Joshi, Nimisha B., 2007, *"Studies on Aromatic Cardo Copolymers",* thesis PhD, Saurashtra University

DEDICATED TO MY BELOVED FAMILY

STUDIES ON
AROMATIC CARDO COPOLYMERS

A

THESIS SUBMITTED TO

THE SAURASHTRA UNIVERSITY

FOR

THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN THE FACULTY OF SCIENCE (CHEMISTRY)

BY

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UNDER THE SUPERVISION

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The work included in the thesis is my own work under the supervision of **Dr. P. H. Parsania** and leads to some contribution in Chemistry subsidized by a number of references.

Dt.: -01-2007

Place: Rajkot.

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This is to certify that the work submitted for the Ph. D. Degree of Saurashtra University by **Ms. Nimisha B. Joshi** is her own work and leads to advancement in the knowledge of Chemistry. The thesis has been prepared under my supervision.

Date : -01-2007
Place : Rajkot.

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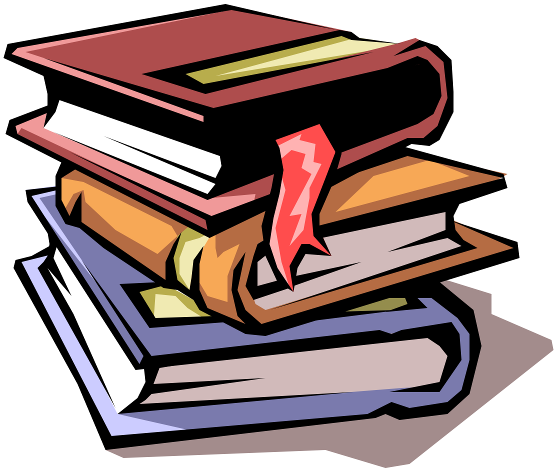
-- Nimisha B. Joshi

CONTENTS

SYNOPSIS

STUDIES ON AROMATIC CARDO COPOLYMERS



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SYNOPSIS OF THE THESIS TO BE SUBMITTED TO SAURASHTRA UNIVERSITY FOR THE DEGREE OF PHILOSOPHY IN THE FACULTY OF SCIENCE-CHEMISTRY

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GENERAL INTRODUCTION

A brief review of the work to be incorporated in the thesis entitled **"STUDIES ON AROMATIC CARDO COPOLYMERS"** is described as under.

We live in a polymer age - Plastics, fibers, elastomers, coatings, adhesives, and rubber. These are all common terms in our modern vocabulary, and all are a part of the fascinating world of Polymer Chemistry.

Synthetic polymers– designated as plastics - have become technologically significant since the 1940s and since then they have come to replace glass, wood, masonry and other construction materials, and even metals in many industrial, domestic, commercial and environmental applications. These widespread applications are not only due to their favorable thermo-mechanical properties but also mainly due to stability and durability of plastics. On the other hand, plastics also play an important role for many "short live" applications such as packaging and commodity as well as hygienic products, which represent the major part of plastic waste.

In 1980s the total volume of plastics consumed world wide overtook that of iron and steel. There are sound economic reasons for the increasing use of plastics. They are weight less and are generally more corrosion resistant than metals [1]. It is well established that aromatic cardo (Latin meaning a loop) polymers [2-4] are well known for their excellent solubility, excellent thermo-mechanical and electrical properties and easy processability led to their industrial importance.

---

1. M. P. Stevens "Polymer Chemistry – 3rd Edn." University of Hartford – 1999
2. D. J. Liaw, J Polym Sci Part A: Polym. Chem., **33,** 605, 1995
3. S. S. Vibhute, M. D. Joshi, P. P. Wadgaonkar, A. S. Patil, N. N. Maldar, J Polym. Sci: Part A: Polym. Chem., **35,** 3227, 1997
4. D. J. Liaw, B. Y. Liaw, J. J. Hsu and Y. C. Cheng, J Polym. Sci. Part A: Polym. Chem., **38 ,** 4451, 2000

Polyesters are one of the most versatile synthetic polymers. They are widely used commercially as fibers, plastics, and coatings. Aromatic polyesters are high performance engineering plastics and find their applications in a variety of fields [5-8]**.**

Commercially terephthalate polyesters are well known as engineering thermoplastics due to their good chemical resistance, high thermal and dimensional stability, high strength and rigidity coupled with good surface hardness and gloss [9].

A number of halogenated aromatic polyesters have been examined with respect to the effect of chemical structure on thermal properties [10, 11]. Partly aromatic polyesters can be synthesized by using aliphatic diols and aromatic dicarboxylic acids [12].

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5. H. Han and P. K. Bhowmik, Prog Polym. Sci. **22**, 143, 1997
6. H. Wang, Z. Shen, S. Z. D. Cheng, F. W. Harris, Polym. Prep. **40**, 88, 1999
7. X. Han, A. B. Padias, H. K. Hall, J Polym. Sci. Part A: Polym Chem. **37**, 2891, 1999
8. E. Bucio, J. W. Fitch, S. R. Venumbaka and E. C. Patrick, Polymer, **46,** 3971, 2005
9. F. Pilati ‘‘Polyesters’’ in: Comprehensive Polymer Science, Vol. 5, G Allen Ed. Pergamon Press, Oxford 1989, Chapter 17: pp275
10. K. E. Kane, L. A. Wells, P. E. Cassidy, High Perform Polym., **3**,191, 1991
11. S. Gharbi, J. P. Andreolety, A. Gandini Eur Polym. J. **36**, 463, 2000
12. S. V. Levchik and E. D. Weil, Polym Adv Technol **15**, 691, 2004

The work to be incorporated in the thesis is subdivided into five chapters:

CHAPTER-1: The literature survey on monomers and aromatic cardo copolyesters

CHAPTER-2: Syntheses of monomers and copolyesters

This chapter is further subdivided into two sections:

SECTION-I: syntheses of monomers

SECTION-II: Syntheses of copolyesters

CHAPTER-3: Characterization of copolyesters

SECTION-I: Solubility of copolyesters

SECTION-II: Spectral characterization of copolyesters

SECTION-III: Preparation of copolyester films

SECTION-IV: Density measurements

SECTION-V: Viscosity measurements

SECTION-VI: Hydrolytic stability of copolyesters

SECTION-VII: Microbial activity of copolyesters

CHAPTER-4: Thermo-mechanical and electrical properties of copolyesters

SECTION-I: Thermal properties of copolyesters

SECTION-II: Mechanical and electrical properties of copolyesters

CHAPTER-5: A brief review of the work done

CHAPTER-1: THE LITERATURE SURVEY ON MONOMERS AND AROMATIC CARDO COPOLYESTERS

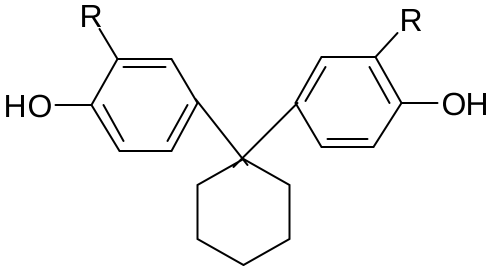
Chapter-1 of the thesis describes up to date literature survey on the synthesis and physico-chemical properties of monomers and cardo copolyesters.

CHAPTER-2: SYNTHESES OF MONOMERS AND COPOLYESTERS

This chapter is further subdivided into two sections:

SECTION-I: SYNTHESES OF MONOMERS

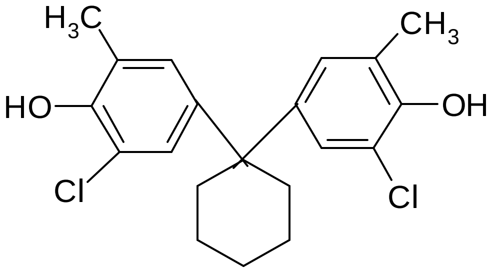
(A) Synthesis of 1, 1'-bis (4-hydroxy phenyl) cyclohexane and 1, 1'-bis (3- methyl-4-hydroxy phenyl) cyclohexane



BC: R=H and MeBC: R= CH_3

BC and MeBC were synthesized by Friedel–Crafts condensation of phenol / o-cresol and cyclohexanone in the presence of HCl: CH_3COOH (2:1v/v) as a catalyst at 50-55ºC for 4h and were repeatedly recrystallized from methanol-water system prior to their use.

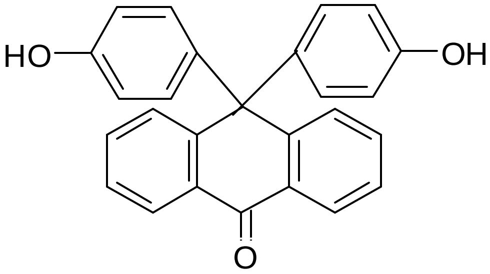
(B) Synthesis of 1, 1'-bis (3-methyl-5-chloro-4-hydroxy phenyl) cyclohexane



ClMeBC

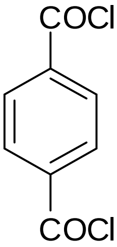
ClMeBC was synthesized by chlorination of MeBC by using thionyl chloride in carbon tetrachloride and sodium sulfide as a catalyst at 55ºC for 3h and at 70ºC for 1h.

(C) Synthesis of 9, 9’-bis (4-hydroxy phenyl) anthrone-10 (BAN)



BAN was synthesized by condensing anthraquinone with phenol at 120^{0}C for 6h in the presence of stannic chloride (molar ratio 1:7:1.5, respectively) and was isolated from hot acetic acid. BAN was recrystallized repeatedly from dioxane-water system prior to its use.

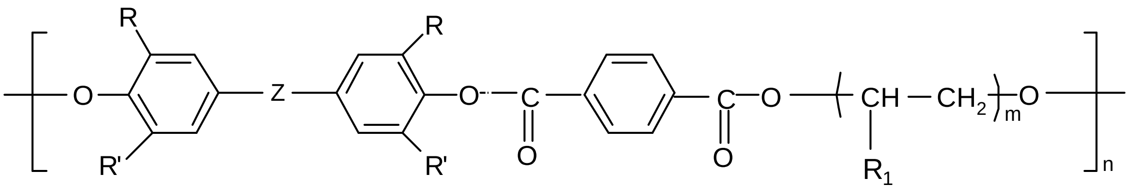
(D) Synthesis of terephthaloyl chloride (TC).



TC was synthesized from terephthalic acid and thionyl chloride at reflux temperature for 12h and recrystallized repeatedly from chloroform-n-hexane system.

SECTION-II: SYNTHESES OF COPOLYESTERS

Copolyesters of varying compositions have been synthesized by interfacial polycondensation technique by using $CHCl_3$-H_2O as an interphase, alkali as an acid acceptor and CTAB as an emulsifier .The reaction time and temperature were 2h and 0°C, respectively. All the copolyesters have been purified repeatedly from $CHCl_3$ - MeOH system.



MET : m=1, R= C H_3 , R’=H, R_1=H and Z= 

MPT : m=1, R= C H_3 , R’=H, R_1= C H_3 and Z= 

MBT : m=2, R= C H_3 , R’=H, R_1= H and Z= 

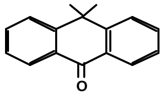
MHT : m=3, R= C H_3 , R’=H, R_1= H and Z= 

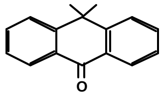
ClMET : m=1, R= C H_3 , R’=Cl, R_1= H and Z= 

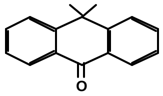
ClMPT : m=1, R= C H_3 , R’=Cl, R_1= C H_3 and Z= 

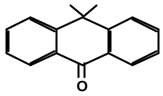
ClMBT : m=2, R= C H_3 , R’=Cl, R_1= H and Z= 

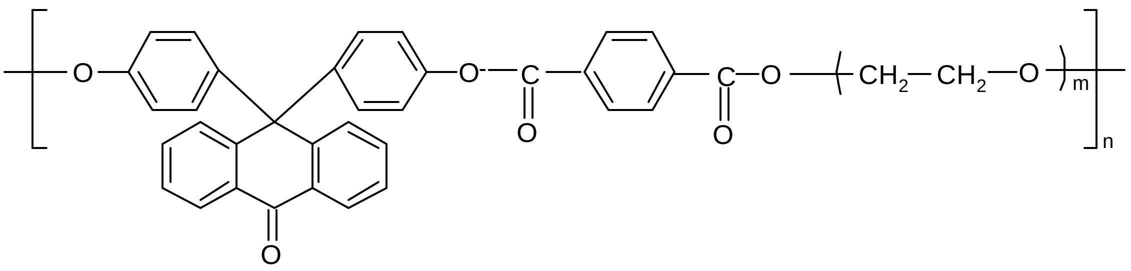
ClMHT : m=3, R= C H_3 , R’=Cl, R_1= H and Z= 

BANET: m=1, R=R'=R_1=H and Z= 

BANPT: m=1, R=R'=H, R_1=CH_3 and Z= 

BANBT: m=2, R=R'=R_1=H and Z= 

BANHT: m=3, R=R'=R_1=H and Z= 



BPEGT

CHAPTER-3: CHARACTERIZATION OF COPOLYESTERS

This chapter deals with the characterization of copolyesters under investigation and it is further subdivided into seven sections:

SECTION-I: SOLUBILITY OF COPOLYESTERS

The solubility is an interesting aspect of the polymer system, which diminishes with increasing molecular weight of the given polymer in a solvent under consideration. The polymer dissolution is extremely slow process. A special feature of polymer solution is high magnitude of positive excess entropy and large negative deviations from Raoult's law. The solubility of polymer was tested in various organic solvents at room temperature and thermodynamic goodness of the solvents is reported.

SECTION-II: SPECTRAL CHARATERIZATION OF COPOLYESTERS

The structures of the polymers are supported by IR and NMR spectral data.

SECTION-III: PREPARATION OF COPOLYESTER FILMS

In order to exploit mechanical and electrical properties and hydrolytic stability of the copolymers, tough and transparent films were prepared from concentrated solutions.

SECTION-IV: DENSITY MEASUREMENTS

The densities of copolyesters are determined by flotation method at room temperature by using CCl_4- n-Hexane system. The structure property relation in density is discussed.

SECTION-V: VISCOSITY MEASUREMENTS

Dilute solution viscosity measurements were made in different solvents at different temperatures. The intrinsic viscosities and Huggin's constant are determined and are discussed in light of thermodynamic goodness of the solvents.

SECTION-VI: HYDROLYTIC STABILITY OF COPOLYESTERS

Hydrolytic stability of copolyester films is determined against water and 10% each of acids, alkalis and salt at room temperature for varying time interval. The effect of acids, alkalis and salt on hydrolytic attack is discussed.

SECTION-VII: MICROBIAL ACTIVITY OF COPOLYESTERS

The microbial activity of the copolymers is tested against different gram-positive and gram-negative microbes by cup-plate method and is compared with standard drugs. The effect of structure on antibacterial activity is discussed in light of structure property relationship.

CHAPTER-4: THERMO-MECHANICAL AND ELECTRICAL PROPERTIES OF COPOLYESTERS

Thermo-mechanical and electrical properties of polymers are of great importance from both scientific and practical point of views [13, 14]. Thermal analysis of polymers is useful in the design and synthesis of new materials to meet specific requirements in polymer technology such as high temperature resistance, synthetic fibers, transportation industries, electrical instruments, etc. On practical side thermal analysis of polymers not only explain the behavior of polymers under conditions of high temperature but also helps in selecting the right kind of materials for the specific uses where high temperatures are encountered. The usage of plastics for mechanical applications offers the parts through design , elimination of finishing operations, simplified assembly, reduced maintenance, weight saving, noise reduction, and freedom from corrosion. The kinetic parameters provide usefulness of the potentially unstable nature of the materials under investigation.

---

13. R. C. Mackenzie, Ed. “Differential Thermal Analysis”, Vol. 182, Academic Press, New York, (1970)
14. H. Nishizaki, K. Yoshida and J. H. Wang, J Appl. Polym. Sci. **15,** 2869 (1980)

Both DSC and TGA are complementary of each other and the combined analyses provide much information on physico-chemical changes in a system during heating. Thus physico-chemical properties of polymers mainly depend on the molecular architecture. This chapter of the thesis is further subdivided into two sections:

SECTION-I: THERMAL PROPERTIES OF COPOLYESTERS

Copolyesters are analyzed by DSC/TGA at a single heating rate in an N_2 atmosphere. The glass transition temperature, thermal stability and kinetic parameters, etc of the copolyesters are determined and discussed in light of structure – property relationship.

