrated against polystyrene standards. A Viscotek differential refractometer, Model 300TDA, right-angle laser light scattering (RALLS) and viscometer detectors connected to a data capture unit (DM 400) were used with TriSEC software (version 3.0). SEC in THF was carried out using three 300mm PL gel packed columns, mixed pore sizes at temperature of 30°C. The system was calibrated against polystyrene standards. MALDI-TOF spectra were recorded using an Applied Biosystems Voyager-DE Biospectrometer Workstation. A 1% solution of 2-(4-hydroxyphenylazo)-benzoic acid in THF was used as a matrix. The data was collected from about 4000 shots. The instrument was calibrated using a commercial sample of poly(ethylene) oxide (Polymer Labs PEO 1080).

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Chapter Five

Conclusions and future work.

5.0 Conclusions and suggestions for future work

The AB_2 monomer, dimethyl 5-(2-hydroxyethoxy)isophthalate, was synthesised on a 3kg scale in good yield via an established route.[1] The product was analysed by TLC, ^1H NMR and ^{13}C NMR spectroscopy, elemental analysis and mass spectrometry.

The monomer was polymerised via a one-step melt condensation reaction on a 20g scale. The influences of monomer batch size, flow of nitrogen gas into the vessel, stirring rate and temperature were studied. The structural and physical characterisation of these polymers was performed by a variety of analytical techniques, primarily SEC and MALDI-TOF MS.

The Viskotek TriSEC data system provided absolute molecular weight data for the polymers. The molecular weight and polydispersity values of the product increased with the polymerisation time. A plateau in increase in number average molecular weight, M_n, was achieved, whereas weight average molecular weight, M_w, continued to increase resulting in polydisperse materials.[1] The flow of nitrogen gas into the vessel, higher stirring rate and higher temperature of reaction resulted in higher rate of increase in molecular weight.

Evidence of cyclisation was provided by MALDI-TOF MS. The relative amount of cyclic species increased with the reaction time, generally until complete cyclisation was achieved. The flow of nitrogen gas into the reaction vessel, lower stirring rate and higher temperature were found to promote cyclisation.

By variation of reaction conditions and apparatus design sufficient reproducibility of polymerisation was achieved for a qualitative study of catalyst effects. Commercially available catalysts were applied to the system and their influences were compared on the basis of the way in which molecular weight and cyclisation degree values changed with time. Catalysts were found to promote different reactions with different rates. Molecular weight and cyclisation increase profiles were generally similar to these observed for uncatalysed polymerisation.

An A_2B monomer, methyl 3,5-bis(2-hydroxyethoxy)benzoate, was synthesised on a 10g scale in good yield via a new route. The product was analysed by TLC, ^1H NMR and ^{13}C NMR spectroscopy, elemental analysis and mass spectrometry. The monomer was polymerised and functionalised with acetoxy groups, which made the resulting polymers soluble in organic solvents. MALDI-TOF MS showed that polymers were completely functionalised. Molecular weights of these polymers increased faster than in the analogous polymerisation of the AB_2 monomer, dimethyl 5-(2-hydroxyethoxy) isophthalate).

In future it will be very interesting to determine the influence of catalysts on the internal structure of poly(dimethyl 5-(2-hydroxyethoxy)isophthalate)s, particularly on the degree of branching. Also it will be interesting to see the influence of various catalysts on each of the reactions: polycondensation, cyclisation and ester-ester interchange.

Cyclisation of poly(methyl 3,5-bis(2-hydroxyethoxy)benzoate)s was very fast, running the reaction at a lower temperature may decrease the rate of cyclisation and allow a more accurate comparison of the AB_2 and A_2B systems. Lower temperature of the reaction may also result in slower development of molecular weights, which would show clearer occurrence of ester-ester interchange reactions. Evidence for this type of reaction may be found by reaction of fully cyclised hyperbranched polyester with a core molecule.[1] A fully cyclised hyperbranched polyester cannot take part in reaction by polycondensation mechanism due to absence of A groups. Introduction of the core molecule in the reaction medium may allow its incorporation into polymer by an ester-ester interchange mechanism. Hence appearance of core terminated species in the mass spectrum after a reaction with a core molecule would provide support for the hypothesis that ester–ester interchange reactions occur in these systems. After the mechanism of the reaction is established, the effects of reaction conditions and catalysts may be studied, which would allow comparison of A_2B and A_2B systems.

In future it would be interesting to compare molecular weights and structures of individual fractions of polymers, for example by a combination of SEC and in-line MS.[2] If determination of DB was straightforward, which currently would involve a large amount of NMR time, it would be possible to investigate the relationship between molecular weight, DB and fraction of cyclisation of a given polymer fraction.

Investigation of properties and determination of DB values of copolymers of AB_2 with linear polymers of a similar structure, such as poly(methyl 2-hydroxyethoxy)isophthalate)s for example, and A_2B systems would be helpful for understanding structure/property relationships.

The size of cycles or the speed of their formation is unknown at the moment. Modelling studies taking into account cyclisation and ester-ester interchange reactions are also of great interest.[3] Prediction of the probability of the formation of cycles of a certain size would be very useful in building a clearer picture of the polymerisation process and the details of the product structure. Modelling studies may also provide insight into why the length of the alkylene chain appears to be the factor that inhibits ester-ester interchange reactions, observed for polymerisation of dimethyl 5-(2-hydroxyethoxy)isophthalate) and unobserved for other homologues of dimethyl 5-(ω-hydroxyalkoxy)isophthalate) with a higher number of methylene units in the alkylene chain.

It may also be possible to investigate ester-ester interchange processes by varying the end groups of the hyperbranched polyesters. Replacement of functional groups with bulky groups such as phenyl or *tert*-butyl esters may reduce the occurrence of ester-ester interchange reactions.

Copolymerisation of AB_2 monomer with linear AB monomer may decrease the DB value. Conversely, copolymerisation of AB_2 monomer with analogous AB_n monomer, with $n>2$, may increase the DB value. Interesting structures may be obtained by copolymerisation of monomers with inverse structures, for example AB_2 and A_2B monomers, depending on monomer feed ratios, although crosslinking and gelation is a distinct possibility.

To conclude, the synthesis of hyperbranched polyesters was successful. Interesting results were obtained from physical and structural characterisation of these materials; but although it was possible to gain information about different aspects of the hyperbranched structure, it was not possible to characterise these novel architecture materials fully. Extensive work is required in order to understand the structure/property relationship.

5.1 References

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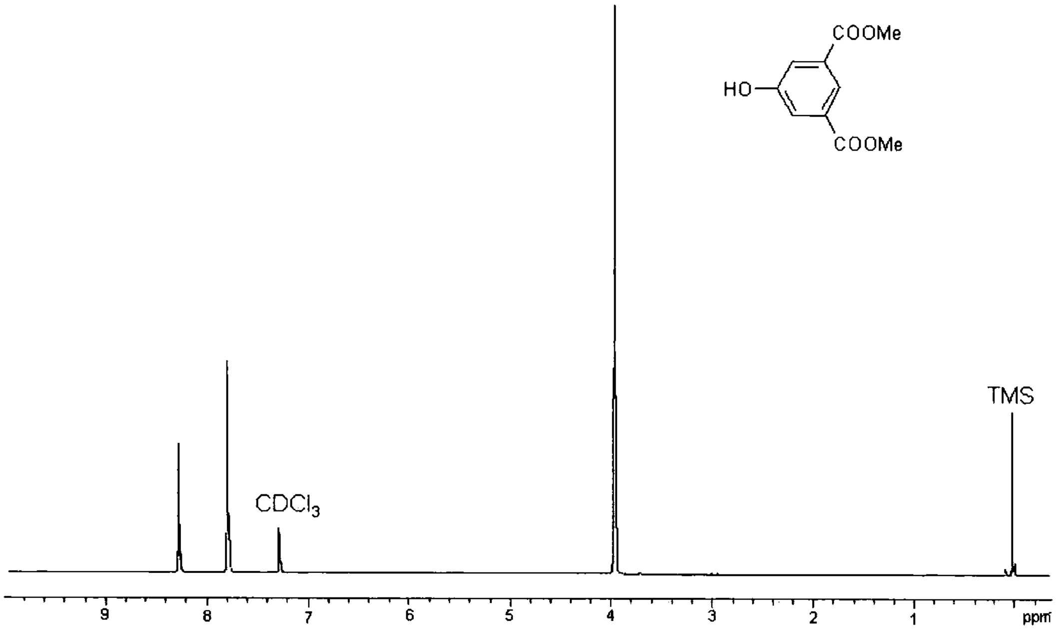
[1] D. Parker, The Synthesis and Characterisation of Hyperbranched Polyesters, *Ph.D. Thesis*, Durham University (2000)