SECTION-II: MECHANICAL AND ELECTRICAL PROPERTIES OF COPOLYESTERS

High polymers are well known for their engineering applications as films, fibers, sheets, composites, etc. The use of polymers in engineering as dielectric is becoming increasingly important because dielectric property is a sensitive method of studying polymer structure. In present case the tensile strength, electric strength, and volume resistivity of copolyester films are determined according to standard test methods and discussed their industrial importance.

CHAPTER-5: A BRIEF REVIEW OF THE WORK DONE

This chapter describes a brief output of the work investigated during the tenure of the research programme.

Signature of the Guide **Signature of the candidate**

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Date: 26/06/2006

CHAPTER – 1

LITERATURE SURVEY ON AROMATIC CARDO COPOLYESTERS

CHAPTER - 1

LITERATURE SURVEY ON BISPHENOLS AND AROMATIC CARDO POLYESTERS

SECTION-I: GENERAL INTRODUCTION

Polymers are substances containing a large number of structural units joined by the same type of linkage. These substances often form into a chain-like structure. Polymers in the natural world have been around since the beginning of time. Starch, cellulose, and rubber all possess polymeric properties. Man-made polymers have been studied since 1832. Today, the polymer industry has grown to be larger than the aluminium, copper and steel industries combined.

For living human body or any living things one necessary molecule is required, which is known as protein got synthesized in natural form by reacting simple chemical compound like methane, ammonia and carbon dioxide. The protein is a natural polymer on which the life is supported.

Polymers are also appeared in their other natural forms like wood, cotton, cellulose, starch, etc. Over the many civilizations, however human beings have been finding different ways to meet their basic requirements. Once upon a time the need to cover the body was met by animal skins; it is being met by polyester today. As the time passes people had tried to develop synthetic polymers for the different purposes. “The motivation behind all the research is necessity”.

However, polymers have obviously not been discovered overnight. They come out of long and pressuring study by a host of motivated scientists whose work has enriched life. Today and also in forth coming days, the over all insight into polymer science and technology is so deep that a material scientists can create an almost limitless range of new materials.

The word ‘polymer’ is derived from the Greek words “poly” means many and “mer” means parts. Thus, a polymer is a large number of subunits or building blocks linked together by covalent bonds. According to IUPAC, a polymer is defined as “a substance composed of molecule characterized by the multiple repetition of one or more species of atoms (constitutional units) linked to each other in amounts sufficient to provide a set of properties that do not vary markedly with the addition or removal of one or a few of the constitutional units.” [1]

The synthetic polymers such as polyethylene and polyesters are relatively new comers to the face of earth and are important to mankind. Naturally occurring polymers have been utilized through many centuries by mankind. On close examination the history of polymers goes back farther than that of any group of substance known to man.

A. Bisphenols:

Bisphenols are most widely useful as intermediate for dyes, drugs, varnish and constituent of veterinary medicines, fungistats and pesticides, antiseptic, anticoccidial, lowering serum cholesterol in mammals. Several bisphenols are used as bactericides, disinfectants, agricultural fungicides, herbicides, and drugs for treatment of seborrhea and acne and typical anti-inflammatory agents. Various bisphenols have been shown to be effective fungicides specifically against mildew preventives on cotton fabric and against the fungi that cause peach brown rot.

Bisphenols find their applications as anti-oxidants for rubbers, oils, fats, soaps and carotene; and stabilizers for polyolefin and against UV radiation, and for increasing the flex life of rubbery material. They are also used as fog inhibitors in electrophotography, electroplating solvent and as wash-fastening agents. They are also useful in manufacturing thermally stable polymers, epoxy resins and polyester resins.

---

1. Hans-George Elias, “Macromolecules-I”, Structure and Properties, 2nd Edn., Plenum Press New York, 1984.

Among the monomers with cardo groups, phenolphthalein is probably used alone as a commercial product in analytical chemistry and medicine. Most monomers of the cardo type are obtained by condensation of compounds with carbonyl groups (ketone or their dichlorides, fluorenone, anthraquinone, phthalic anhydride) and phenols, amines, alkyl aromatic compounds, etc., in the presence of Friedel-Crafts catalysts or mineral acids ($AlCl_3$, $TiCl_4$, $ZnCl_2$, $SnCl_4$, H_2SO_4, HCl and others). Monomers of the cardo type possess high melting points, which exceeds those of analogous compounds having no cardo groups.

Cardo bisphenols [2-5] find their industrial usage for the preparation of epoxy resins, polyester resins, and thermally stable polymers and also for the preparation of flame retardant epoxy resins.

---

2. V. V. Korshak, V. A. Sergeyev, V. K. Shitikov and A. A. Severov, ”Thermosetting polymers from phenols of different structure and formaldehyde”, Polymer Sci. U.S.S.R. **9**, 2202, 1967; Vysokomol Soedin, **A-9**, 1952, 1967.
3. V. V. Korshak, V. A. Sergeyev, V. K. Shitikov, A. A. Severov, I. Kh. Nazmutdinova, S. G. Zheltakova, V. F. Burlutskii, B. A. Kiselev and V. V. Yaremenko, “Thermosetting phenolphthalein - based copolymers”, Polymer Sci. U.S.S.R., **10**, 1258, 1968; Vysokomol Soedin, A-10, 1085, 1968.
4. V. V. Korshak, V. A. Sergeyev ,V. K. Shitikov, A. A. Severov, V. F. Burlutskii and S. G. Djeltakova, “Phenol-aldehyde resins”, Polymer Sci. U.S.S.R., **172**, 489, 1962; Bull. Izobr., **13**, 70, 1965; C. A. **63**, 16, 564, 1965.
5. V. A. Sergeyev, V. V. Korshak and V. K. Shitikov, “Thermosetting copolymers of phenol and its derivatives, with formaldehyde”, Polymer Sci U.S.S.R., **10**, 2680 ,1968; Vysokomol Soedin, **A-10**, 2304, 1968.

B. Aromatic cardo polymers

Modern technologies (airspace industry, microelectronics, automotive industry) demand easily processable polymeric materials suitable at broad temperature range involving both cryogenic and temperature as high as 350-400^{o}C. A great variety of cardo polymers has been developed namely: aromatic polyesters, polyarylates, polyamides, polyethers, polyether-ketones, polyimides and other carbon chain polymers [6].

The processing of polymers via melt (injection and pressure molding, extrusion) and/or their solution leads to polymer materials having high thermal characteristics, tough and dielectric properties, improved chemical and radiation resistant. The colorless and transparent films, reinforced plastics, adhesives, coatings, fibers, membranes based on cardo polymers have been formulated.

It is well known fact that the synthesis of polymers with rigid chains having large segments, which increases the glass transition temperature, is one of the ways of obtaining heat-resistant polymers. In some cases the glass transition temperature of polymers with rigid chains can be even higher than the initial decomposition temperature. Thermal stability of polymers will determine the applications of the polymers in different fields.

There are number of factors, which increase the heat resistance of linear polymers: introduction of different cycles to the main chain of macromolecules, increasing the intermolecular interaction due to polar groups and hydrogen bonds, introduction of different side cyclic groups, polymer crystallization, ordering the structures, use of monomers with a symmetrical structure (for instance, terephthalic acid instead of isophthalic acid), formation of chemical cross-links between linear macromolecules, regular arrangement of units in the chain, preparation of stereo regular polymers and, so on.

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6. S. V. Vinogradova, V. A. Vasnev and Ya. S. Vygodskii, "Cardo polyhetero-arylenes. Synthesis, properties, and characteristic features", Russ. Chem. Revs. **65(3)**, 249-277, 1996.

The following factors are mainly responsible for better solubility namely preparation of amorphous polymers, decrease of the rigidity of the macromolecular chain, introduction of polar groups showing affinity for the macromolecular chain, introduction of polar groups showing affinity for the solvent (that is, leading to positive thermal mixing effect), introduction of various substituents containing polar groups showing affinity for the solvent, random position of various units in the back-bone and introduction of dissimilar units.

The introduction of such cyclic side groups is very effective if one of the elements of the cyclic group belongs to the main chain of the macromolecules (that is, the cardo group).

Various properties of polymers are largely dependent upon their chemical structure. Recently much attention is being paid towards polymers containing cardo groups (cyclic side groups in which at least one of the ring atom is a part of the basic polymer chain) as they possess very interesting properties. It has been proposed that such polymers be termed as cardo polymers from the Latin word ‘cardo’ meaning a loop, since such cyclic groups can be considered as loops on the back-bone of the polymer [7].

The properties of cardo polymers largely depend on the back bone structure. The presence of cardo groups in polymers endows them with very specific properties such as enhanced thermal stability together with excellent solubility, which is of great importance in aromatic heterocyclic polymers with rigid chains.

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7. S .V. Vinogradova, S. N. Salazkin, G. Sh. Chelidze, G .L. Slonimsky, A. A. Askadsky, K. A. Bichko, L. I. Komarova, I. V. Zhuraleva and V. V. Korshak, Plast Massy., **8**, 10 , 1971

[C] The aim of the present investigation

Recently much attention is being paid towards polymers containing cardo (Latin meaning a loop) groups [8], due to their excellent physico-chemical properties and promising industrial applications as coatings, adhesives, thermoplastic molding compositions alone or mixed with fillers, films, fibers, packaging, glass reinforced plastics and antifriction self lubricating materials. It has been proposed that cyclic side groups in the main chains are regarded as loops (cardo groups). The introduction of cardo groups in different hetero and carbon chain polymers such as polyesters, polyamides, polyethers, polycyanurates and polysulfonates endow them with very specific properties such as excellent solubility, high flexibility and good thermal and chemical stability, excellent mechanical and dielectrical properties. These characteristics signify the industrial importance of this class of polymers [8].

OBJECTIVES OF THE PRESENT INVESTIGATION

1. To synthesize monomers and aromatic cardo copolyesters.
2. To support the structure of copolyesters by IR and NMR spectroscopy.
3. To elucidate biological activity of cardo copoly esters
4. To characterize polymers by viscosity measurements in different solvents at specific temperature.
5. To determine the density of cardo copoly esters by floatation method.
6. To determine the thermal properties of cardo copoly esters
7. To determine the chemical resistance of cardo copoly esters
8. To determine the mechanical and electrical properties of cardo copoly esters

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8. V. V. Korshak, S. V. Vinogradova, and Ya. S. Vygodskii, J. Macromol. Sci., Rev. Macromol. Chem. Phys. **11**, 45, 1974

SECTION-2: LITERATURE SURVEY ON BISPHENOLS

Bisphenols are the important constituents or intermediates in dyes, drugs, paints and varnishes, coatings, pesticides, plasticizers, fertilizers, bactericides and in other applications. They are widely applied in manufacturing thermally stable polymers, epoxy resins and polyester resins.

Farbenind [9] has reported the condensation of phenols and ketones in the presence of acetic acid and hydrochloric acid at 50°C and also reported the melting point of 1,1'-bis (4-hydroxy phenyl) cyclohexane (186°C), 1,1'-bis (4-hydroxy phenyl)-4-methyl cyclohexane (179°C). The products are useful as intermediate for dyes and drugs.

Mc Greal et. al [10] have reported the condensation of ketones (0.5mole) and phenols (1.0mole) in acetic acid. The solutions were saturated with dry HCl for 3-4h and kept the reaction mixture for varying periods up to 4 weeks until the mass crystallized. The yield with aliphatic and aromatic ketones were 10-25 % and with cyclic ketones 50-80%. They have also proposed the following mechanism

1) The addition of phenol to ketone

$\text{PhOH} + \text{R}_2\text{CO} \text{ ? } \text{R}_2\text{C (OH) C}_6\text{H}_4\text{OH}$

2) $\text{R}_2\text{C (OH)-C}_6\text{H}_4\text{OH} + \text{Ph OH ? } \text{R}_2\text{C (C}_6\text{H}_4\text{OH)}_2 + \text{H}_2\text{0}$

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9. I. G. Farbenind, “Condensation of ketones with phenols”, Fr. Pat. 647,454, 1929 ; C.A. **23,** 2540, 1929.
10. M. E. McGreal, V. Niederl and J. B. Niederl, “Condensation of ketones with phenols”, J. Am. Chem. Soc., C.A. **33**, 2130, 1939.

Johnson and Musell [11,12] have reported synthesis of 1,1'-bis (4-hydroxy phenyl) cyclohexane (I) using 5 moles of phenol, 1 mole of a cyclohexanone, H_2S and BuSH below 40^oC with 0.1 - 0.3 mole dry HCl gave (I) m.p. $186\text{-}187^oC$, 2Me-I $236\text{-}240^oC$; 4-Me-I 178^oC; 1,1'-bis(4-hydroxy-3-methyl phenyl) cyclohexane m.p. 187^oC and 1,1'-bis(4-hydroxy-3-isopropyl phenyl) cyclohexane, m.p. $109\text{-}111.5^oC$. Mash containing small quantity of bisphenol (I) protects chickens from coccidiosis better than does a sulfaguanidine. They have also reported that coccidial infection in poultry may be suppressed by feeding a bisphenol (p-OH $(C_6H_4)_2$-CRR' in which R' is a phenyl or alkyl and R is H or alkyl).

Bender et.al [13] have reported preparation of various bisphenols by reacting phenol, NaOH and acetone. The mixture was refluxed for 16h and acidified to p^H 2-3 with 6 N HCl. The yield was 47.5%. Similarly they have also synthesized 1,1'-bis(4-hydroxy phenyl) cyclohexanane (m.p. 187^oC); 1,1'-bis(3-methyl-4-hydroxy phenyl) cyclohexane (m.p. $186\text{-}189^oC$) and 1,1'-bis(3-chloro-4-hydroxy phenyl) cyclohexane (m.p. $134\text{-}141^oC$).

Bender et.al [14] have reported the preparation of bisphenols by irradiating a mixture of ketone and phenol at $20\text{-}100^oC$ with ß-rays or ultra violet in the presence of 37% aq. HCl or 70% aq. H_2SO_4 as a condensing agent and stirring at $30\text{-}37^oC$. 1,1'-Bis (4-hydroxy phenyl) cyclohexane (m.p. $186\text{-}187^o$ C) was obtained in 93% yield from 1 mole cyclohexanone and 4 moles of phenol.

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11. J.E.Johnson and D.R.Musell, "Bis (hydroxy phenyl) cyclohexane compositions", U.S. Pat. 2,538,725, 1951; C.A. **45**, 4412, 1951.
12. J.E.Johnson and D.R.Musell, "Diphenol compound composition for coccidiosis", U.S. Pat. 2,535,014, 1950; C.A. **45**, 2635, 1951.
13. H.L.Bender, L.B.Conte and F.N.Apel, "Bisphenols", U.S. Pat. 2,858,342, 1958 ; C.A. **53**, 6165, 1959.
14. H.L.Bender, L.B.Conte and F.N.Apel, "Diphenol compound composition for coccidiosis control", U.S. Pat. 2,936,272, 1960; C.A. **54**, 19,604, 1960.

Farbenfabriken [15] has reported the preparation of 4,4'-dihydroxy diphenyl cyclohexane (m.p.186°C) using cyclohexanone (78 kg) and excess phenol (400 kg) in the presence of 38% HCl as a catalyst at room temperature for 6 days.

Tumerman et.al [16] have reported condensation of o-cresol with aliphatic, aromatic and cyclic ketones in the presence of HCl and BF_3 as catalyst. The highest reaction rate was observed in the case of Me_2CO and cyclohexanone. The condensation of o-cresol with pinacolone yielded 10-12% after 450 h of condensation.

Freudewald et.al [17] have reported the condensation of phenol (94 g) with cyclohexanone (98 g) in the presence of 2.0 g EtSH and anhydrous HCl (4.7 g) and heating at 70°C in closed system for 3h to give 97% 1,1'-bis(4-hydroxy phenyl) cyclohexane.

Popova and Nedonoskova [18] have reported the synthesis of monomers by condensing PhOH and o-cresol with cyclohexanone to give 1,1'-bis(4-hydroxyphenyl) cyclohexane and 1,1'-bis(3-methyl-4-hydroxy phenyl) cyclohexane, respectively. These bisphenols are treated with HNO_3 in AcOH at 0°C to give 1,1'-bis(3-nitro-4-hydroxy phenyl) cyclohexane and 1,1'-bis(5-nitro-3-methyl-4-hydroxy phenyl) cyclohexane, respectively, and were reduced with $SnCl_2$ in HCl and with Raney Ni to give 1,1'-bis(3-amino-4-hydroxy phenyl) cyclohexane. These monomers are useful for coordination poly condensation.

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15. Farbenfabriken, "Bisphenols", Ger. Pat. 1,031,788, 1958 ; C.A. **54**, 19,603,1960.
16. B.M.Tumerman, E.S.Gervits and I.V.Vesela, Neffepererabotkai, Naftekhim, Nauchn, Tekhum, **8**, 46, 1965 C.A. **64**, 4977, 1967.
17. Freudewald, E.Joachim, Konrad and M.Fredeic, "p-Phenylphenol", Fr. Pat. 1,537,574 ,1968 ; C.A. **71**, 21,868, 1969.
18. T.K.Popova and G.P.Nedonoskova, "New monomers for coordination polycondensation", Zh. Khim, 5Zh338, 1970; C.A. **75**, 6, 391, 1971.

Alexandru [19] has reported the preparation of bisphenols by reaction of a ketone with phenol, BuSH, $ClCH_2CH_2Cl$ and Me_3SiCl. The mixture stirred and heated to 50-55^{o}C and finally at 65^{o}C to give bisphenol-Z.

Subramaniam et.al [20] have reported the synthesis of 4,4'-isopropylidene bisphenyl dicinnamate, 4,4'-cyclohexylidene bisphenyl dicinnamate, 4,4'-isopropylidene bisphenyldisalicylate, 4,4'-cyclohexylidene bisphenyl disalicylate, dioxyacetic acid and dimethyl ether of bisphenol-A and bisphenol-C. They have tested the compounds for their activity against a fungi Fusarium oxysporum by filter paper disc method and reported that dimethyl ether and the dioxy acetic acid are inactive even at the highest concentration level used, whereas both the esters are active even at the minimum concentration level used.

Rao et.al [21] have reported a convenient method for the preparation of bisphenols. Cyclohexanone was treated with PhOH at 55^{0}-60^{o}C and with o-cresol at room temperature in the presence of HCl and AcOH to give 1,1'-bis(4-hydroxy phenyl) cyclohexane and 1,1'-bis(3-methyl-4-hydroxy phenyl) cyclohexane, respectively.

Garchar et.al [22,23] have studied optimization reaction conditions for the synthesis of 1,1'-bis(R,R'-4-hydroxy phenyl) cyclohexane by condensing

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19. B.S.Alexandru, U.S.Pat. 4,766,255, 1988, C.A. **110**, 38,737, 1989.
20. G.Subramaniam, R.Savithri and S.Thambipillai, "Synthesis and antifungal activity of bisphenolic derivatives", J. Indian Chem. Soc., **66**, 797, 1989.
21. M.V.Rao, A.J. Rojivadiya, P.H.Parsania and H.H.Parekh, "Convenient method for the preparation of the bisphenols", J. Ind. Chem. Soc., **64**, 758, 1987
22. H.H.Garchar and P.H.Parsania, "Optimization reaction conditions for synthesis of 1,1'-bis (4-hydroxy phenyl) cyclohexane", Asian J. Chem., **6**, 135, 1994.
23. H.H.Garchar, S.H.Kalola and P.H.Parsania, "Synthesis and evaluation of bisphenol-C and its derivatives as potential antimicrobial and antifungal agents", Asian J. Chem., **5**, 340, 1993.

cyclohexanone (0.05 mole) and phenol, o-cresol and 2,6-dimethyl phenol (0.1mole) in the presence of varying mixture of hydrochloric acid and acetic acid (2:1 V/V) at four different temperatures; 40^{o}, 50^{o}, 60^{o}, 70^{o}C . They have reported optimum concentration (10-15ml), time (30-90min) and temperature (55-70^{o}C) for obtaining yields greater than 80%. They have also synthesized chloro, bromo and nitro derivatives and screened for their potential antimicrobial and antifungal activities against different microbes. Some of these compounds are significantly found active against B. subtilis, S. pyrogens and A.niger. The nitro compounds are found to be the most active as antifungal agents.

Smirnova and Robas [24] have reported acidity constants of chlorine containing bisphenols. The p^{K} values for the first and second ionization of bisphenol-A, bisphenol-C and bisphenol-S derivatives are reported. Introduction of a Cl atom into the parent molecule decreases the 1st and 2nd p^{K} values where as introduction of a Me group increases the p^{K} value.

Farbenfabriken [25] has reported chlorination of bisphenols by chlorine gas with stirring for 1 h at 15^{0}C in nitrogen atmosphere and steam distillation of 1,1’-(4-4’-dihydroxydiphenyl) cyclohexane gave 1,1’-(3,3’,5,5’–tetrachloro 4,4’-dihydroxyphenyl) cyclohexane (m.p. 148.5-149.5^{0}C) .

Nayef S. Al-Muaikel [26] has reported the preparation of 2,5-bis (p-hydroxybenzylidene)cyclopentanone I, 2,6-bis(p-hydroxybenzylidene)cyclo hexanone II, 2,6-divanillylidenecyclohexanone III or 2,7-bis(p-hydroxy benzylidene)cycloheptanone IV were synthesized by the condensation of two moles from p-hydroxybenzaldehyde or vanillin with one mole of cycloalkanone

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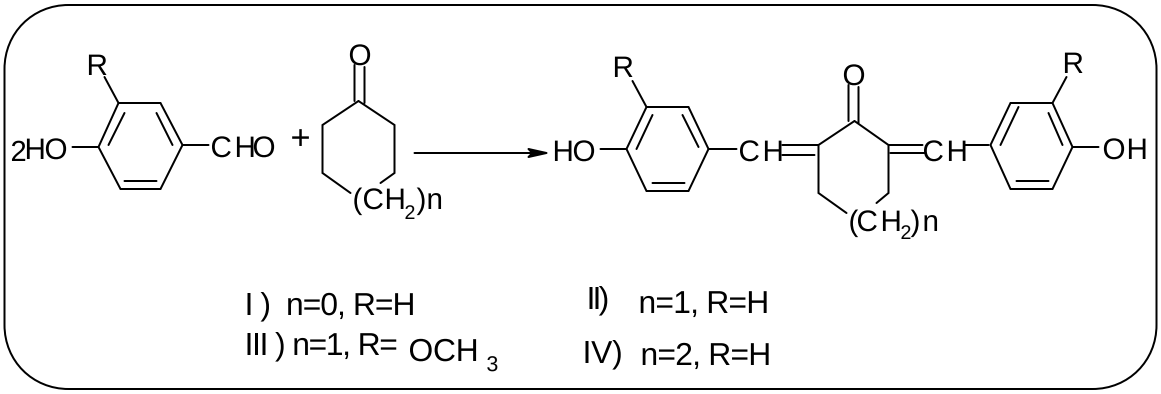
24. O.V.Smrinova and E.Ya. Robas Zh.Prikl Khim, **48** , 578, 1975 ; C.A. **82**,139,009, 1975.
25. Farbenfabriken, “Ring-halogenated dihydroxydiarylalkanes", Ger. Patent 1,073,504, 1958, C.A. **55**, 16,491, 1961.
26. Nayef S. Al-Muaikel ,” Synthesis and characterization of new unsaturated polyesters and copolyesters containing azo groups in the main chain” , Eur. Polym. J., **39**, 1025–1033, 2003.

was dissolved in 100 ml ethanol at 50^0C. The warmed reaction mixture was stirred, while dry hydrogen chloride gas was introduced as a catalyst. After 2h of stirring, a solid product separated out. The solid material was filtered off, washed with several portions of water, dried, and recrystallized twice from dioxane; yield 89%.



SECTION-3: POLY ESTERS

Polyesters are heterochain macromolecular substances characterized by the presence of carboxylate ester groups in the repeating units of their main chain. The traditional procedure for preparing linear aliphatic polyesters consists in the thermal polycondensation of diacids with diols, or in the self-condensation of hydroxyacids followed by the elimination of water.

Polyesters have received a great deal of attention since the early work of Carothers, who initiated study on many step-growth polymerizations [27].

The first fiber-forming polyesters were prepared by Carothers and Hill in the late 1920s using the melt condensation of dicarboxylic acids and aliphatic diols [28]. In the early 1940s, Whinfield and Dickson discovered the fiber- and film-forming poly(ethylene terephthalate) (PET), which possessed a higher melting point and displayed better chemical resistance due to the presence of more rigid groups (e.g., phenylene) in the backbone, is now the most important member of polyester group by production volume and sales value [29]. PET was first commercialized by ICI (Imperial Chemical Industries, Ltd.) as “Terylene”.

Today, polyesters are widely used as both important thermoplastic and thermosetting materials.

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27. W.H. Carothers, “Studies on polymerization and ring formation I. An introduction to the general theory of condensation polymers”, J. Am. Chem. Soc. , **51**, 2548, 1929.
28. F. M.Herman, G.Norman, M.B.Norbert, Encyclopedia of Polymer Science and Technology, p 2, 1964
29. T. E.Long, S. R.Turner, “Applied Polymer Science 21st Century”, Craver, C. D.; Carraher, C. E., Elsevier, p979, 2001.

The common methods of synthesizing polyesters are as under:

a. By condensing dibasic acid with diol [30].

b. By the self condensation of dihydroxy acid to form linear polyesters [30].

c. By the action of dihydroxy compounds and diacid chlorides. There are three general methods of preparing polyesters from diacid chlorides [30].

    (i) Fusion of the two reactants and removal of HCl as it forms.

    (ii) Condensation in solution with HCl being removed by distillation or by salt formation with added base.

    (iii) Interfacial polymerization: solution of dihydroxy compounds in aqueous base and diacid chloride in an inert solvent are brought into contact, allowing polymer formation at the interface.

The technique of interfacial polymerization is quite different from the bulk and solution polycondensation methods and is only applicable to very fast reactions to obtain very high molecular weight polymers.

The most important polyesters formed from diacid chlorides are the polycarbonates which have achieved enough commercial significance.

Mitrach et. al [31] have prepared acid chlorides from dicarboxylic acids. Thus, 2 mol of the respective dicarboxylic acid was refluxed with thionyl chloride (800 ml) and dry dimethylformamide (DMF, 2ml). After 5h the excess of thionyl chloride was distilled off and the residue was washed with dry hexane.

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30. P.W.Morgan , “Condensation polymers by interfacial methods”, Wiley Interscience , New York, 1965.

31. K. Mitrach, L.Pospiech, L.Haubler, D.Voigt, D.Jehnichen and M.Ratzsch, “Thermotropic block copolymers: polyesters with flexible poly(tetramethylene glycol) units in the main chain", Polymer, **94**, 3469, 1993.

SECTION-4: AROMATIC CARDO POLY ESTERS

As far back as the 1930's in enumerating various monomers such as diols, Wagner [32] reported the possibility of using phenolphthalein in polyesters synthesis. Some early papers were devoted to formaldehyde polymers of phenolphthalein [33-37]. In 1946, the syntheses of alkylated polymers of fluorescein and phenolphthalein [38] was reported and two years later polymers were obtained by polymerization of diallyl phenolphthalein dicarbonate[39].

Later, data reported the semi conducting properties of epoxy polymers based on phenolphthalein [40-44] were published. Characteristic of such investigation is the fact phenolphthalein-a monomer in polymer synthesis was used as one of the representative of a vast diol series without regard to its specific contribution to polymer properties.

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32. F.C. Wagner, "Synthetic resins", U.S.Pat., 2, 35, 578, 1936; C.A.. , **30,** 3, 542, 1936.
33. R.H. Kienle, Ind. Eng. Chem., **22 ,** 590 , 1930.
34. S.L. Bafna and H.A. Shah, "Ion exchangegers. II Phelopthalein-formaldehyde resins", J.Sci. Ind . Res. , **138** , 48, 1954; C.A.., **49,** 7,777, 1955.
35. S.L. Bafna and H.A. Shah, "Ion exchange resins", Ind. Pat., **44**, 359, 1952; C.A.. , **47,** 798, 1953.
36. S.L. Bafna and H.A. Shah, J.Ind. Chem .Soc., **29** ,611, 1953.
37. S.L. Bafna and H.A. Shah, "Iminodiacetic acid derivatives", Swiss Pat., 2,92,453,1953; C.A.., **48** , 6,326 ,1954.
38. I.F.Morozov , Chem. Prom., **11** , 22, 1946; **41** , 3,995 ,1947.
39. J.A.Brally and F.B. Poppe , Brit. Pat. , 611,539 ,1948. C.A. **43 ,** 4,398, 1949.
40. E.S. Lo, Ind. Eng. Chem. , **52** ,319 ,1960.
41. E.S. Lo , "Epoxy-resin composition", U.S.Pat., 3,015,648 ,1962; C.A. , **56** , 11,793 ,1962.
42. E.S. Lo , Ger. Pat, 1,132,728 ,1962; C.A. , **57** , 1,687 ,1962.
43. E.S. Lo, "Hardners for epoxy resins", U.S.Pat., 3,008,925 ,1962; C.A. , **56**, 4,974 ,1962.
44. E.S. Lo, "Curable product from a halohydrin and phenol condensation product", U.S.Pat., 3,015,647 ,1962; C.A. , **56** , 8,928 ,1962.

The syntheses of high molecular weight polyesters of phenolphthalein and various diacids performed in 1961, may be thought as the beginning of systematic purposeful investigation in the field of cardo polymers. Essentially for the first time; attention was drawn to the specific role of the cardo phthalide groups in the development of the properties of hetero chain polymers [45-46].

Many cardo polymers with esters, amide, imide 1, 3, 4,-oxadiazole, ether and other groups have been synthesized, and the number is growing each year. The introduction of cardo groups into the polymer chains of polymer such as aromatic polyesters, polyethers, aromatic polyamides, heterocyclic polymers [47-48]. Cardo chain polymers endow them with some specific properties. These polymers made it possible to investigate such characteristics, which could not be evaluated on polymers having no such groups.

Vinogradova et.al [49] have reported the aromatic cardo polyethers of phenolphthalein prepared by a nucleophilic substitution reaction of activated aromatic dihalogen compounds and alkali-metal bisphenoxides in DMSO.

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45. V. V. Korshak, S. V. Vinogradova and S. N. Salazkin, Avt. Svidet. USSR, **140,** 990, 1961; Bull. Izobr. , **17**, 51, 1961.
46. V. V. Korshak, S. V. Vinogradova and S. N. Salazkin, “Polyester of aromatic dihydroxy condensed ring compounds” Vysokomol Soedin, **4** , 339, 1962 ; C.A. , **58** , 3,513 ,1963.
47. V. V. Korshak, “Heat stable polymers”, Thermostokie Polymery, p. 411, Nauka, Moscow. 1969.
48. V. V. Korshak, “Thermostable polymers”, Thermostokie Polymery, Izd. Khimiya, Moscow, 1969.
49. S. V. Vinogradova ,S. N. Salazkin, A. A. Kulkov and V. V. Korshak, “Aromatic polyethers of the cardic type”, Polym. Sci. USSR. , **14**, 2962, 1972; Vysokomol Soedin, **A14**, 2, 545, 1972.

The formation of polyethers with use of cardo bisphenols (phenolphthalein and phenol such as 4,4’- dihydroxy diphenyl- 2,2’- propane (Bisphenol-A), which can arise both from the lower reactivity of the first bisphenoxides because of high acidity of bisphenol monomers[50] and from the heterogeneity of the reaction medium due to poor solubility of such metal phenoxides. In the earlier days phenolphthalein was used to prepare cardo polymers [51-57].

After that 2,2’-bis(p-hydroxy phenyl)propane(Bisphenol-A) has come into existence for the preparation of the polyesters in 1961 [58].

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50. V.V. Korshak, A.P. Kreshkov, S.V. Vinogradova, N. Sh. Aldarova, Vasnev, E.L. Baranov, M.V. Slavgorodskoya, A.I. Tarasov and T.I. Mittaishvili, “Acidity constants of some bisphenols”, Org. Ractivity, **7**, 285 ,1970; C.A. **74** ,13,539 ,1971.
51. S.V.Vinogradova, V.V. Korshak and S.N.Salazkin., “Heterochain polyesters”, C.A., **56** , 11,792 ,1962.
52. V.V. Korshak, S.V.Vinogradova and M.A.Iskenderov, “Polyester of aromatic dihydroxy condensed ring compounds” C.A., **58** , 3,513 1963.
53. S. Fujisawa, S.I. Oniwa and Y.Matswda, Jap. Pat., 11,297 ,1963; C.A., **59** , 1,03,209, 1963.
54. S.V.Vinogradova, V.V. Korshak, S.N.Salazkin and S.V.Bereza, “Heterochain polyesters—LX. Polyarylates based on phenolphthalein anilide” ,Vysokomol Soedin, **6(11),** 1,555 ,1964; C.A., **61** , 16,169 ,1964.
55. G.I.Timofeeva, L.V.Dubrovina, V.V.Korshak and S.A.Pavlova, “Viscometric properties of polyarylates” , Vysokomol Soedin, **6(11),** 2,008 ,1964; C.A., **62** , 6,573 ,1965.
56. V.V. Rode, A.S.Yarov and S.R.Rafikov, Vysokomol Soedin, **6(12),** 2, 168, 1968; C.A., **63**, 1, 889 ,1965.
57. V.V.Korshak, S.V.Vinogradova, V.A.Vasnev and T.I.Mitaishvili, “Synthesis of polyarylates under heterogeneous conditions”, Vysokomol Soedin, **A_{11}(1),** 81 ,1969; C.A., **70**, 68,813 ,1969.
58. B. E. Jennings, Brit. Pat., 902121, 1965; C.A., **57** , 12,724 ,1962.