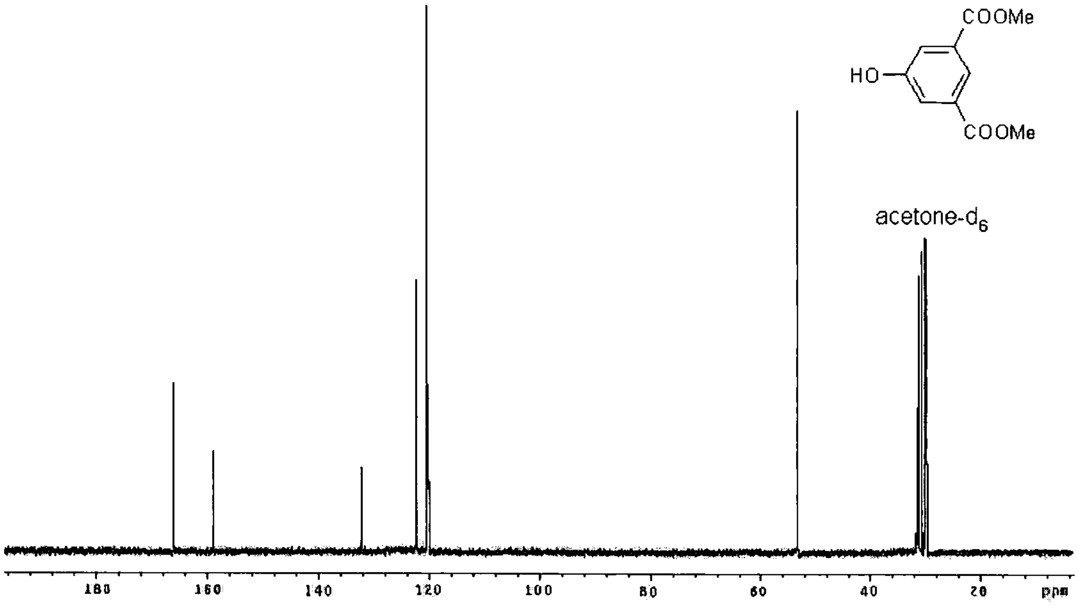
[2] Jayakannan, M., Van Dongen, J. L. J., Behera, G. C., Ramakrishnan, S., *J. Polym. Sci.: A: Polymer Chemistry*, **40(24)**, 4463 (2002)

[3] Dušek, K., Somravsky, J., Smrckova, M., Simonsick, W. J., Wilczek, L., *Polymer Bulletin*, **42**, 489 (1999)

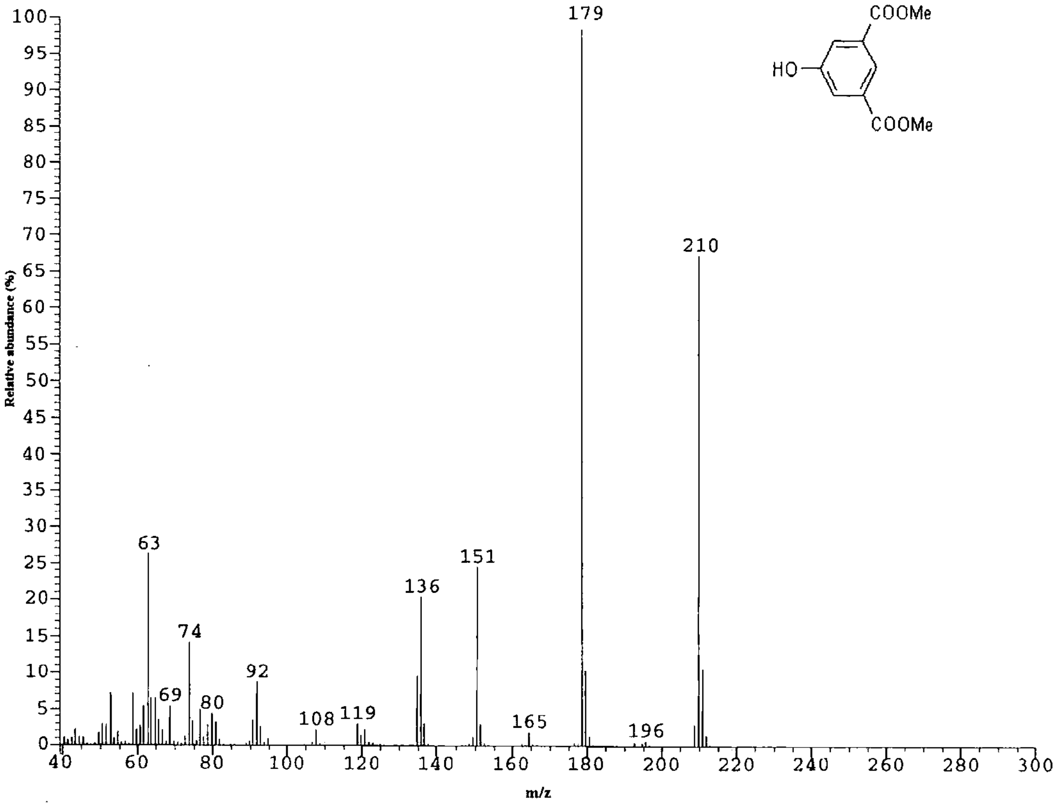
Appendices 1.1 to 1.27
NMR, MS, MALDI-TOF MS spectra and SEC chromatograms



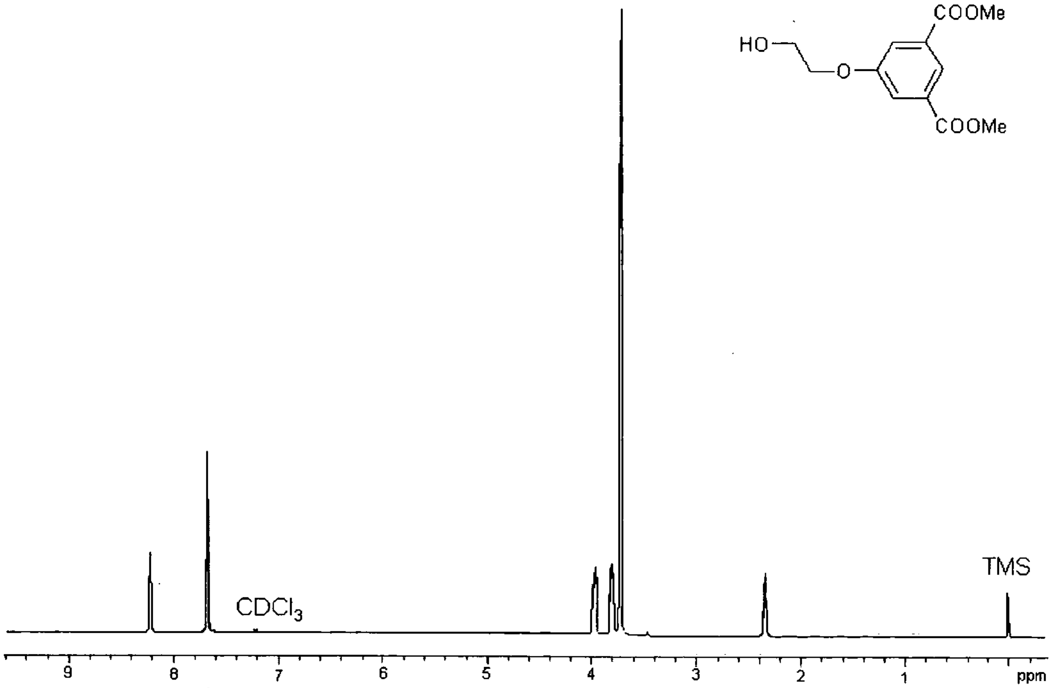
Appendix 1.1. ^{1}H NMR spectrum of dimethyl 5-hydroxyisophthalate ($CDCl_3$, 300MHz).