Korshak et.al [59] have studied the effect on solubility and softening points for polyesters based on the para isomers of $CH_2(C_6H_4OH)_2$, $(CH_3)_2C(C_6H_4OH)_2$, $Ph_2C(C_6H_4OH)_2$, 3,3'-bis(4-hydroxyphenyl) phthalide as the phenolic components and iso or terephthalic acids. Generally isophthalides are mechanically weaker than the terephthalates. Products from bisphenols with bulky groups at the central carbon atom displayed improved solubility in organic solvents, lower crystallinity and relatively better thermal stability.

Corporation [60] has reported the syntheses of linear sulfur containing aromatic copolyesters. The polymer containing $-SO_2O-$ and O-(C:S-)-O- groups and having reduced viscosity of 0.3 dl/g (in CCl_4 at 25^0C) were prepared by treating diphenyl with diacid chloride in an inert solvent in the presence of at least stoichiometric amount of triethylamine. When triethylamine was replaced by pyridine, dimethylaniline or 2, 5-lutidine, low molecular weight polymers were obtained. Thus, 0.11 mole Et_3N was added to a vigorously stirred mixture of 0.05 mole bisphenol-A and 0.015 mole 4, 4'-biphenyl disulfonyl chloride in 130 ml CH_2Cl_2. The mixture was cooled at 20^0C and solution of 0.035 mole isophthaloyl chloride in 10 ml CH_2Cl_2 was added and the mixture was stirred for 20 min. In place of triethyl amine, other organic bases like tetrabutyl amine, N-methyl piperazine, N,N'-dimethyl piperazine, N,N'-methyl morpholine, N,N'-dimethyl benzyl amine were also used and the highest intrinsic viscosity was observed in case of dimethyl piperazine (0.44 dl/g).

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59. V.V. Korshak, S.V.Vinogradova, and V.A. Pankratov, "The effect of the structure of bisphenol raw materials on the properties of aromatic polyesters", Polym. Sci. USSR., **156(4),** 880, 1964; C.A., **61**, 8, 419, 1964.
60. B. W. Corporation, Neth . Appl. Pat., 6,557, 157, 1966; C.A. **66**, 3, 016 , 1967.

Andre and Leonard [61] have reported the preparation of polyterephthalate of bisphenol-A of high molecular weight by interfacial polycondensation using water-dichloromethane as a solvent system in the presence of catalysts such as quaternary phosphonium compounds containing $PhPOCl_2$ at low temperatures (0-5^{0}C).

Koshak et.al [62] have studied the effect of the tertiary amines on the formation of polyarylates in low temperature polycondensation. At 2:1 triethyl amine-terephthaloyl chloride ratio, 95 % polymer of inherent viscosity 0.86 dl/g is observed. Low yields and low viscosity polymers formed in the presence of pyridine, $PhNEt_2$, dimethyl cyclohexyl amine with bisphenols.

In further development several scientists [63-65] have established the experimental conditions for the preparation of cardo polyesters from bisphenol with high flexibility and high thermal stability.

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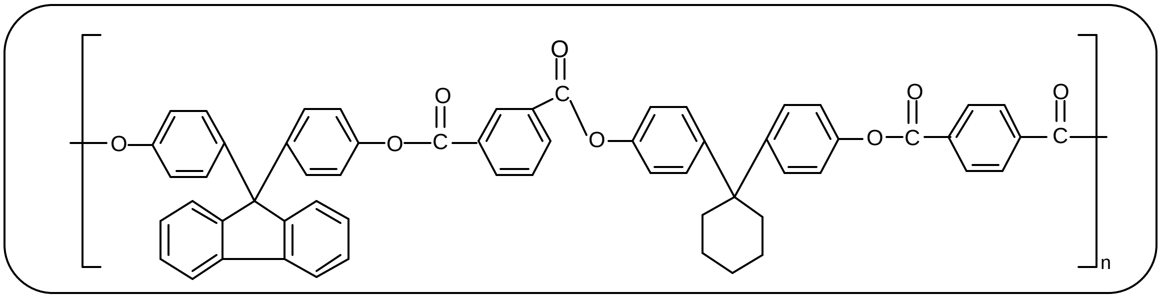
61. C.J. Andre and D. M.Leonard, "High molecular weight copolymeric polycarbonates", Ger. Pat. , 1,199, 500, 1961; C.A. **63** , 16,502 ,1965.
62. V.V. Korshak, V.A. Vasnev, S.V.Vinogradova and T.I. Mitaishvili, "Study of structure formation in polyarylates of bis-(4-hydroxyphenyl)-2,2-propane and its ring-substituted derivatives", Vysokomol Soedin, **A10(9),** 182 ,1968; C.A., **70**, 12,032 ,1969.
63. N.Royji, E.Yu and M. Kenichi, Jap. Pat. , 6,924,113 ; C.A., **72** , 4,435 ,1970
64. H.G. Weyland, C.A.M.Hoefs, K.Ynlema and W.J.Mija, Eur. Polym. J., **6(10**), 1,339, 1970.
65. H.Ulrich, L.Guenther, S.Herman and W. Kurt, "Halogen containing aromatic polyester carbonates". Ger, Offer, 2,052,378, 1970; C.A., **77**, 49,131, 1972.

Nakamura and Watose [66] have reported the synthesis and properties of poly(iso-terephthalate) of bisphenol-C.



They have used tetrachloroethane and water as an interface system and sodium lauryl sulfate as an emulsifier. It was observed that as the reaction temperature is increased the intrinsic viscosity of the polymer found to be decrease, i.e. at 0^0C [?] 1.21 dl/g, where at 26^0C 0.41 dl/g.

Akin George [67] has prepared amorphous, high softening homogeneous polyester from mixtures of bisphenol-A - isophthalic acid – terephthalic acid copolymer and bisphenol-A - isophthalic acid polymer at 370^0C with inherent viscosity 0.63 dl/g and tensile elongation 80%.

Shiozaki et.al [68] have reported heat and light resistant aromatic poly (ester-carbonates) from tetrabromo and tetrachloro- bisphenol A with different acid chlorides.

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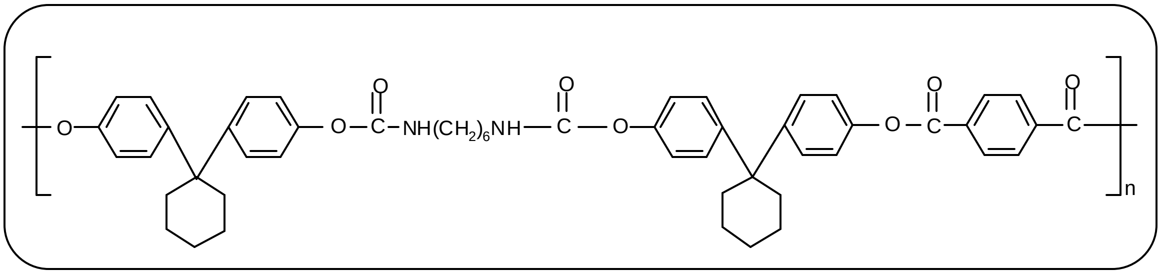
66. N.Tadayoshi and W. Hideo, “Poly(phenyl esters) for films and other molded products from difunctional phenols and dicarboxylic acid chlorides”, Japan, Kokai, **990**, 7,242, ,1971; C.A., **79** ,54,272 ,1973.
67. A. George, “High softening non crystalline condensation copolymers”, U.S. Pat., 3,728,416, 1973; **C.A., 79**, 19, 406, 1973.
68. M. Shiozaki, S.Tsuneo, T.Takeshi and F.Kazutoshi, “Heat and light resistant, aromatic poly (ester carbonates)”, Japan, Kokai, 7,347, 598, 1971; C.A., **80**, 27,682,1974.

Mikiteev et.al [69] have synthesized and studied the properties of polyurethane arylate based on 4,4'–dihydroxydiphenyl-1,1'-bis(cyclohexyl phenyl) ester of hexamethylene dicarbamic acid and terephthalic acid chloride.



Hazama et.al [70] have carried out the preparation of aromatic polyesters with controlled molecular weight by interfacial polymerization of an organic solution of an organic solution of a mixture of terephthaloyl chloride and isophthaloyl chloride with an aqueous alkali solution of bisphenols such as bisphenol- A, halogenated bisphenol –A, and bisphenol-S in the presence of p-methoxy phenol as a viscosity stabilizer.

Turska and Rozyeka [71] have carried out the polycondensation of terephthaloyl chloride with bisphenol-C, bisphenol-A and 2, 2'-bis (4-hydroxy-3-chlorophenyl) propane (Bisphenol-B) in the presence of triethyl amine by thermo-mechanical method using a colvet type calorimeter.

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69. A.K.Mikiteev V.V.Korshak and Z.I.Afaunova, "Synthesis and properties of polyurethane acrylate based on 4,4'-dihydroxy diphenyl -1,1' [bis (cyclohexyl phenyl)] ester of hexa methylene dicarbamicacid and terephthalic acid dichloride", Fiz. Khim Polim., **1**, 112 ,1973; C.A., **85** ,63,358 ,1976.
70. K .Hazama, N.Hiroshi, N.Kazuhiko and Y.Keniji, "Aromatic polyesters with controlled molecular weight", Japan, Kokai, 7,623, 595 ,1976; C.A., **85** ,6,364 ,1976.
71. E. Turska and R. B. Rozyeka, "Application of a thermochemical method for studying a low-temperature polycondensation process." Polymer, **21(10)**, 1,190, 1980.

Shah and Shah [72] have prepared copolycyanurate by interfacial polycondensation of 2-methoxy-4,6-dichloro-s-triazine (MDT) jointly with bisphenol-A and bisphenol-C using a chloroform–water system and different molar proportions of the reactants to get high polymer. The copolymer compositions of the tercopolymer samples were estimated by the analysis of NMR spectral data. They have studied the solution properties of polymer prepared.

Morgan [73] has reported the softening point 375^0C and 400^0C of 9,9'-bis(4-hydroxyphenyl) anthrone-10 isophthalate and 9,9'-bis(4-hydroxy phenyl) anthrone-10 terephthalate copolyesters, respectively.

Jedlinski and Danuta [74] have observed three step thermal degradation of polyterephthalate of bisphenol-A i.e., at 300^0C slow decomposition, $560\text{-}600^0$C rapid decomposition and was completely decomposed at 890^0C. Keck [75] has reported the softening point 188^o C and crystallization point 350^oC of 2,2'-bis(4-hydroxy phenyl) propane isophthalate and 2,2'-bis (4-hydroxy phenyl) propane terephthalate copolymer.

Slonimski et.al [76] have reported glass transition temperature 240^o C of the polyarylate obtained by the condensation of phenolphthalein with isophthalic acid.

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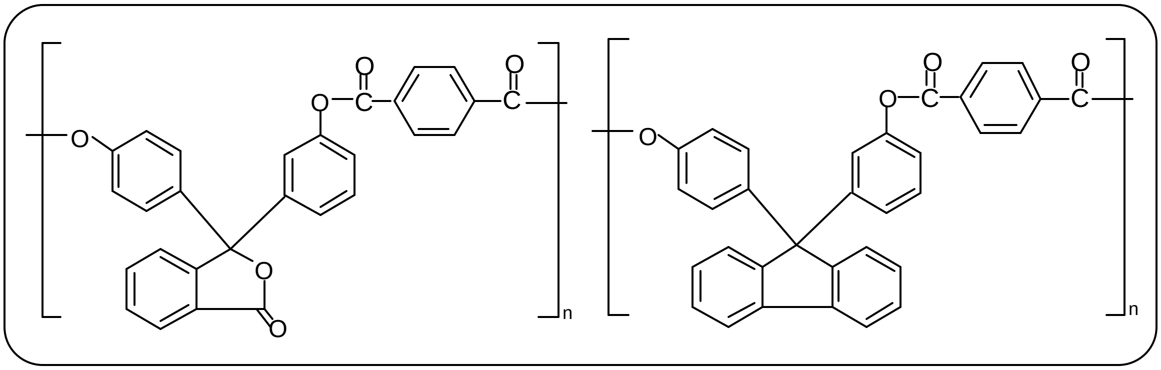
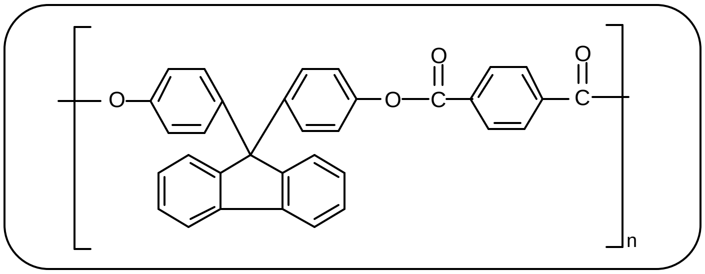
72. N.A. Shah and P.P. Shah, J.Macromol. Sci.-Phys., **B23(4-6)**, 383 ,1985.
73. P.W.Morgan, "Aromatic polyesters with large cross-planar substituents" Macromolecules. **3,** 536, 1970.
74. Z. Jedlinski, S.Danuta, Polimery, **14(3),** 105-10, 1969; C.A., **71**, 35,934 ,1969.
75. M. H. Keck,"Biphenyl terephthalate - biphenyl isophthalate copolyesters", U.S Pat., 3,133,989; C. A., **61**, 13,500, 1964.
76. G.L.Slonimskii, V. V. Korshak, S. V. Vinogradova, A. I. Kitaigorodskii, A. A. Askadsky, S. N. Salazkin and E. M.Belavtseva, "Physical-chemical regulation of super molecular structures and mechanical properties of amorphous polyacrylate", Dokl. Akad. Naut. USSR., **156 (4)**, 924 ,1963; C. A. **61**, 9,631 ,1964

Rode et.al [77] have studied thermo-oxidative degradation of polyarylates I & II. The study of aging process of polyarylates at low-degree of conversion showed that cross-linking predominates during both thermal and thermo-oxidative processes. They have also reported the degree of cross-linking and cross-linking density according to Flory.



Korshak et.al [78] have reported the properties of polyarylate D-9 (Ia) prepared from 9, 9' –bis(4-hydroxy phenyl) fluorine (II) and terephthalic acid.



According to them D-9 films are stable up to < 350^{o} C and have excellent dielectric properties over a broad temperature range. The biphenyl radical at central C increased the resistance of D -9 against UV irradiation. They have also synthesized 1a from terephthaloyl chloride (II) and other bisphenols, and from $COCl_2$ and II. They have studied physico-chemical properties of (Ia).

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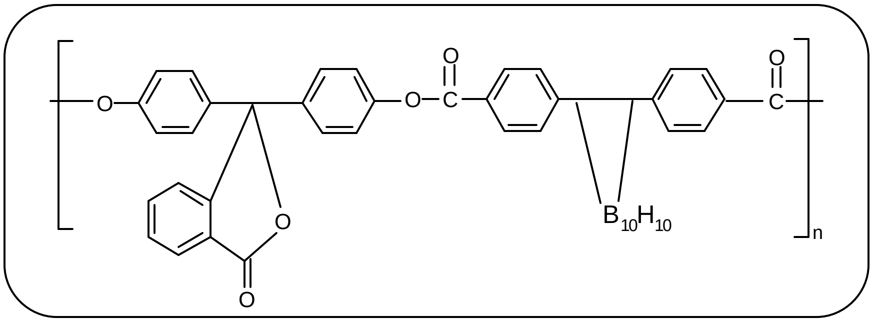
77. V. V. Rode, S. R. Rafikov and I. V. Zhuravleva, J. Polym. Sci. Part-C, **16,** 3255-63, 1965; C. A. **70**, 4, 755, 1969.
78. V. V. Korshak, S. V. Vinogradova and V. A. Pankratov, Dokl. Akad. Nauk. USSR., **181(6),** 1,339 (Russ) ,1968; C. A. **70**, 12,08, 669 ,1969

Korshak et. al [79] have reported synthesis of six high molecular weight polyarylates of carborane by low temperature or high temperature polycondensation of 1, 2-bis [(4-chloro-carbonyl) phenyl]-o-carborane and bisphenols. The polyarylates have high softening point, soluble in dichloroethane and chloroform, high tensile strength and thermal stability and four polyarylates have crystalline structure.



Vinogradova et.al [80] have reported polyarylates by high and low temperature polycondensation in solution and also by interfacial polycondensation from 9, 9'-bis(4-hydroxy phenyl) anthrone-10 and aromatic dicarboxylic acids. It is shown that the presence of anthrone ring in these polyarylates imparts high heat resistance to the polymers, while maintaining good solubility in various solvents.

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79. V.V.Korshak, S.V.Vinogradova, A.I.Kalachev, P. M. Valetskii and V. I. Stanko, "Some correlations in the synthesis of polyarylates from dichlorodiphenylolpropane in the presence of triethylamine", Vysokomol Soedin, Ser A, **15(A),** 848-53(Russ), 1971; C.A. **75**, 49, 700, 1971

80. S. V. Vinogradova, S. N. Salazkin, L. A. Beridze, A. I. Mzhel'skii, A. A. Askadskii, G. L. Slonimskii and V. V. Korshak, "Side reactions in low-temperature polycondensation", Polym. Sci. USSR. **11**, 1327, 1969

Conix and Laridon [81] have reported the preparation of high molecular weight thermoplastic mixed polyester with improved solubility in organic solvents, water resistant and having viscosity > 0.40 dl/g at 25^{o} C in sym. tetrachloroethane. Thus, interfacial polycondensation of a solution containing 0.02 mol bisphenol-A in 1.089 N NaOH (37.2 ml) added dropwise to a CH_2Cl_2 solution containing 0.01 mole, 4, 4' diphenyl disulfonyl chloride and 0.01 mole 4, 4'-diphenyl dicarboxylic acid chloride using 0.1 g benzyl trimethyl ammonium chloride as an emulsifier. The copolymer had viscosity of 1.62 dl/g and formed flexible films from CH_2Cl_2 solution.

Bajaj et.al [82] have synthesized copolyesters by interfacial polycondensation of 2,2'-bis(4-hydroxyphenyl)-propane or phenolphthalein as an aromatic diol and ethylene glycol or polyethylene glycol as an aliphatic diol in various mole ratios with terephthaloyl or isophthaloyl chloride. Chemical compositions, dilute solution viscosities and solubility behavior of these polymers have been investigated. The introduction of aliphatic diol in aromatic polyesters influences T_g, softening point, chemical resistance and thermal stability.

Bajaj and Khanna [83] have synthesized aromatic-aliphatic copolyesters, using hydroquinone, resorcinol, 4,4'-dihydroxybiphenyl (DHBP), 2,2' bis(4-hydroxyphenyl) propane and 4,4'-dihydroxydiphenyl sulphone (DHDPS) as bisphenols and ethylene glycol as a diol, have been synthesized by interfacial, low temperature and high temperature solution condensation. Relative reactivities of these bisphenols and ethylene glycol have been evaluated by various polycondensation methods at a fixed ratio of bisphenol/glycol. Decrease in the extent of polymerization and viscosity was observed by incorporation of aliphatic diol. Viscosity was also influenced by the chemical structure of the bisphenol.

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81. A.Conix and U. L. Laridon, "High molecular weight, thermoplastic mixed polyesters" Ger. Pat., 1,445,384 , 1975; C. A. **84**, 45,921 ,1976

82. P. Bajaj, D. N. Khanna and G. N.Babu., "Aromatic-aliphatic copolyesters—I. Synthesis and characterization" Eur. Polym. J., **15**, 1083-1088, 1979.

83. P. Bajaj and D. N. Khanna, "Aromatic-aliphatic copolyesters—II. Various polycondensation processes", Eur. Polym. J. ,**17**, 275-279, 1981

Kricheldorf et.al [84] have prepared homo- and copolyesters made up by terephthalic acid (T) on the one hand, and ethylene glycol (Et), diethylene glycol (Di), triethylene glycol (Tr), 1,4-butanediol (Bu) and 1,6-hexanediol (He), on the other hand, were investigated by means of 60, 90, 250 and 400 MHz ^{1}H NMR spectra or by 22.63 MHz ^{13}C NMR spectra. Copolyesters of ethylene glycol and oligo (ethylene glycols) can be analyzed by means of ^{1}H NMR spectra because of the fact that the terephthalic acid protons are sensitive to sequence effects, while the ^{13}C NMR signals are insensitive.

Ponnusamy et.al [85] have prepared random copolyesters from dimethyl terephthalate (DMT), ethylene glycol (EG) and butane1,4-diol(BD) by melt-polycondensation technique, using varying amounts of EG and BD. Compositions have been established by ^{1}H NMR spectroscopy. Intrinsic viscosity and number average molecular weight were measured. Thermal properties have been studied by differential thermal analysis. Melting and crystallization temperatures and thermodynamic parameters are discussed in terms of structural differences, particularly the effect of composition and chain flexibility. The degree of crystallinity from differential thermal analysis, IR and wide angle X-ray scattering (WAXS) are discussed.

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84. H. R. Kricheldorf, M.Droscher and W. E. Hull, "^{1}H NMR sequence analysis of poly(ethylene terephthalates) containing various additional diols" , Polym. Bull. , **4**, 547 - 554, 1981.

85. E. Ponnusamy, C. T. Vijayakumar, T. Balakrishnan and H. Kothandaraman "Preparation and characterization of poly (ethylene/tetramethylene terephthalate) copolyesters", Polymer, **23**, 1391-1394, 1982.

Tsvetkov et.al [86] have investigated the hydrodynamic (sedimentation, diffusion, viscometry) and optical (birefringence) properties of solutions of aromatic copolyesters obtained by polycondensation of three components terephthaloyl chloride, 4,4'-dihydroxy 1,1'-dinaphthoyl and 2,2'- propane diol for different molar ratios. A quantitative molar evaluation of the parameter of equilibrium rigidity of the copolymers the length of the statistical Kuhn segment is made.

Pramanick and Ray [87] have reported the syntheses of copolymers derived from a-amino dicarboxylic acid with 1,2-ethane diol,1,3- butane diol, 1,4-butane diol, 1,6- hexane diol and glycerol to get copolyesters I, II, III, IV and V, respectively. The polymer samples have been characterized by their number average molecular weight ($\bar{M}_n$), elemental analysis and their IR spectra. The copolyester V is crosslinked. All of the copolyesters I–V undergoes slow hydrolytic degradation in aqueous solution at ambient temperatures as studied by the measurement of the decrease in reduced viscosity and increase in specific conductance of their aqueous solutions. They are also degraded in aqueous suspension by the fungus *Aspergillus niger* and by the bacterium *E. coli*. Degradation by *Aspergillus niger* mainly depends on the polarity of the polymers, the more polar polymers being less degradable.

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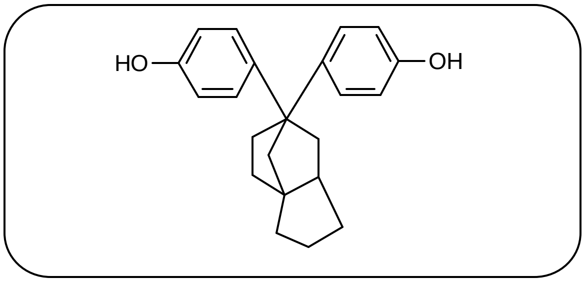
86. V. N. Tsvetkov, L. N. Andreyeva, S. V. Bushin, A. I. Mashoshin, V. A. Cherkasov, Z. Yedlinski and D. Sek, "Conformational properties of aromatic terephthalic acid polyesters" , Polym. Sci. U.S.S.R., **26**, 2569-2578, 1984.
87. D. Pramanick and T.Ray, "Synthesis and biodegradation of polymers derived from aspartic acid", Biomaterials, **8**, 407-410, 1987.

Vinogradova et.al [88] have reported the synthesis of mixed polyarylates of 5, 5'-bis (p-hydroxy phenyl) hexahydro-4, 7- methanoindane (I), hydroquinone (II) and terephthaloyl chloride (III) or sebacoyl chloride (IV) by low temperature solution polycondensation. According to them m.p. and solubility are dependent on the monomer ratio and long blocks of homopolymers in the polymer chain. II is more reactive towards III than I. They have observed the change in polymer structure with variation in monomer ratio, condensation temperature, and sequence of monomer addition.



According to them low temperature polymerization of I, II and III causes the m. p. to decrease without change in the specific viscosity, which is attributed to the exchange reaction in which sequence of I and II in the copolymer chain changes.

Rao et.al [89] have reported the synthesis and properties of cardo polyester (I) of 1,1'-bis(3-methyl) 4-hydroxy phenyl cyclohexane with isophthaloyl and terephthaloyl chlorides. They have observed that I has good solubility range, good thermal, mechanical and dielectric properties.

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88. S.V.Vinogradova, V.V. Korshak, G. Sh. Papava, N. A. Maisurade and P. D. Tsiskarishvili, Vyskomol Soedin, Ser. A. **14(11),** 2,301-5(Russ); 1972; C. A. **78**, 98,081 ,1993.
89. M.V.Rao, A.J.Rojivadia, P.H.Parsania and H. H. Parekh, "Synthesis and characterization of the poly 1,1'-bis (3-methyl-4-hydroxyphenyl) cyclohexane iso-terephthalate"**,** J. Macromol. Sci. Chem. **A27(1),** 53 ,1990; C. A. **112**, 1,59,057 ,1990.

Rao et.al [90] have reported synthesis and properties of cardo polyester based on 1,1'-bis(3-methyl-4-hydroxy phenyl) cyclohexane and isophthaloyl chloride (I) and terephthaloyl chloride (II). They have concluded that the polyester based on II is more thermally stable (400°C) than that of I (300°C). Polyester based on II involved two steps degradation. Polymer based on II has limited solubility in common organic solvents. They have improved the solubility and molecular weights by copolymerizing cardo bisphenol with I and II at the expense of thermal stability.

Rojivadia et.al [91] have reported thermal and mechanical behavior of copolymer (I) of 1, 1'- bis (4- hydroxy phenyl) cyclohexane, phthaloyl chloride and terephthaloyl chloride. The polymer is stable up to about 300°C in an air and involves two steps degradation. A 1 mm thick film of (I) has 54.7 kg/cm^2 tensile strength, 600 kg/cm^2 young modulus, 5 % elongation at break and 4.1 kV dielectric breakdown strength.

Rojivadia et.al [92] have reported the synthesis and characterization of cardo polyester of 1,1'-bis(4-hydroxy phenyl) cyclohexane with phthaloyl chloride. The polyester was prepared by interfacial poly condensation of 1,1'-bis(4-hydroxy phenyl) cyclohexane by using water 1,2-dicholro ethane as an interface, alkali as an acid acceptor and sodium lauryl sulfate as an emulsifier at 0°C for 5 h. The polymer has excellent solubility, high Tg (175°C), stable up to about 375°C in an air and involves two step degradation.

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90. M.V.Rao, A.J.Rojivadia, P.H.Parsania and H.H.Parekh, "Synthesis and charaterization of two cardo polyesters", J. Polym. Mater. **6**, 217-222, 1989; C. A. **113**, 41, 436 ,1990.
91. A. J. Rojivadia, M. V. Rao, P. H. Parsania and A. R. Parikh, "Thermal and mechanical behaviour of the cardo polyarylate made from 1,1'-bis(4-hydroxyphenyl) cyclohexane with phthalic/ terephthalic acid", J. Polym. Mater. **8 (4),** 357- 360 , 1991, C. A.**117**, 8,847 ,1992.
92. A. J. Rojivadia, M. V. Rao, P. H. Parsania and A. R. Parikh, "Synthesis and characterization of cardo polyarylate of 1,1'-bis(4-hydroxyphenyl) cyclohexane and phthaloyl chloride" , J. Polym. Mater. **8(4),** 338, 1991; C. A. **117**, 27, 294 ,1992.

Komehl and Lundt [93] have prepared polyesters from 4,4′-dihydroxy biphenyl, hydroquinone, 2,5-dimethyl hydroquinone and the substituted terephthaloyl dichloride in 1,1’,2,2’-terachloroethane. Their structures were characterized by ^{1}H-NMR, GPC and elemental analyses; their thermal behavior was studied by DSC measurements, microscopy under polarized light, and thermogravimetric analyses.

Komehl and Lundt [94] have reported the synthesis of copolyesters derived from 2,5-bis(pentyloxy)terephthaloyl dichloride (I), 4,4′-dihydroxybiphenyl (II) and trans-1,4-dihydroxycyclohexane (III). The structures were characterized by ^{1}H-NMR, GPC and elemental analyses; their thermal behavior was studied by DSC measurements, microscopy under polarized light and thermogravimetric analyses. The composition of the copolyesters with 30, 50 and 70 mol % (III) was not as expected, due to the differing reactivities of the diols (II) and (III) during the polycondensation. This led to the existence of two species of polyesters from one reaction mixture. The higher the content of (III) in the polymer, the lower is the molecular weight. By increasing the amount of (III), the thermal stabilities and melting points decrease drastically, whereas the solubility increases.

Lu et.al [95] have synthesized copolyesters containing rigid segments (naphthalene and terephthalene) and flexible segments (aliphatic diol) structure

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93. G.Komehl and B. Lundt , “Synthesis and properties of main chain copolyesters derived from 2,5-bis-(pentyloxy)-terephthaloyl dichloride and aromatic diols”,Polym. Bull. , **33**, 497-504, 1994.
94. G.Komehl and B. Lundt “Synthesis and properties of main chain copolyesters derived from 2,5-bis(pentyloxy)terephthaloyl dichloride and *trans*-1,4-dihydroxycyclohexane” , Polym. Bull. , **34**, 503-508, 1995.
95. T.Lu, Y. Sun and C.Wang, “Novel copolyesters containing naphthalene structure II. Copolyesters prepared from 2, 6-dimethyl naphthalate, 1, 4-dimethyl terephthalate, and ethylene glycol” J. Polym. Sci.: Part-A: Polym. Chem., **33**, 2841-2850, 1995

from DMN/DMT/EG (2,6-dimethyl naphthalate / 1,4-dimethyl terephthalate / ethylene glycol) ternary monomers with various mole ratios. Copolyesters having intrinsic viscosities of 0.52-0.65 dl/g were obtained by melt polycondensation in the presence of metallic catalysts. Most copolyesters have better solubilities than poly(ethylene naphthalate) (PEN) and poly(ethylene terephthalate) (PET) in various solvents. The effect of the starting mole ratio of DMN, DMT, and EG on the thermal properties of the resulted copolyesters was also investigated using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). Glass transition temperatures of copolyesters were in the range of 70.7-115.2°C, and 10% weight loss in nitrogen were all above 426°C.

Dieckmann et.al [96] have reported the aromatic polyesters with isophthaloyl, pyridine-2, 6-dicarbonyl and pyridine, 2, 5-dicarbonyl units in the main chain. Thus the complex acid dichloride (20 mmol) and the respective dihydroxy compound (20 mmol) were placed together with 1-chloronaphthalene (40 ml) ,in a three necked flask. The flask was equipped with a stirrer, N_2 inlet and distilling head. The high temperature solution polycondensation was carried out at 220^0C for 2h. After cooling the condensation polymer was precipitated in ethanol (200 ml), filtered off and extracted for 12h with ethanol using a Soxhlet apparatus and vacuum-dried at 60^0C for 18 h.