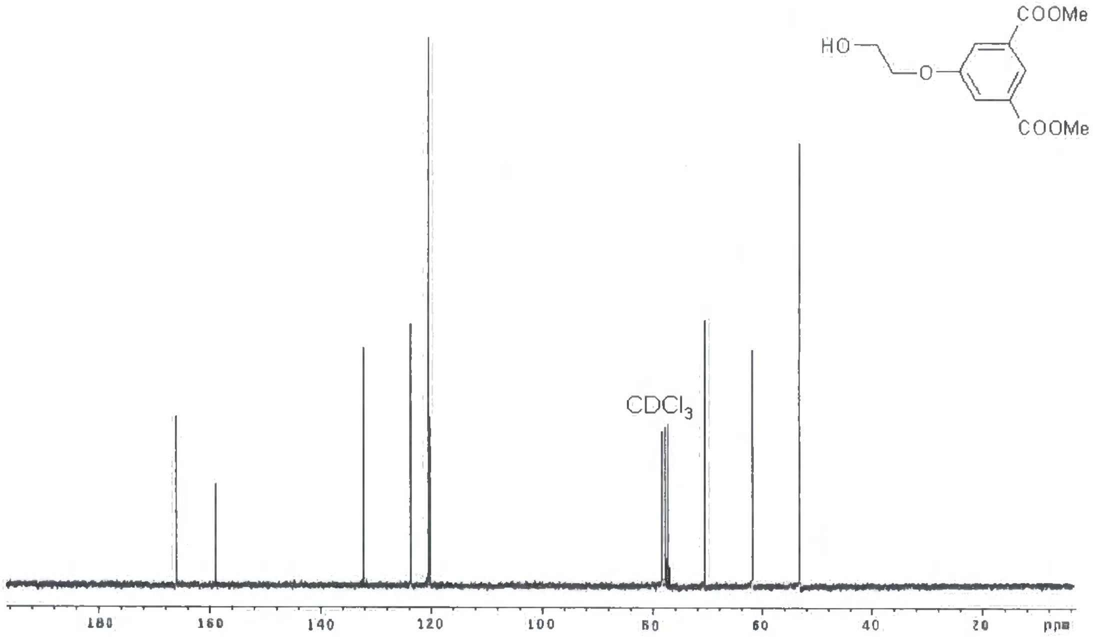
Appendix 1.2. ^{13}C NMR spectrum of dimethyl 5-hydroxyisophthalate (acetone-d_6, 125MHz).



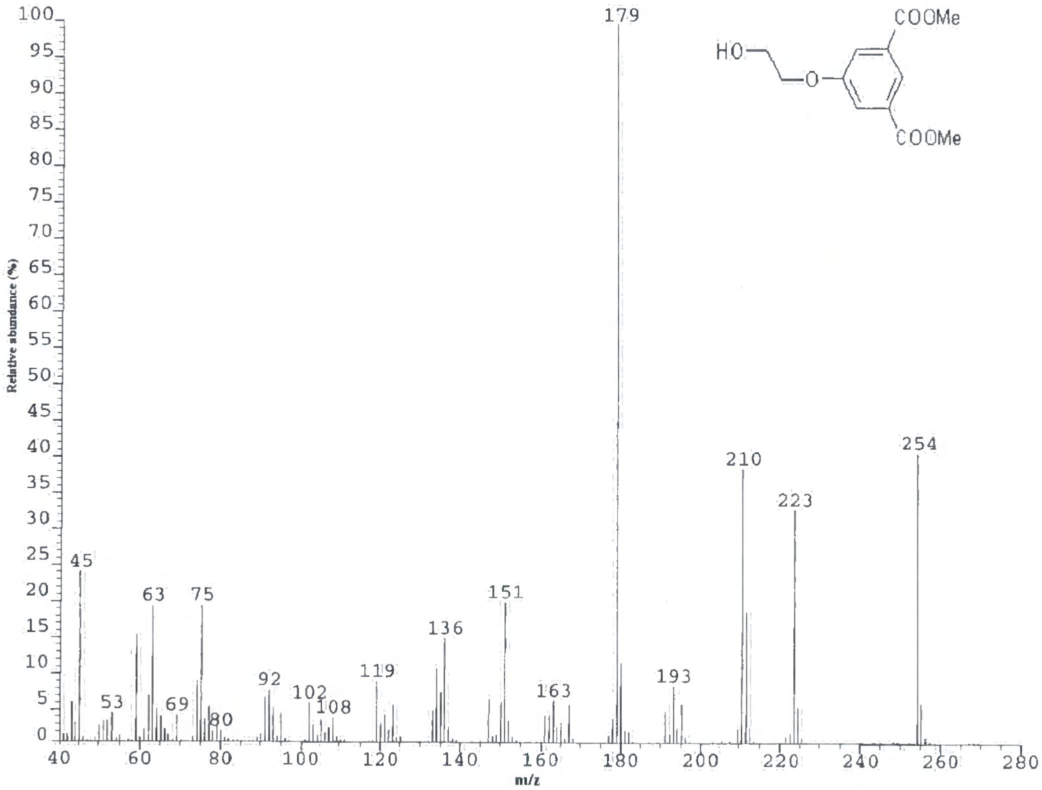
Appendix 1.3. Mass spectrum (EI+) of dimethyl 5-hydroxyisophthalate.



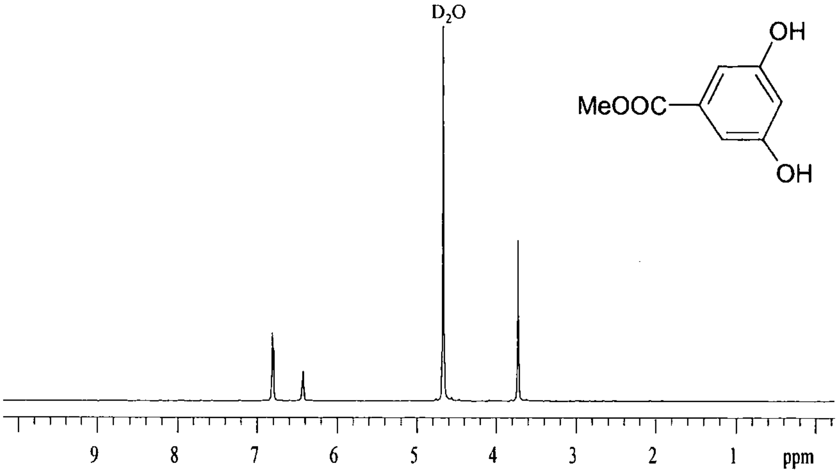
Appendix 1.4. ^1H NMR spectrum of dimethyl 5-(2-hydroxyethoxy)isophthalate ($CDCl_3$, 300MHz).



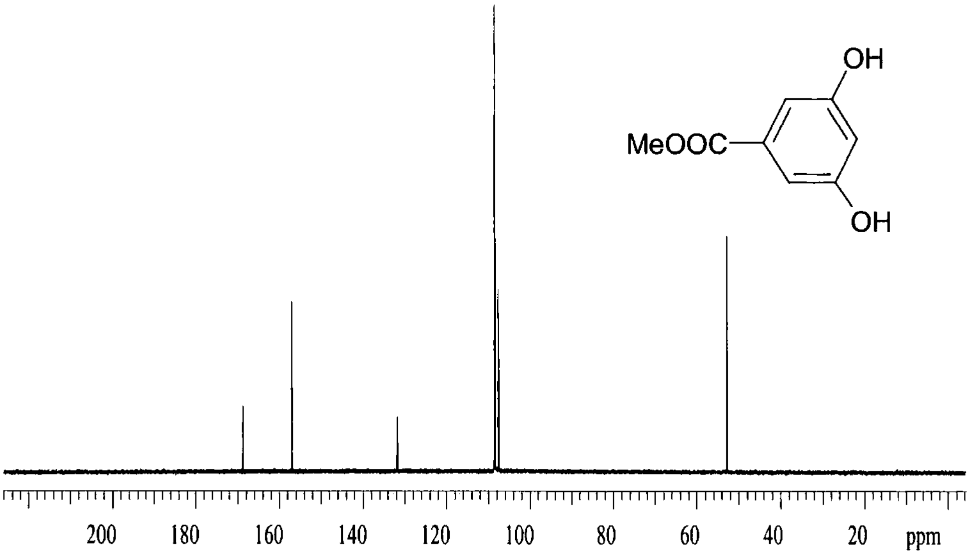
Appendix 1.5. ^{13}C NMR spectrum of dimethyl 5-(2-hydroxyethoxy)isophthalate ($CDCl_3$, 125MHz).