Anna Kultys [97] has reported the new linear polyesters containing sulfur in the main chain were obtained by melt polycondensation of diphenylmethane-4,4'-di(methylthiopropionic acid) with ethanediol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,2-propanediol, l,3-butanediol, and 2,2'-oxydiethanol. Low-molecular weights, low-softening temperatures and, very good

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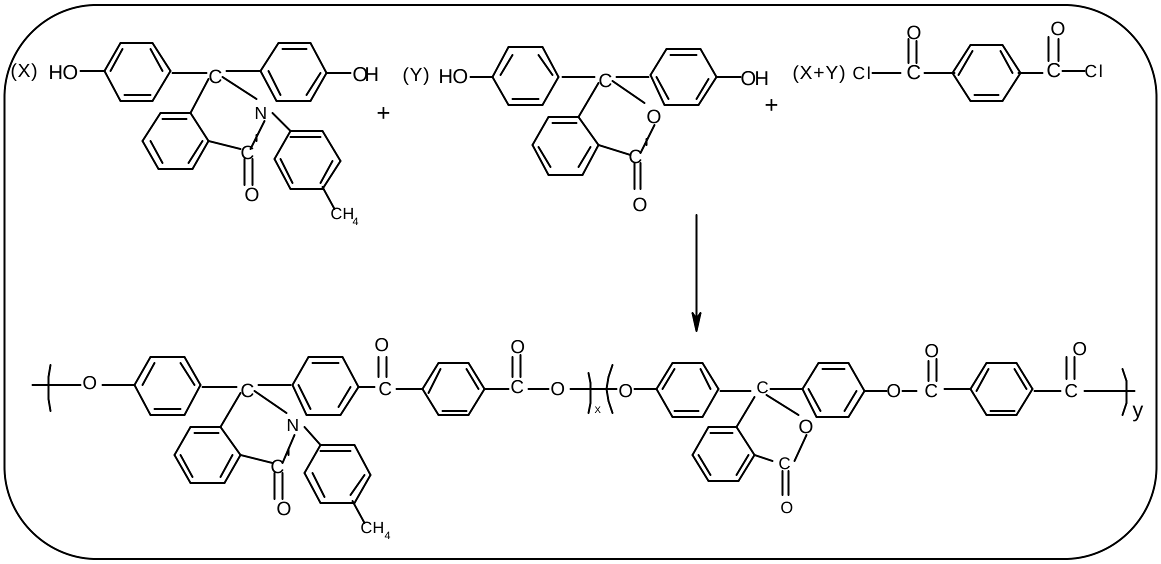
96. F.Dieckmann, D.Pospiech, P.Uhimann and F.Bohmel , "Synthesis and inverse gas chromatographic characterization of polyesters containing pyridine units in the main chain" , Polymer, **38 ,** 5887-5892, 1997

97. A.Kultys, "Preparation and properties of polyesters from diphenylmethane-4,4'-di(ethylthiopropionic acid) and aliphatic diols" , J. Polym. Sci.: Part-A: Polym. Chem., **35**,547-555, 1997

solubility in organic solvents are their characteristics. The structure of all polyesters was determined by elemental analysis, FT-IR and ‘H-NMR spectroscopy and x-ray diffraction analysis. The thermal behavior of these polymers was examined by differential thermal analysis (DTA), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC).

Vibhute et.al [98] have reported new polyesters containing ‘‘cardo’’ groups were synthesized by interfacial polymerization. Thus, a solution of 0.636 g (2 mmol) of phenolphthalein, 0.160 g (4 mmol) of NaOH, and 0.100 g of phase transfer catalyst (cetyltrimethylammonium bromide) dissolved in 25 ml of water, with rapid stirring, a solution of 0.406 g (2 mmol) of terephthaloyl chloride (TPC) in 16 ml of dichloromethane was introduced . 50 ml hexane was added to precipitate the polymer. The polymer was filtered out and dried under vacuum at 80^0C for 20 h. Yield: 0.600 g (61.9%). $?_{red}$: 0.67 dl/g.



Joshi et.al [99] have prepared new polyesters containing both silane and ‘‘cardo’’ groups were synthesized by solution polycondensation involving the

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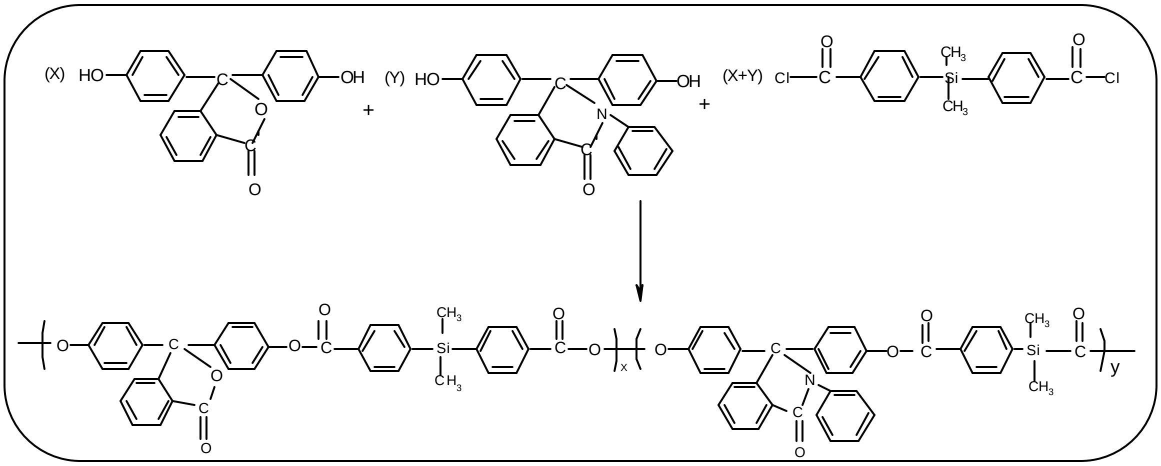
98. S. S. Vibhute, M. D. Joshi, P. P. Wadgaonkar, A. S. Patil and N. N. Maldar, “Synthesis and characterization of new cardo polyesters”, J. Polym. Sci.: Part-A: Polym. Chem., **35**, 3227–3234, 1997.

99. M. D. Joshi, A. Sarkar, O. S. Yemul, P. P. Wadgaonkar, S. V. Lonikar and N. N. Maldar ,” Synthesis and characterization of silicon-c polyesters”, J. Appl. Polym. Sci. , **64**: 1329–1335, 1997

reaction of bis(4-chlorocarbonylphenyl)dimethylsilane with cardo bisphenols, namely, phenolphthalein, phenolphthalimidine, and phenolphthalein anilide. Copolyesters were obtained by using different proportions of phenolphthalein and phenolphthalein anilide. Polyesters had inherent viscosities in the range 0.22–0.70 dL/g and were readily soluble in chlorinated hydrocarbons and polar aprotic solvents. Polyesters showed glass transition temperatures in the range 168–255^{0}C as measured by DSC and thermogravimetric analysis indicated no weight loss below 416^{0}C in a nitrogen atmosphere.



Anna Kultys et.al [100] have carried out the two series of new linear polyesters containing sulfur in the main chain were obtained by melt polycondensation of naphthalene-1, 4-bis (methylthioacetic acid) (N-1, 4-BMTAA) or naphthalene-1,5-bis(methylthioacetic acid) (N-1,5-BMTAA) with some aliphatic diols . Softening temperatures ranging from 55 to 130°C, reduced viscosities in the range of 0.15–0.39 dl/g, and low-molecular weights were their characteristic. The structure and thermal properties of all polyesters were examined by using elemental analysis, FT IR and NMR spectroscopy, X-ray diffraction analysis, differential thermal analysis (DTA), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC).

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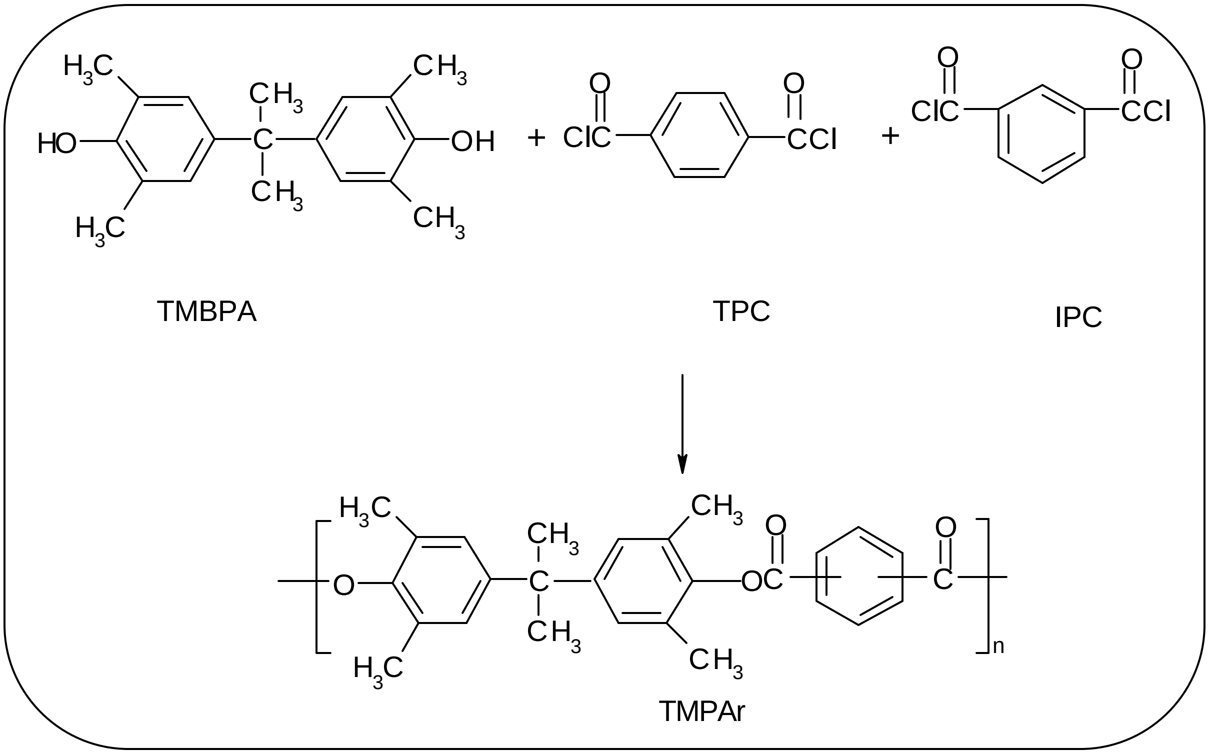
100. A. Kultys, Wawrzyniec Podkoscielny and Stanislaw Pikus, “Polyesters containing sulfur VI. synthesis and characterization of polyesters from naphthalene-1,4-or naphthalene-1,5-bis(methylthioacetic acid) and aliphatic diols”, J. Polym. Sci.: Part-A: Polym. Chem., **36**, 2359–2369, 1998.

Ahn et. al [101] have reported polyester of tetramethyl bisphenol-A(TMBPA). Thus, TMBPA and terephthaloyl chloride (TPC)/isophthaloyl chloride (IPC) mixture (50/50) were dissolved in dry chloroform ($CHCl_3$) and cooled down to 0 ~ 5^0 C in an ice bath. When triethylamine was added dropwise to the solution with stirring, an exothermic reaction took place. After 7 h, the reaction mixture was poured into a large volume of methanol.



Choi et.al [102] have synthesized a series of halogen containing aromatic polyesters with decamethylene spacer groups was synthesized by the solution polymerization from 4,4’-dicarboxyl-1,10-diphenoxydecane and bisphenol-A. Incorporation of fluorine atoms in the bisphenol-A units in the polymer backbone enhanced the solubility of the polyesters in various organic solvents, as did the substitution of chlorine and bromine on the aromatic rings of the bisphenol-A, ortho to the ester linkages.

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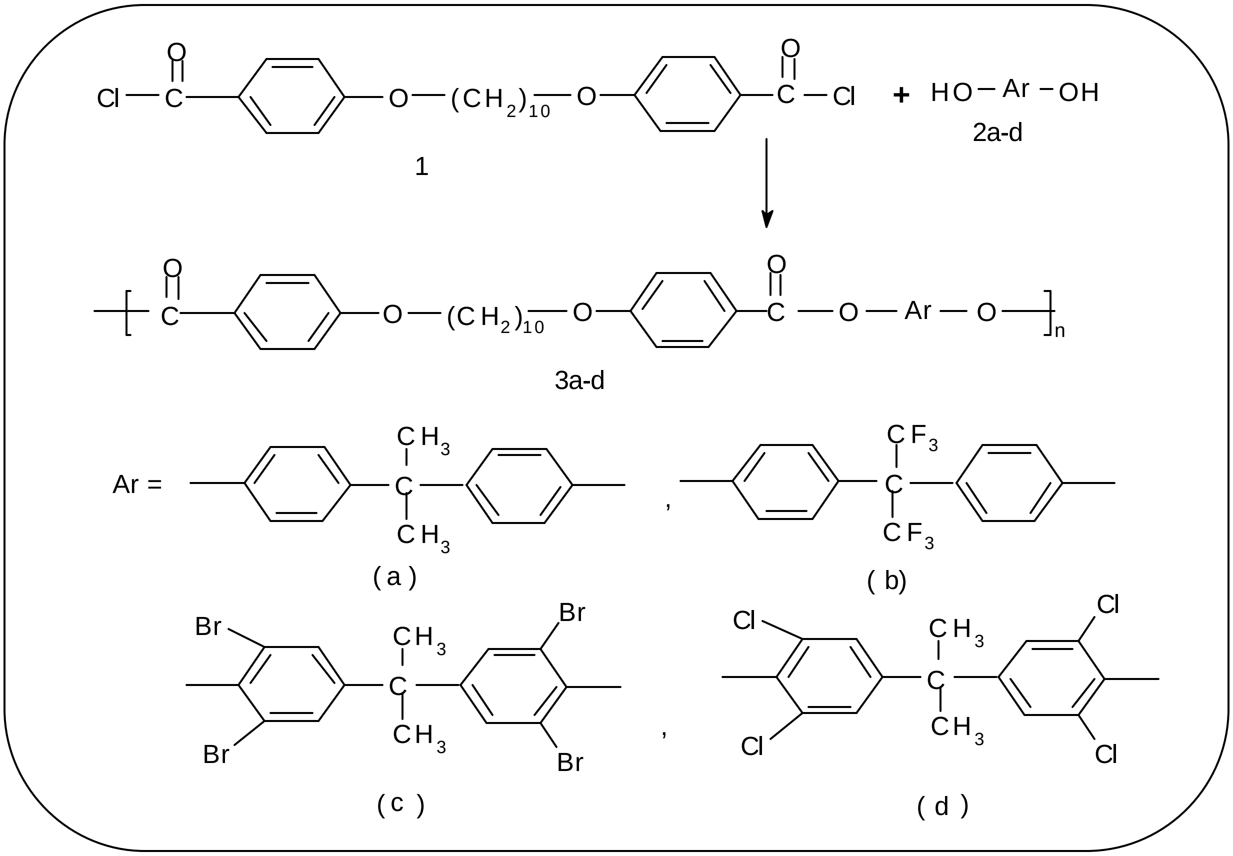
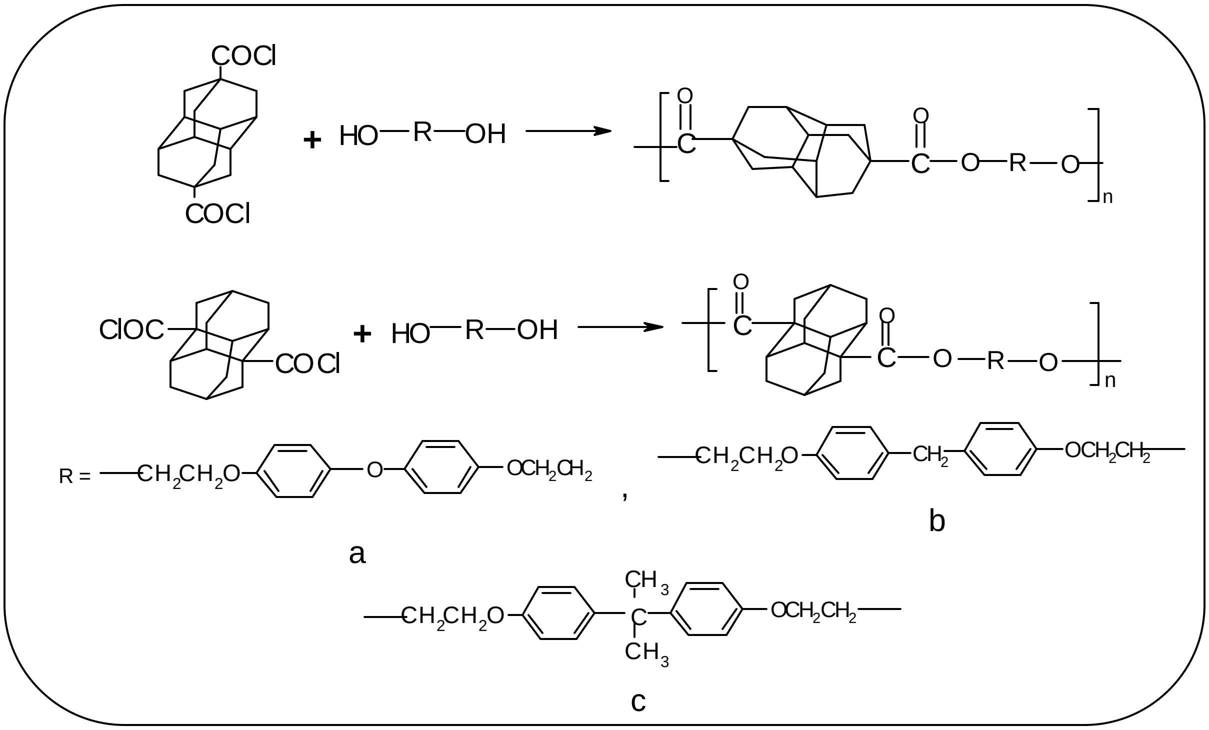
101. T. O. Ahn, M. Lee, H. M.Jeong and K. Cho, ”The phase behavior of tetramethyl bisphenol-A polyarylate/aliphatic polyester blends” , J. Polym. Sci.: Part-A: Polym. Phy. , **36**, 201–212, 1998
102. E.Choi, J.David, T.Hill, Y.Kim, H. James and J. Peter, Pomery “Synthesis, thermal and radiation sensitivities of halogen containing decamethylene-spacered aromatic polyesters”, Polym. Adv. Technol. **9**, 52–61, 1998



The effect of the halogen substituents on the thermal and radiation sensitivities of the polyesters has been investigated. The inherent viscosities of THF solutions at 30°C ranged from 0.25 to 0.63 dl/g. The number average (6,000~31,000) and weight average molecular weights (12,000~48,000) were measured by gel permeation chromatography, resulting in polydispersity indices of M_w/M_n=1.6~2.0. The chemical structures of the polyesters were characterized by means of IR spectroscopy, ^{1}H NMR and ^{13}C NMR spectroscopies and elemental analyses.

Chern and Huang [103] have synthesized a series of new polyesters by high temperature solution polycondensation of 1,6- or 4,9-diamantane dicarboxylic acyl chlorides with aryl ether diols. All polyesters had good solubilities and could be soluble in chloroform, nitrobenzene, o-chlorophenol, DMF, and o-dichlorobenzene. The glass transition temperatures of polyesters were 90-108^{0}C and 102-132 ^{0}C, as determined by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA), respectively. The temperatures at 5% weight loss of polyesters ranged from 338 to 395 ^{0}C in air, from 385 to 403 ^{0}C in N_2 atmosphere. Polyester had tensile strengths of 34.9 ~ 45.5 MPa, elongation to breakage values of 3.5 ~ 4.6 %, and initial moduli of 1.4 ~ 1.6 GPa.



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103. Y.T.Chern and C.M.Huang , “Synthesis and characterization of new polyesters derived from 1,6- or 4,9- diamantanedicarboxylic acyl chlorides with aryl ether diols” , Polymer, **39,** 2325-2329,1998.

Bhunia et.al [104] have synthesized novel copolyesters by solution polycondensation of terephthaloyl chloride with 4-[(4-hydroxy -2-penta decenyl phenyl) diazenyl] phenol (HPPDP) and 1,4-butane diol. The copolyester was characterized through elemental analysis, ^{1}H NMR, IR, and UV spectroscopy. Dilute solution viscosity of its solution was also determined by viscometry. The intrinsic viscosity [?] was 0.98 dl/g.

Park et. al [105] have reported the syntheses of aromatic polyester and copolyesters having pendant carboxyl groups are directly synthesized from isophthaloyl chloride, diphenolic acid and diols by aqueous/organic two-phase interfacial polycondensation, using phase transfer catalysts. The yield and molecular weight of the polyester were remarkably affected by the structure of quaternary ammonium salts and crown ether catalysts. The phase transfer reaction steps are suggested to explain this phenomena. The properties of copolyesters were dependent on the original structure of diols.

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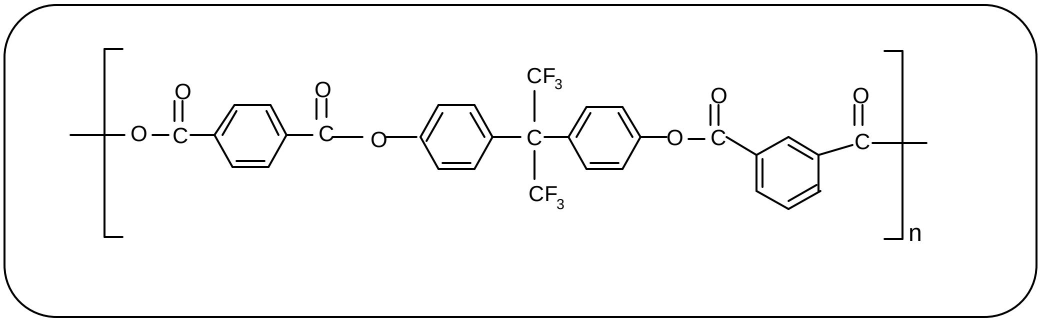
104. H. Bhunia, A. Basak, T. Chaki and G.Nando, "Synthesis and characterization of polymers from cashewnut shell liquid: a renewable resource V. Synthesis of copolyester", Eur. Polym. J., **36**, 1157-1165, 2000
105. D. Park, D. Ha, J. Park, J. Moon and H. Lee, "Synthesis of aromatic polyesters bearing pendant carboxyl groups by phase transfer catalysis", Reaction Kinetics and Catalysis Letters, **72**, 219 – 227, 2001.

Liaw et.al [106] have prepared a series of new polyesters from terephthaloyl (or isophthaloyl) chloride with various cardo bisphenols by solution polycondensation in nitrobenzene using pyridine as hydrogen chloride quencher at 150 °C. These polyesters were produced with inherent viscosities of 0.32–0.49 $dl{\cdot}g^{-1}$. Most of these polyesters exhibited excellent solubility in a variety of solvents. The polyesters containing cardo groups including diphenylmethylene, tricyclodecyl, *tert*-butylcyclohexyl, phenylcyclohexyl, and cyclododecyl groups exhibited better solubility than bisphenol A–based polyesters. These polymers showed glass transition temperatures (*Tg*'s) between 185°C and 243°C and decomposition temperatures at 10% weight loss ranging from 406°C to 472°C in nitrogen.

Vygodskii et.al [107] have synthesized copolymer based on bisphenol - 6F and 1:1 iso : terephthalic acids. This polymer was synthesized by polycondensation of bisphenol-6F and iso/terephthaloyl chlorides in 2-chloronapthalene as the reaction solvent at 220^{o} C. The polyarylate is highly soluble in many organic solvents including MMA.



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106. D. J. Liaw, B. Y. Liaw, J. J. Hsu and Y. C. Cheng, "Synthesis and characterization of new soluble polyesters derived from various cardo bisphenols by solution polycondensation**",** J. Polym. Sci.: Part-A: Polym. Chem., **38**, 4451–4456, 2000.

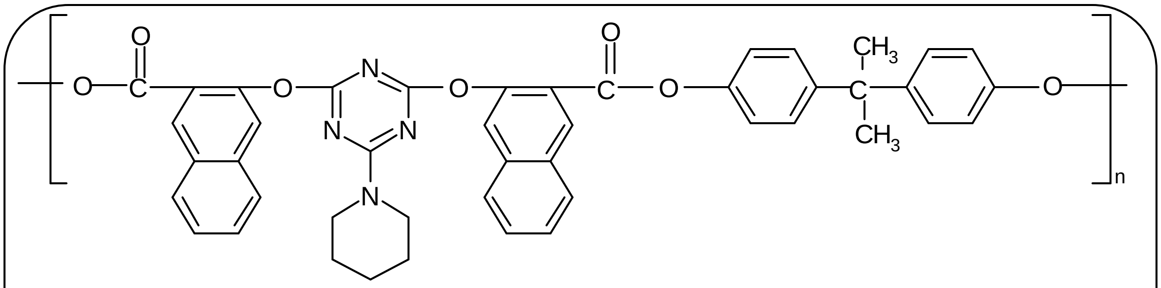
107. Y. S. Vygodskii, A. M. Matieva, A. A. Sakharova, D. A. Sapozhnikov and T.V. Volcova, High Perform. Polym. **13**, 317– 323 ,2001

Patel et.al [108] have synthesized various polyesters by interfacial polycondensation of 2-(N-piperidine)-4,6-bis-(naphthoxy-3-carbonylchloride)-s-triazine (PNCCT) with each of the aromatic and aliphatic diols: bisphenol-A (BPA),bisphenol-C (BPC), bisphenol-S (BPS), phenolphthalein (Ph), catechol (C), resorcinol (R), hydroquinone (Hq),ethylene glycol (EG), and 1,4-butanediol (Bu-1,4). Interfacial polycondensation of PNCCT with BPA was investigated in detail in order to select optimum reaction conditions. The yield of polyesters varies from 63 to 76%. The polyesters are soluble in methylated solvents such as dimethyl formamide, dimethyl sulfoxide, methanol, etc. The reduced viscosity of polyesters determined with a 1 g/dl solution in dimethyl formamide at 25±3^{0}C was found to be in the range 0.340-0.628 dl/g. All the polyesters were characterized by IR spectra. The densities of the polyesters, determined using the suspension method at 25±3^{0}C, range between 1.118 and 1.208 g cm^{-3}. The overall reactivity of diols, based on reduced viscosity values, was found to decrease in the following order:

PEBPA > PEPh > PEBPC > PER > PEHq > PEC > PEBPS > PEEG > PEBu-1,4

The thermal stability of polyesters based on various temperature characteristics, was found to decrease in the following order:

PEPh > PER > PEHq > PEEG > PEBPS > PEBPA > PEBPC > PEC



Polyester of BPA
[PEBPA]

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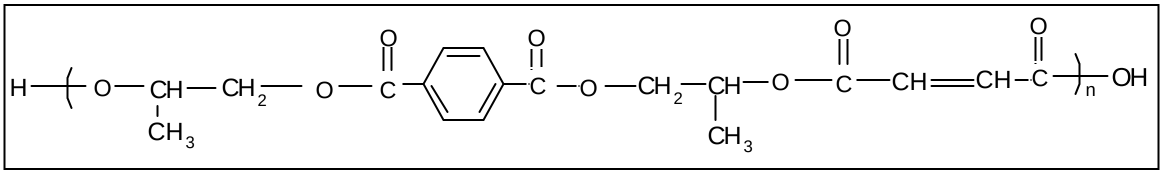
108. P.M. Patel, S.K. Patel and K.C. Patel, “Synthesis and characterization of polyesters based on s-triazine”,Eur. Polym. J., **36,** 861-865, 2000

Shaik et.al [109] have reported properties of copolyesters with an alternating sequence of terephthalic acid and aliphatic dicarboxylic acids were prepared with three different methods. First, dicarboxylic acid dichlorides were reacted with bis (2-hydroxyethyl) terephthalate (BHET) in refluxing 1,2-dichlorobenzene. Second, the same monomers were polycondensed at 0-20°C in the presence of pyridine. Third, dicarboxylic acid dichlorides and silylated BHET were polycondensed in bulk. Only third method gave satisfactory molecular weights. The alternating sequences and thermal properties were characterized with ^{1}H NMR spectroscopy and differential scanning calorimetry measurements, respectively.

Polyester based on bis-(2-hydroxypropyl terephthalate) (BHPT) and maleic anhydride (MA) was prepared by Magda and Maher [110]. Thus, BHPT (1.1 mole) was heated in an oil bath maintained at 80^0C by means of a contact thermometer. MA (1 mole) was added. The temperature was raised to 150 ^{0}C over a period of one hour, and then increased at a rate of 10 ^{0}C/h up to 210 ^{0}C, until the acid number reached 32 ±2 mg KOH/g. A representative example of the polymer structure is given in the following scheme. The reaction order was found to be second and third order in the presence and absence of the catalyst, respectively. The prepared polyester was examined by infrared and NMR spectroscopy.



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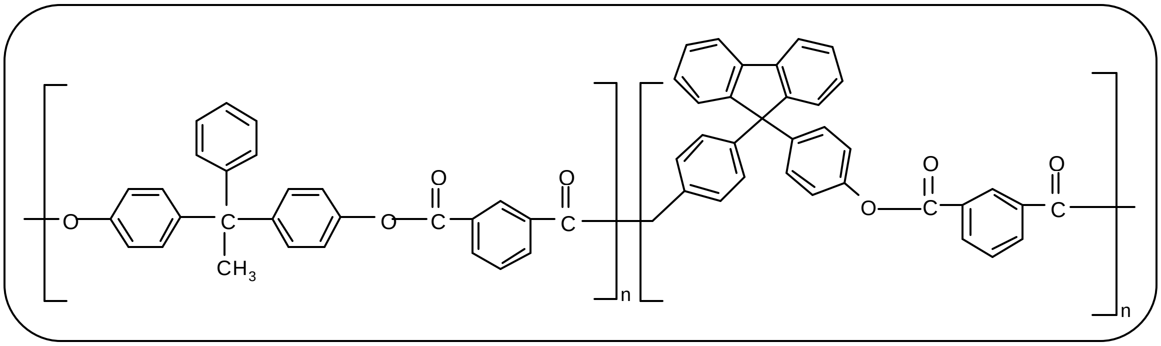
109. A.Shaik, M.Richter, H.Kricheldorf and R.Kruger, “New polymer syntheses CIX. Biodegradable, alternating copolyesters of terephthalic acid, aliphatic dicarboxylic acids, and alkane diols”, J. Polym. Sci. Part A: Polym. Chem., **39**, 3371-3382, 2001.

110. T. E. Magda and Z. E. Maher, “Preparation and characterization of polyester based on bis- (2- hydroxypropyl terephthalate)” J.Polym. Res., **9**, 129–133, 2002.

Loria et.al [111] have synthesized isophthalic polyesters from 4,4’-(1-hydroxyphenylidene) diphenol (BAP/ISO) and 4,4’-(9-fluorenylidene) diphenol (BF/ISO),and the isophthalic copolyesters BAP75/ISO, BAP50/ISO, and BAP25/ISO correspond to 75,50, and 25 mol % of yielded polymers and copolymers produced flexible and transparent films when they were cast from solution. Wide angle X-ray diffraction measurements indicated that all the polyesters and copolyesters were amorphous.



Higashi et.al [112] have reported a two-stage solution copolycondensation of IPA/TPA (50/50), ineffective aliphatic *p*-xylyleneglycol (PXG), and effective bisphenols (BPs) using tosyl chloride/ dimethylformamide/ pyridine condensing agent was studied by examining factors, such as, kinds of BPs, reaction temperature, and the order of addition of PXG and BPs. Better results were obtained by initial reaction of PXG followed by BPs at a lower temperature (80 °C).

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111. M. I. Loria, H. Vazquez and J. A.Vega, “Synthesis and characterization of aromatic polyesters and copolyesters from 4,4’-(1-hydroxy phenylidene)diphenol and 4,4’-(9-fluorenylidene)diphenol” , J. Appl. Polym. Sci.**, 86**, 2515–2522, 2002.

112. F. Higashi, Y. Yoshida and O. Matsuzaka, “Propagation in the two-step solution copolycondensation with *p*-xylylene glycol and bisphenols with the TsCl/DMF/Py condensing agent”, Eur. Polym. J., **38**, 1137-1143,2002.

Bastarrachea et. al [113] have synthesized two isophthalic polyesters from 4,4′-(1-hydroxyphenylidene) diphenol (BAP/ISO) and 4,4′-(9-fluorenylidene) diphenol (BF/ISO), and three different copolyesters containing 75, 50, and 25 mol % of BAP/ISO by interfacial polycondensation. This preparation method yielded polymers and copolymers that produced flexible and transparent films when they were cast from solution. It was also found that thermal properties such as glass-transition temperature, thermal stability, dynamic mechanical storage modulus, and maximum on the α-transition of the damping factor tanδ of BF/ISO were higher than those of BAP/ISO.

Zhu et. al [114] have synthesized poly(butylene succinate) (PBS) and its copolymers, poly(butylene succinate-*co*-adipate) (PBSA) and poly(butylene-*co*-hexylene succinate) (PBHS), by direct polyesterification of corresponding diols and dicarboxylic acids. Dimethyl benzene was used as a solvent and water-removing agent. Several catalysts were used to study the esterification of butanediol and succinic acid. Among them, $SnCl_2$ demonstrated superior catalysis behavior. The molecular weight of some polyesters surpassed 30,000. The variation of molecular weight distribution during the polymerization was monitored by GPC and M_w/M_n demonstrated a trend of decrease with the reaction time. The melting point (T_m) and the glass-transition temperature (T_g) were measured by DSC technique.