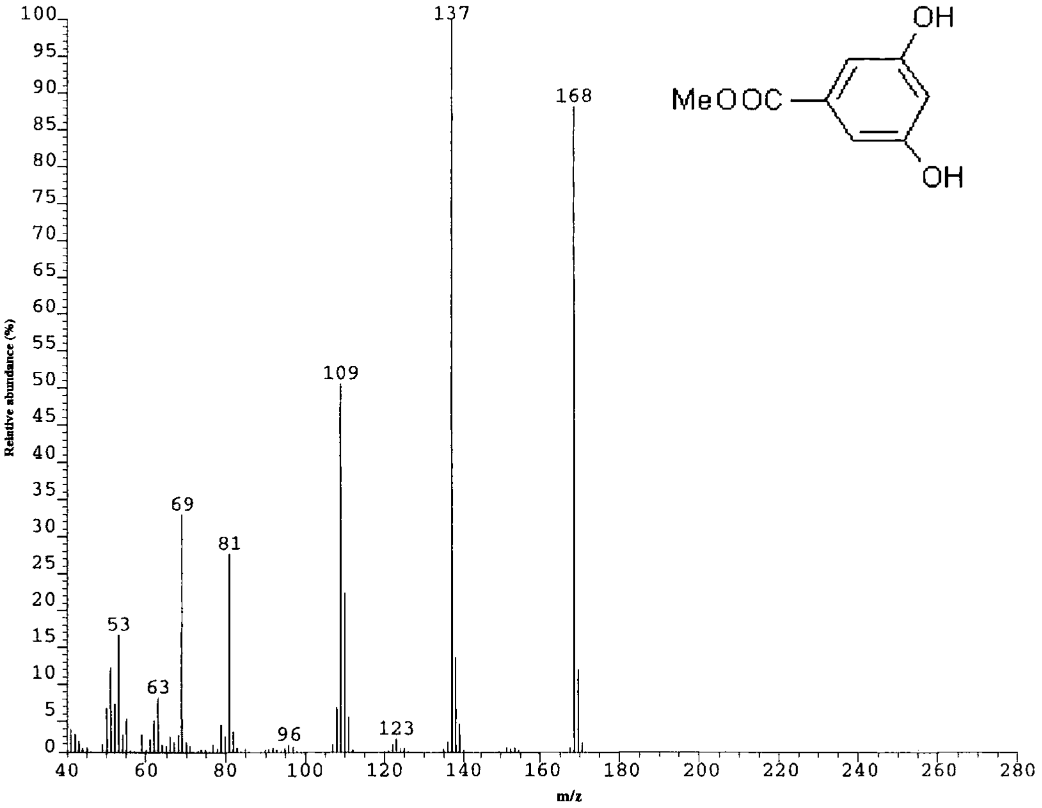
Appendix 1.6. Mass spectrum (EI+) of dimethyl 5-(2-hydroxyethoxy)isophthalate.



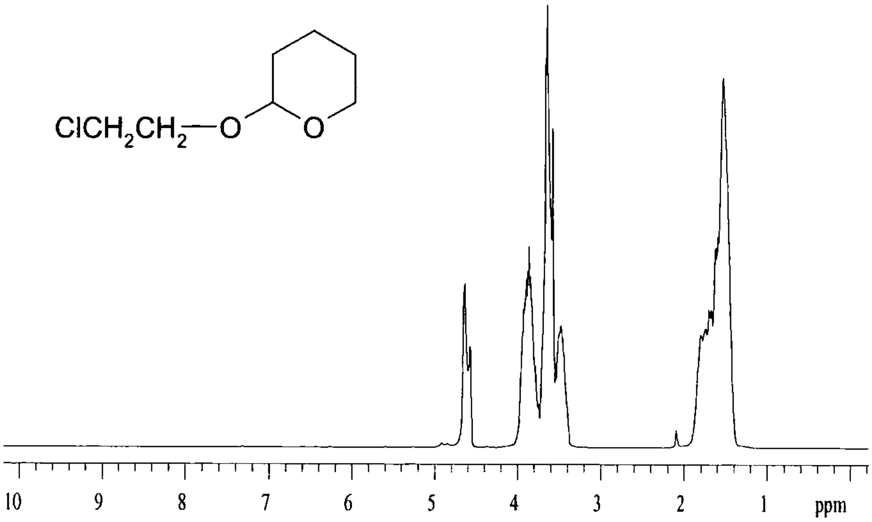
Appendix 1.7. ^{1}H NMR spectrum of methyl ester of 3,5-dihydroxybenzoic acid (D_2O, 300MHz).



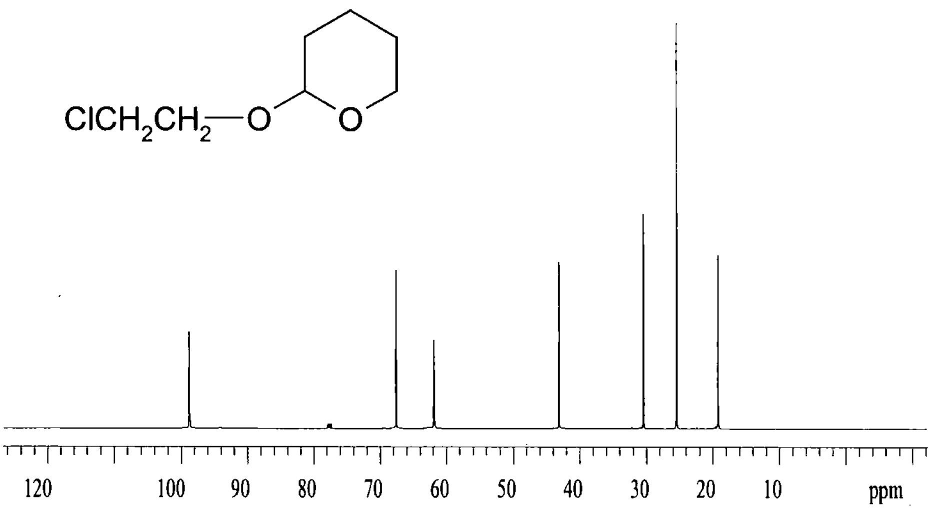
Appendix 1.8. ^{13}C NMR spectrum of methyl ester of 3,5-dihydroxybenzoic acid (D_2O, 125MHz).



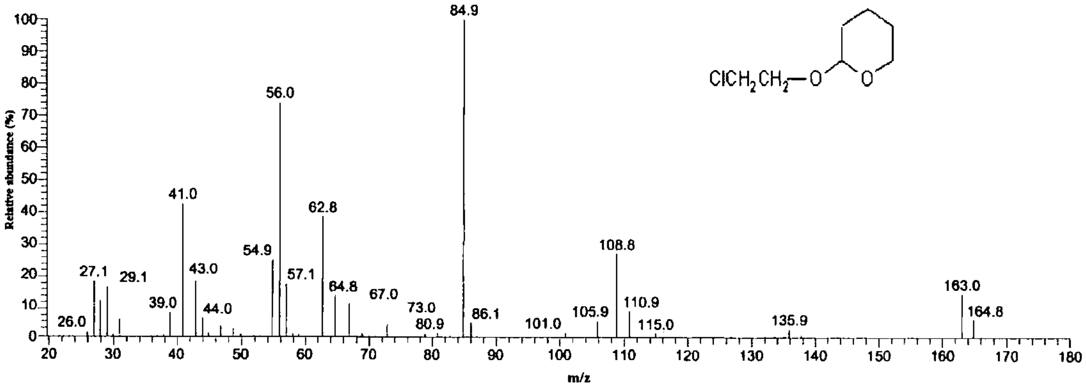
Appendix 1.9. Mass spectrum (EI+) of methyl ester of 3,5-dihydroxybenzoic acid.



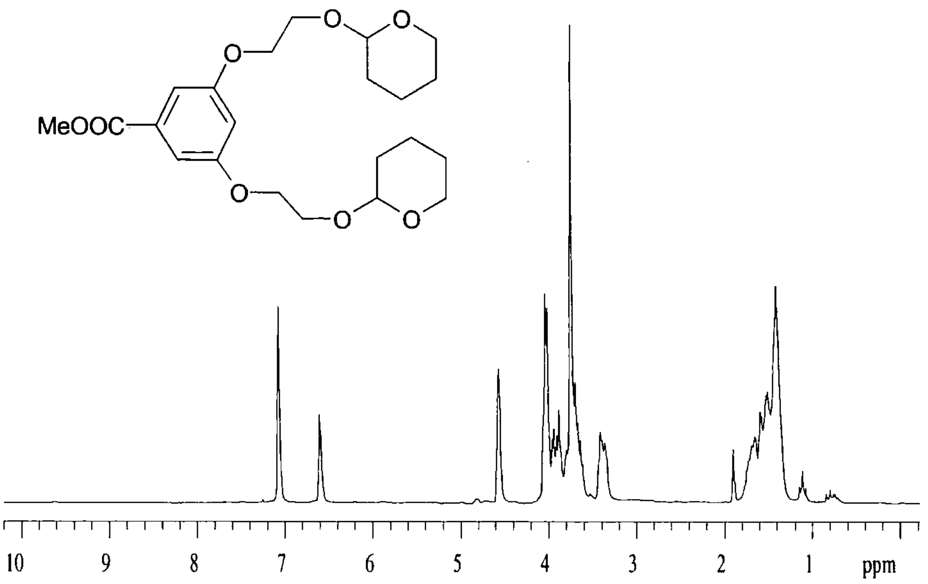
Appendix 1.10. ^{1}H NMR spectrum of tetrahydropyranyl ether of 2-chloroethanol ($CDCl_3$, 300MHz).



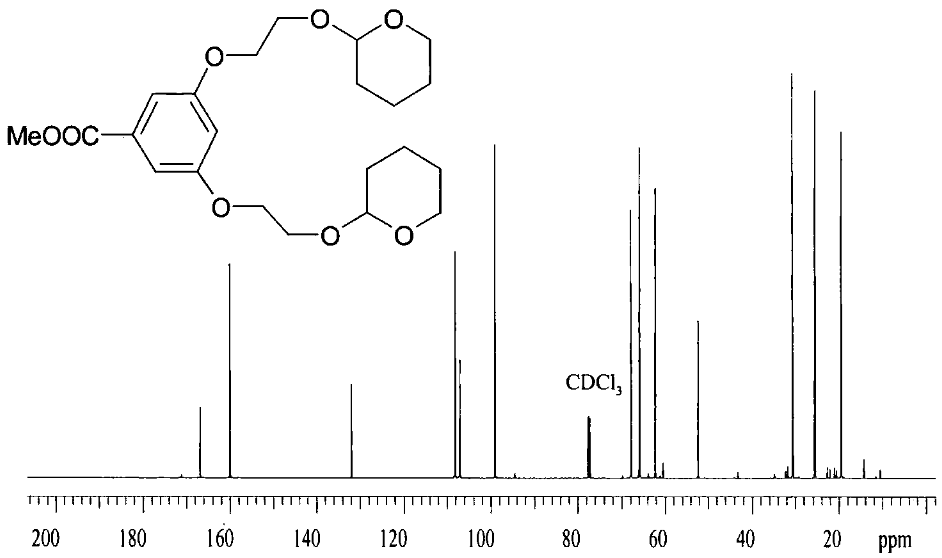
Appendix 1.11. ^{13}C NMR spectrum of tetrahydropyranyl ether of 2-chloroethanol (CDCl$_3$, 125MHz).



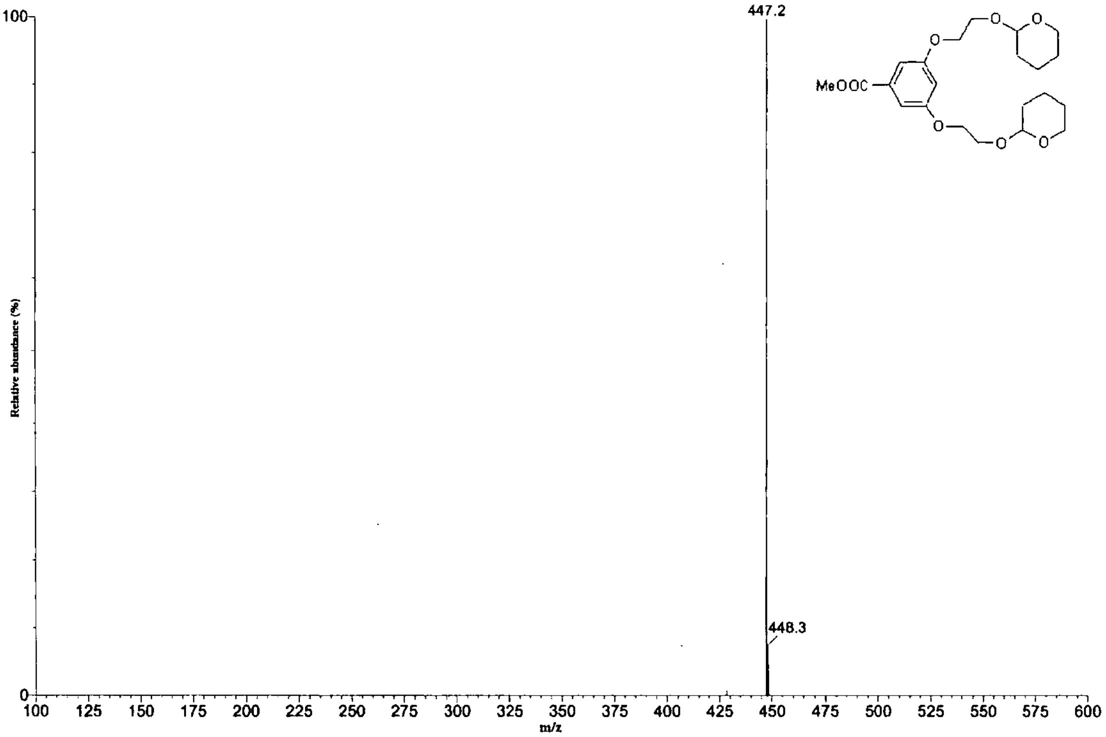
Appendix 1.12. Mass spectrum (ES+) of tetrahydropyranyl ether of 2-chloroethanol.



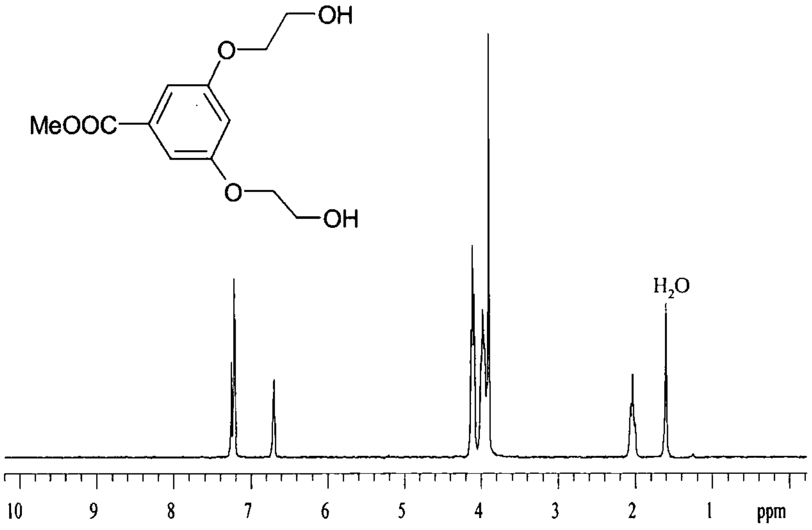
Appendix 1.13. ^1H NMR spectrum of tetrahydropyranyl ether of methyl 3,5-bis(2-hydroxyethoxy)benzoate ($CDCl_3$, 300MHz).



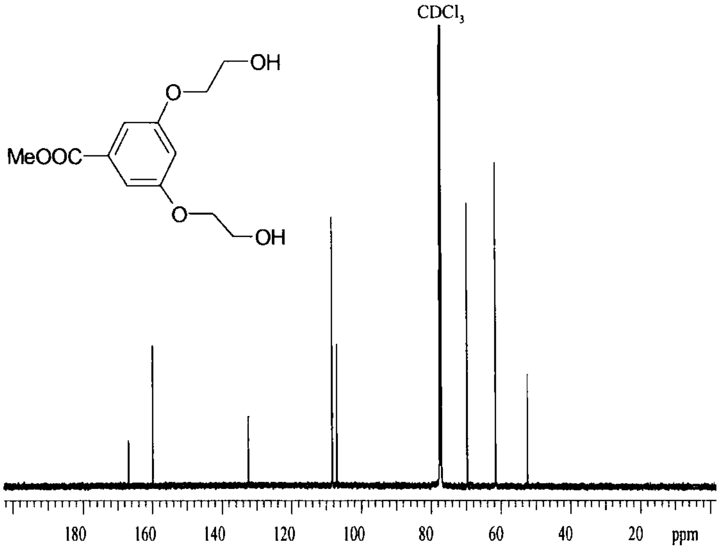
Appendix 1.14. ^{13}C NMR spectrum of tetrahydropyranyl ether of methyl 3,5-bis(2-hydroxyethoxy)benzoate ($CDCl_3$, 125MHz).



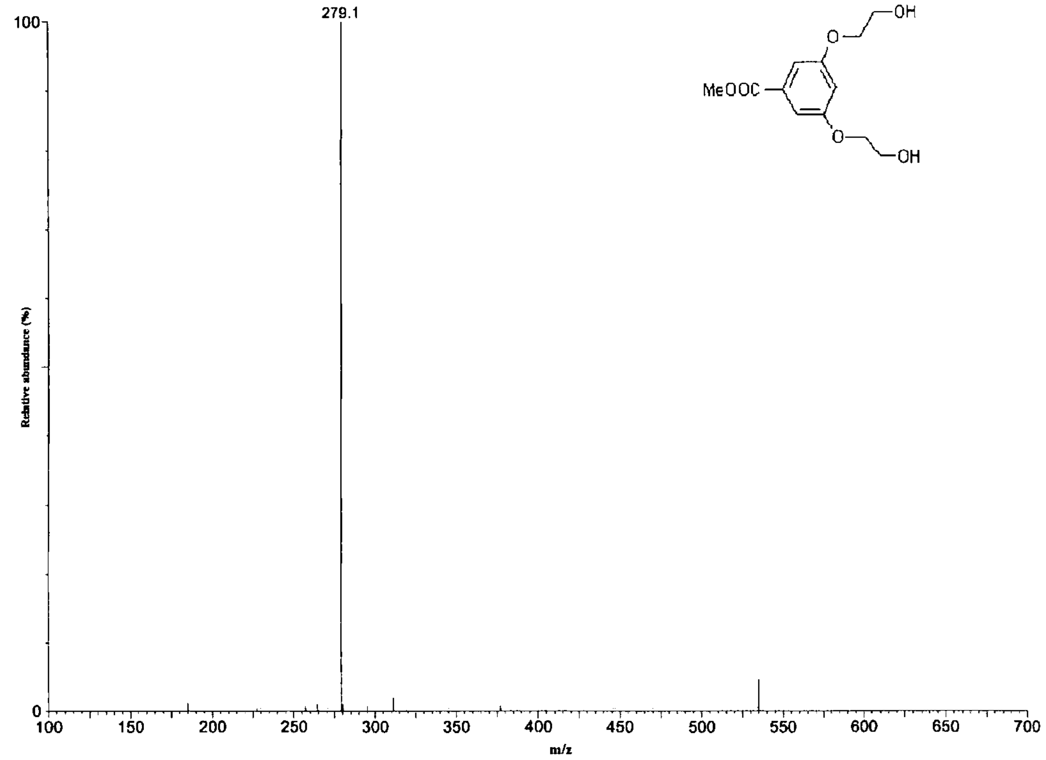
Appendix 1.15. Mass spectrum (ES+) of tetrahydropyranyl ether of methyl 3,5-bis(2-hydroxyethoxy)benzoate.



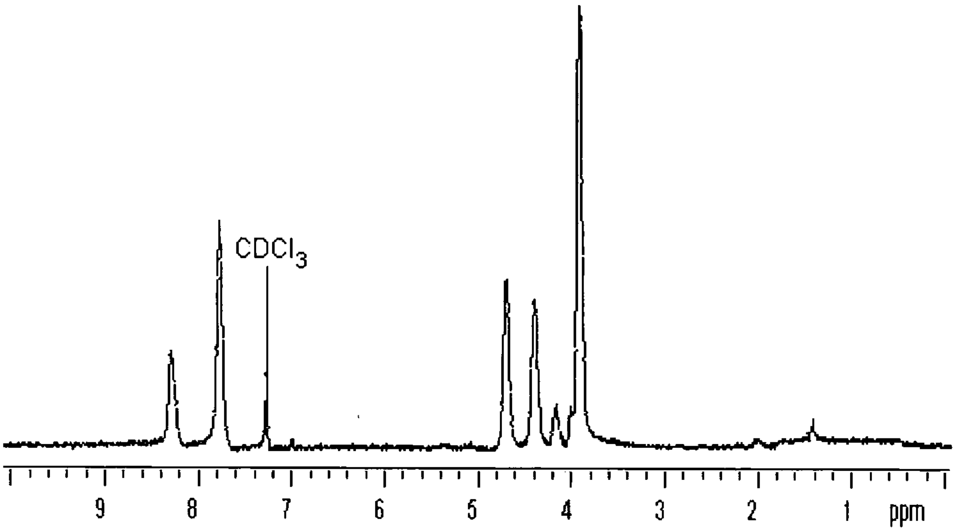
Appendix 1.16. ^1H NMR spectrum of methyl 3,5-bis(2-hydroxyethoxy)benzoate ($CDCl_3$, 300MHz).



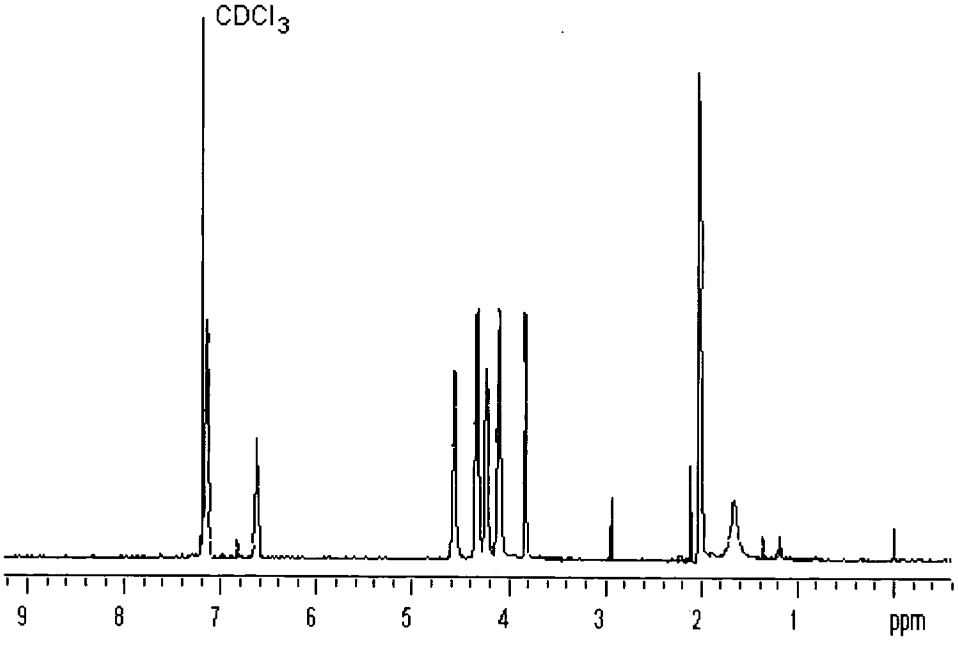
Appendix 1.17. ^{13}C NMR spectrum of methyl 3,5-bis(2-hydroxyethoxy)benzoate ($CDCl_3$, 125MHz).



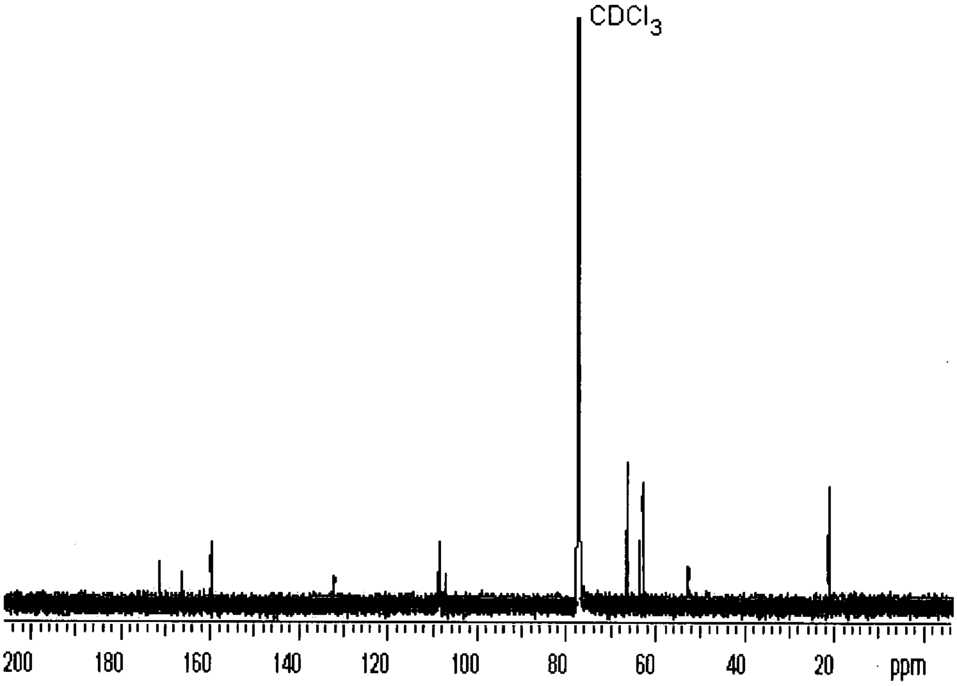
Appendix 1.18. Mass spectrum (ES+) of methyl 3,5-bis(2-hydroxyethoxy)benzoate.



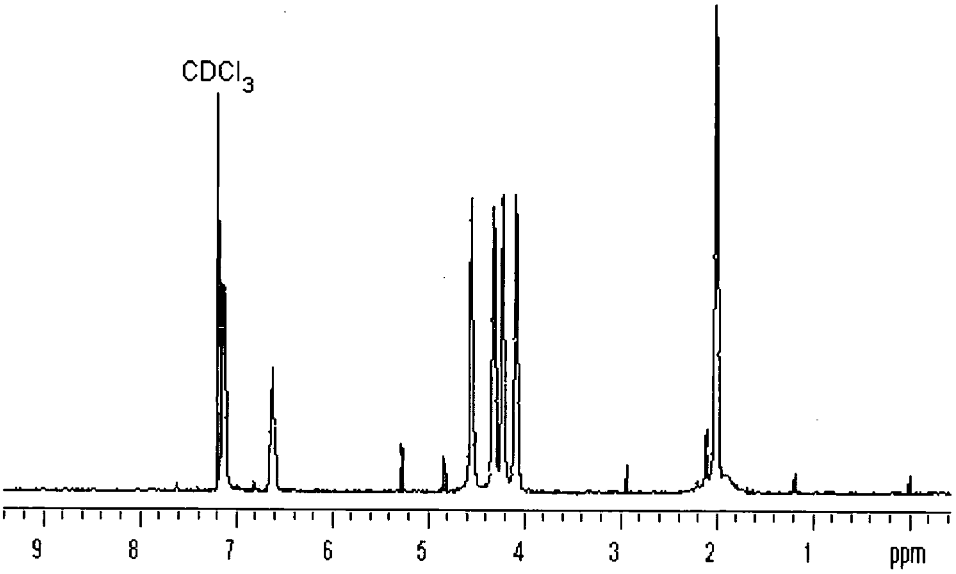
Appendix 1.19. ^{1}H NMR spectrum of poly(dimethyl 5-(2-hydroxyethoxy)isophthalate), after 1 hour of polymerisation ($CDCl_3$, 300MHz).



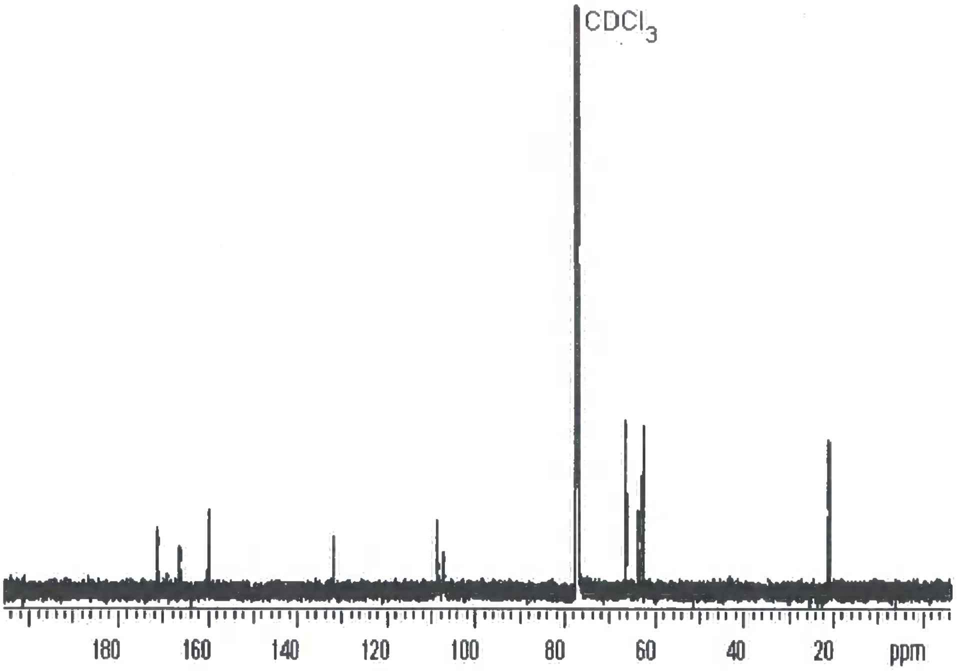
Appendix 1.20. ^{1}H NMR spectrum of poly(methyl 3,5-bis(2-acetoxyethoxy)benzoate), after 10 hours of polymerisation ($CDCl_3$, 500MHz).



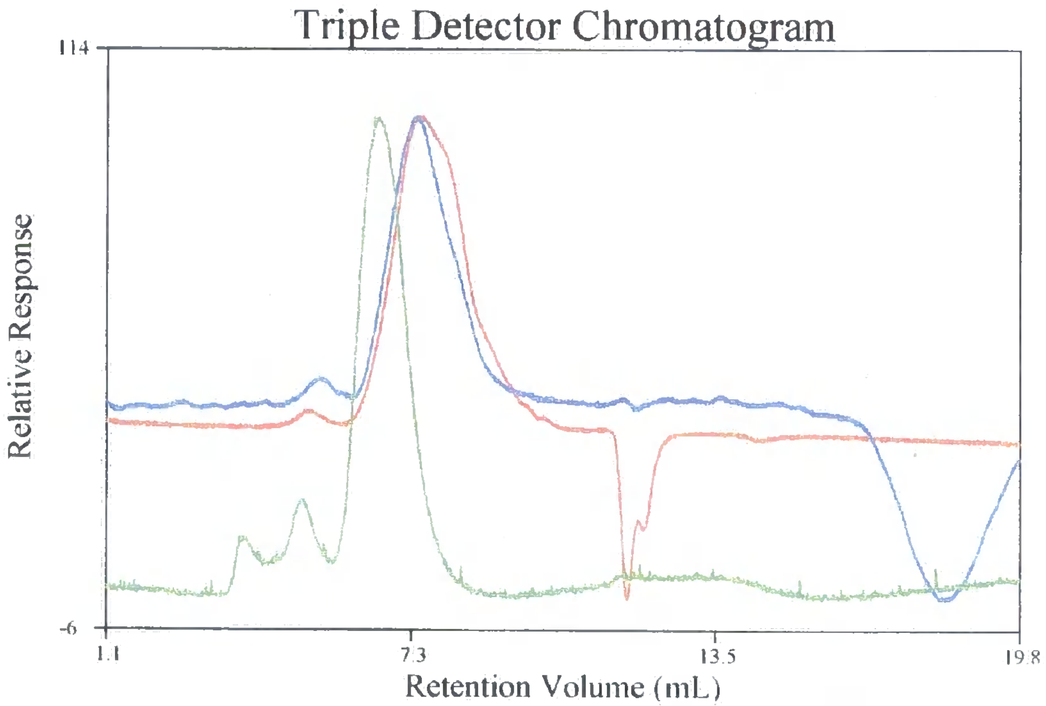
Appendix 1.21. ^{13}C NMR spectrum of poly(methyl 3,5-bis(2-acetoxyethoxy)benzoate), after 10 hours of polymerisation (CDCl$_3$, 125MHz).



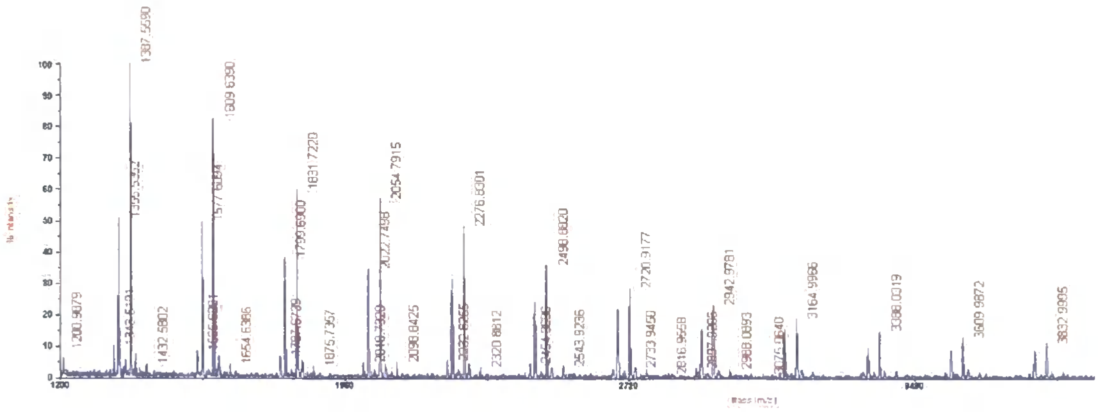
Appendix 1.22. ^{1}H NMR spectrum of poly(methyl 3,5-bis(2-acetoxyethoxy)benzoate), after 25 hours of polymerisation (CDCl$_3$, 500MHz).



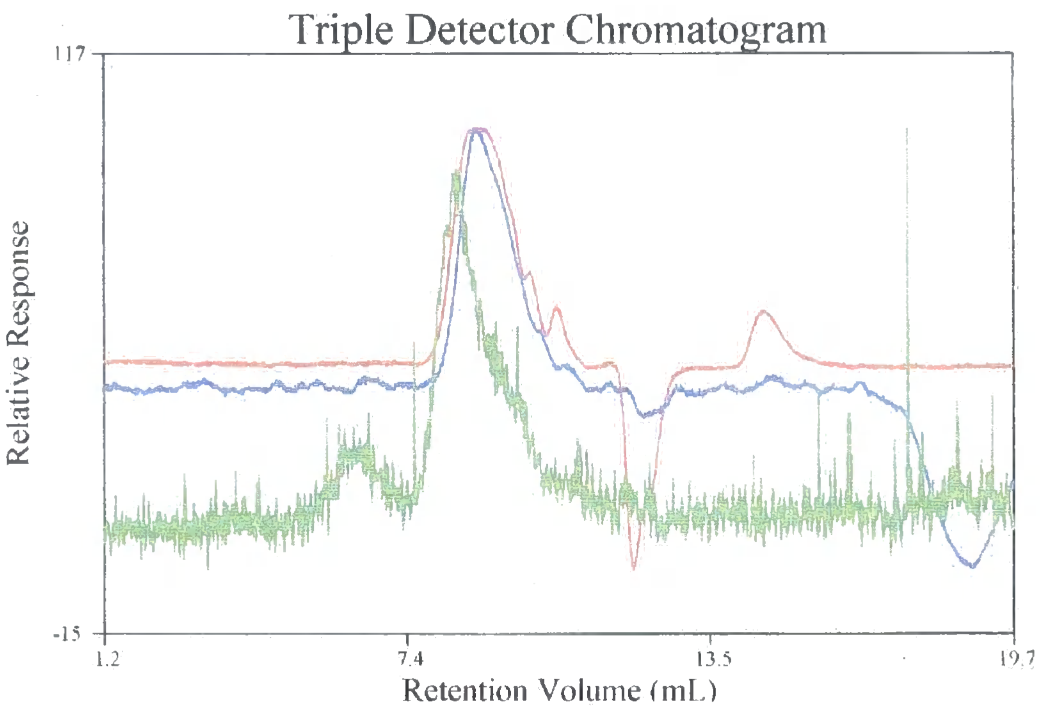
Appendix 1.23. ^{13}C NMR spectrum of poly(methyl 3,5-bis(2-acetoxyethoxy)benzoate), after 25 hours of polymerisation ($CDCl_3$, 125MHz).



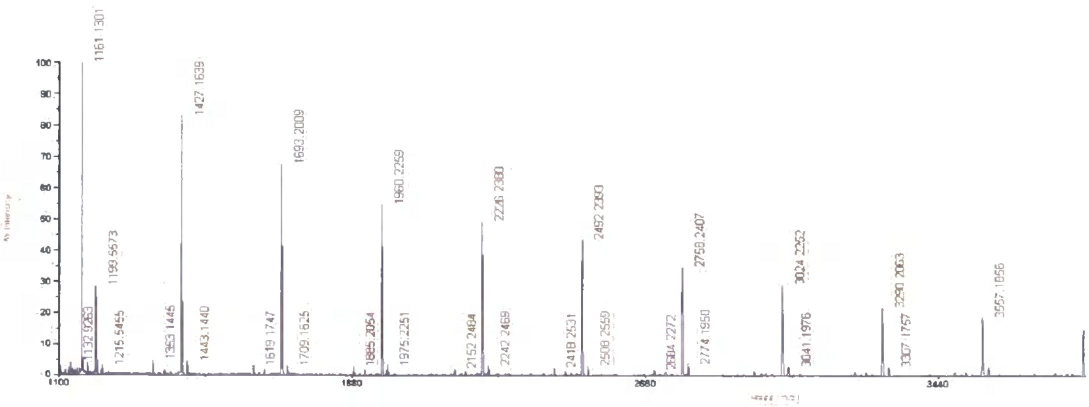
Appendix 1.24. SEC chromatogram of poly(5-(2-hydroxyethoxy)isophthalate), after 70 hours of polymerisation ($CHCl_3$).



Appendix 1.25. Representative MALDI-TOF spectrum of poly(dimethyl 5-(2-hydroxyethoxy)isophthalate) after 70 hours of polymerisation.



Appendix 1.26. SEC chromatogram of poly(methyl 3,5-bis(2-acetoxyethoxy)benzoate), after 10 hours of polymerisation ($CHCl_3$).



Appendix 1.27. Representative MALDI-TOF spectrum of poly(methyl 3,5-bis(2-acetoxyethoxy)benzoate) after 10 hours of polymerisation.