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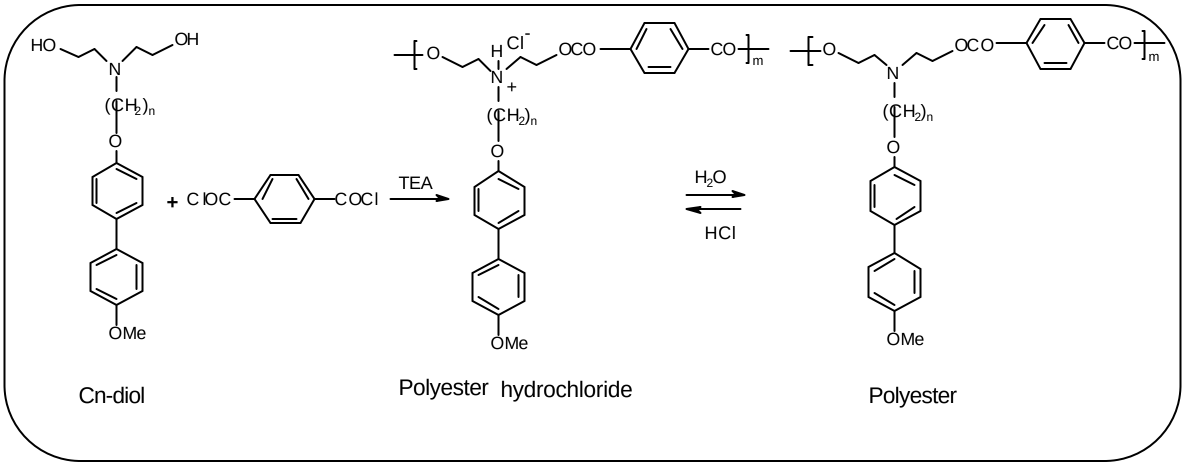
113. M. Bastarrachea, H.Torres, J.Manuel and A.Vega, “Synthesis and characterization of aromatic polyesters and copolyesters from 4,4’-(1-hydroxyphenylidene)diphenol and 4,4’-(9-fluorenylidene)diphenol”, J Appl Polym Sci, **86**, 2515-2522, 2002.

114. C. Zhu, Z. Zhang, Q. Liu, Z. Wang and J. Jin, “Synthesis and biodegradation of aliphatic polyesters from dicarboxylic acids and diols”, J Appl Polym Sci , **90**, 982-990, 2003

Miroslav and Majda [115] have studied side-chain polyesters and polyester hydrochlorides were synthesized from a-(bis(2-hydroxyethyl)amino)-? -(4'-methoxy biphenyl-4-oxy) alkanes with different spacer lengths (Cn-diol, n =6; 8, 10) and terephthaloyl chloride. Since N-substituted diethanolamine acts as a stronger acid acceptor than triethylamine or pyridine, polyester hydrochlorides are formed during polyesterification instead of polyesters. Polyesters can be prepared from a chloroform solution of polyester hydrochlorides by extraction of HCl. During the polyesterification, linear polymers as well as cyclic oligomers are formed. All polymers were analyzed by NMR, size exclusion chromatography (SEC), differential scanning calorimetry (DSC), X-ray spectroscopy (XRD) and polarizing optical microscopy (POM).



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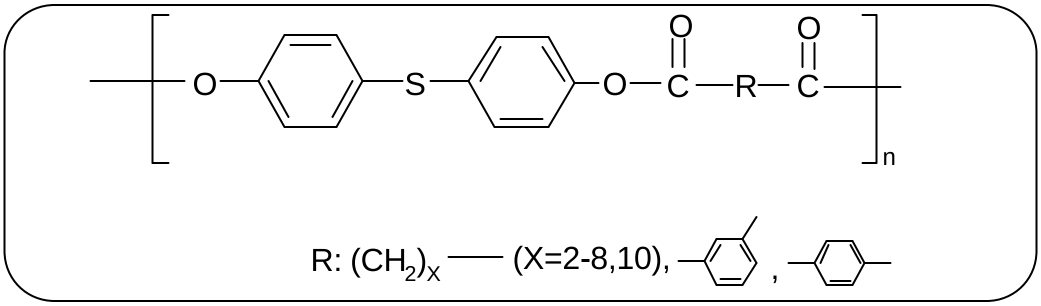
115. H. Miroslav and I.Majda, "Side-chain polyesters and polyester hydrochlorides based on terephthalic acid", Polymer, **44**, 6187-6193, 2003.

Tsai et.al [116] have prepared copolyesters of *p*,*p*′-bibenzoic acid, dimer acid, and an alkylene glycol by melt polycondensation of dimethyl *p*,*p*′-bibenzoate, dimer acid, and an alkylene glycol. The copolyesters are characterized by the inherent viscosity, FTIR, proton NMR, DSC, polarized microscopy, and X-ray diffraction. The polymer composition and sequence distribution of the copolyesters can be seen from the NMR spectra. The glass transition temperature (T_g) and the melting point (T_m) of the copolyesters are found from the DSC. When the content of the flexible dimer acid unit increases, the T_g of the copolyesters decreases significantly.

Hiroshi et.al [117] have reported the synthesis and properties of sulfur-containing polyesters derived from bis(4,4'-hydroxyphenyl)sulfide (TDP) and various acid dichlorides (AC) (with methylene numbers of 2–10) by interfacial polycondensation in a 1,1',2,2'-tetrachloroethane /water mixture using tetra-*n*-butyl ammonium bromide as a phase transfer catalyst. These polyesters were found to show an odd–even effect with the glass transition temperature and the melting point based on the methylene numbers. The tensile strength and storage modulus decreased with the methylene numbers.



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116. H.Tsai, D.Lee and R.Tsai, "Synthesis and properties of copolyesters of *p*,*p*'-bibenzoic acid, dimer acid, and alkylene glycol", J. Appl. Polym. Sci. , **88**, 750-758, 2003

117. H. Hiroshi, S. Watase and M. Tanaka, "Linear polymers with sulfur in the main chain. Synthesis of polyesters by interfacial polycondensation of bis(4,4'-hydroxyphenyl) sulfide with several aliphatic acid dichlorides and their properties" , J. Appl. Polym. Sci, , **91**, 1865–1872, 2004

Berti et.al [118] have studied copolyesters of terephthalic acid with bis-(hydroxyethyl ether) of bisphenol - A (BHEEB) in different molar ratios have been synthesized by reactive blending from terephthalate polyesters and by melt polycondensation from the monomers. By this way, bisphenol -A groups were inserted in the polyester chains with the aim to obtain polyesters with improved mechanical properties. The insertion of the BHEEB into the polyester backbone is quantitative and does not give rise to side reactions.

2,2-Dibutyl-2-stanna-1,3-dioxepane 1 (or 1,3-dioxepene 2) from 1,4 – butane diol and dibutyltin dimethoxide were prepared by Kricheldorf et.al [119] and they were polycondensed at 80^0C in n-heptane with adipoyl-,suberoyl, sebacoyl chloride and with decane-1,10- dicarbonyl chloride. In the case of suberoyl chloride and 2,2-dibutyl-2-stanna-1,3-dioxepane reaction time, temperature and stoichiometry were varied to optimize both the molecular weight and the fraction of cyclic polyesters. With a slight excess of the dicarboxylic acid chlorides, only macrocyclic polyesters were obtained in all cases. The resulting cyclic polyesters were characterized by viscosity measurements, by ^{1}H and ^{13}C NMR and by MALDI -TOF mass spectrometry.

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118. C.Berti, M.Colonna, M. Fiorini, C.Lorenzetti and P. Marchese “Chemical modification of terephthalate polyesters by reaction with bis(hydroxyethyl ether) of bisphenol-A”, Macromol. Mater. Eng. ,**289**, 49–55, 2004.

119. H. R. Kricheldorf, S. Chatti and G. Schwarz, “Ring expansion polycondensation of 2- stanna-1,3- dioxepane (or 1,3- dioxepene) with dicarboxylic acid chlorides” Macromol. Symp., **210**, 93-99, 2004.

Kavthia et.al [120] have studied copolyesters of varying compositions have been synthesized by interfacial polycondensation technique by using H_2O–$CHCl_3$ as an interphase, alkali as an acid acceptor and cetyl trimethyl ammonium bromide – sodium lauryl sulfate as mixed emulsifiers at 0^0C for 4 h. Copolymers are characterized by IR and NMR spectral data, viscosity and density (1.2465–1.2403 g/cm^3) by a floatation method. Copolymers possess excellent solubility in common solvents and chemical resistance against water, acids, alkalis, and salt. They possess moderate to good tensile strength (9.3– 61.8N/mm^2), excellent volume resistivity (1.2x10^{15} – 1.1x10^{17} Ocm), electric strength (29.6–50.0 kV/mm), and dielectric constant (1.51–2.03). They are thermally stable up to about 303–307^{0}C in an N_2 atmosphere and possess high Tg (176–190^{0}C). DTA endo/exothermic transition(s) supported either decomposition or formation of new product(s).

Pramanick et.al [121] have reported a series of copolyesters having a broad range of biodegradable crosslinks synthesized by $FeCl_3$-catalyzed polyesterification of trimellitic acid and glycerol containing a small mol percent of poly(ethylene glycol) (PEG) of varied molecular weights. The polymer samples designated as I (1.5% PEG 2000), II (4.5% PEG 2000), III (7.5% PEG 2000), IV (1.5% PEG 4000), V (4.5% PEG 4000), VI (7.5% PEG 4000), VII (1.5% PEG 6000), VIII (4.5% PEG 6000), and IX (without PEG) are insoluble and moderately tough-to-elastic solids and were characterized by their swelling values in ethanol, glass transition temperatures (T_g), IR spectra, and X-ray diffractograms.

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120. S. H. Kavthia, B. G. Manwar, and P. H. Parsania . “Synthesis and physico-chemical properties of copolyesters of 1,1’-bis(3-methyl-4-hydroxy phenyl)cyclohexane with 2,2’-bis(4-hydroxy phenyl)propane with terephthaloyl chloride” J. Macromole. Sci. Part A —Pure and Appl. Chem., **41**, 29-38, 2004.

121. D. Pramanick, R. Pramanick and G. Betal, “Copolyester of trimellitic acid, glycerol, and poly(ethylene glycol): Synthesis and characterization”, J. Appl. Polym. Sci. , **91**, 343-346, 2004.

Bucio et.al [122] have synthesized series of aromatic polyesters of 1,6-diazaspiro[4,4]-nonane-2,7-dione (SDL) with hexafluorodiacid chloride (6FDAC), oxydibenzoyl chloride, diphenic acid chloride, Isophthaloyl chloride and terephthaloyl chloride under phase transfer conditions. The copolymers were obtained in essentially quantitative yield, these were soluble in common organic solvents, and would readily form clear, colorless films from solution. The optimum condition of polymerization was obtained via polycondensation at room temperature and reaction time of 4 h in chloroform. All polymers were characterized by FTIR, GPC, viscosity, water contact angle, and water absorption, TGA, DSC and TMA. The prepared polyesters showed excellent thermal stability, as measured by TGA (10 wt% loss), are only moderate due to the alicyclic component and range from 365 to 401^{0}C in air; however, glass transition temperatures are quite high (245–309 ^{0}C).

Bing et. al [123] have reported biodegradable aliphatic copolyesters synthesized from e-caprolactone, adipic acid, and 1,6-hexanediol by melt-polycondensation method. The chemical structure and thermal properties of these copolymers were studied in detail. The water absorption behavior and hydrolytic degradation behavior of this copolyester were also studied. This aliphatic copolyester prepolymer would be used to prepare the biodegradable poly(ester urethane).

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122. E. Bucio, J. W. Fitch, S. R. Venumbaka and P. E. Cassidy, "Synthesis and properties of aliphatic spirodilactam diphenol containing polyesters", Polymer **46** , 3971–3974, 2005

123. C.Bing, Z. Qian, Y.C. Gu, L.Yu.Fan, L. Jun, G.T. Chao, W.J. Jia and M.J.Tu, "Synthesis, characterization, and thermal properties of biodegradable aliphatic copolyester based on e-caprolactone, adipic acid, and 1,6-hexanediol" , Materials Letters, **60**, 31-38, 2006.

Wang et.al [124] have reported a series of biodegradable aliphatic/aromatic copolyesters, poly(butylene terephthalate)-*co*-poly(butylene cyclohexanedicarboxylate) - poly(ethylene glycol) (PTCG), prepared by a two-step melt polycondensation method and characterized by means of GPC, FTIR, NMR, DSC, TGA, etc. The effects of aliphatic ester content on the physical, mechanical and thermal properties, as well as in vitro and in vivo degradation behaviors were investigated.

Waghmare et.al [125] have reported a novel series of siloxane copolyesters containing 1,1,3-trimethyl-3-(*p*-hydroxyphenyl)-5-indanol (phenylindane bisphenol), diphenyl terephthalate (DPT), diphenyl isophthalate (DPI), and eugenol end capped siloxanes in varying ratios were prepared at a temperature range of 200-290°C under reduced pressure using dibutyl tin dilaurate catalyst by melt polycondensation. The siloxane-containing copolyesters were characterized by infrared and ^{1}H NMR spectroscopy, elemental analysis, solution viscosity, thermogravimetric analysis, differential scanning calorimetry, and X-ray diffraction. All copolyesters were found to be soluble in commonly used organic solvents and had film forming properties.

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124. L. Wang, Z. Xie, X. Bi, X.Wang, A. Zhang, Z.Chen, J. Zhou and Z. Feng , "Preparation and characterization of aliphatic/aromatic copolyesters based on 1,4-cyclohexanedicarboxylic acid" ,Polymer Degradation and Stability, **91**, 2220-2228, 2006.

125. P. Waghmare, S. Deshmukh, S.Idage and B.Idage, "Synthesis and characterization of siloxane copolyesters containing phenylindane linkages", J Appl Polym Sci , **101**, 2668-2674, 2006

Wei et. al [126] have synthesized a series of copolyesters composed of pure terephthalate acid (PTA), ethylene glycol (EG), and 1,3-propanediol (1,3-PDO) by melt polycondensation process. The molecular weight, molecular weight distribution, and thermal properties of the copolymers were characterized. The results show that the contents of trimethylene terephthalate (TT) units in the resulting copolyesters are higher than PDO compositions in original diol. The glass transition temperature (T_g) of the copolyesters varies from 78.5°C for PET (polyethylene terephthalate) to 43.5°C for PTT (polytrimethylene terephthalate) and decreases monotonically with the components.

Wei et.al [127] have reported the thermal stability of poly(ethylene-*co*-trimethylene terephthalate) was first studied by thermogravimetry under nitrogen atmosphere at different heating rates. The results showed that the thermal behavior of the copolyester had a strong dependence on the chemical composition. The average activation energy from Ozawa technique increases with the concentration of EG units in the polyester, and a greater TG concentration in the copolyesters would decrease the onset degradation temperature. These phenomena may be attributed to the presence of one more methylene of TG unit than of EG in the copolymer. It is also noted that the yield of solid residue increases with the concentration of EG units in the polymer chain at any heating rate, which may be associated with the content of aromatic ring in the polymer chain.

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126. G. Wei, L. Wang, G. Chen and L. Gu, "Synthesis and characterization of poly (ethylene-*co*-trimethylene terephthalate)s", J. Appl. Polym. Sci. ,**100**, 1511- 1521, 2006.

127. G. Wei, D. Hua and L. Gu, "Thermal stability of poly (ethylene-*co*-trimethylene terephthalate)s", J. Appl. Polym. Sci. ,**101**, 3330-3335, 2006.

PROPERTIES OF CARDO POLYMERS

Korshak et.al [128] have reviewed heat resistance and solubility of polymers.

One of the ways of obtaining heat resistant polymers is the synthesis of polymers with rigid backbone having large segments, which increase the glass transition temperature. There is a grave contradiction between the search for the most heat stable polymers and the possibility of their processability to ready-made articles. The higher the thermal stability, the more difficult is there processing by standard melt method. The processability of highly thermally stable polymers is more convenient from solutions.

There are number of factors which increase the heat resistance of linear polymers:

(1) Introduction of different cyclic groups into the main chain of macromolecules.
(2) By increasing the intermolecular interactions.
(3) By introducing side cyclic groups
(4) Polymer crystallization
(5) Ordering the structure
(6) Using monomers with the symmetrical structure
(7) Formation of chemical cross-links between linear macromolecules
(8) Regular rearrangement of units in the chain
(9) Preparation of stereo regular polymers, and so on.

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128. V. V. Korshak, S. V. Vinogradova and Ya. Vygodskii, J. Macromol. Sci. Rev. Macromol. Chem. C11, **45**, 1974

The factors responsible for better solubilities are:

(a) Preparation of amorphous polymers
(b) Introduction of polar groups showing affinity for the solvent
(c) Random position of various units in the backbone and
(d) Introduction of dissimilar units

In order to improve appreciably the solubility in some cases, it is insufficient to change one of these factors, their combined action is necessary. Comparison of the factors increasing the solubility shows that some of them improve one property but impair the other e.g., a decrease in rigidity lowers the heat resistance, while increasing the solubility. The films of cardo polymers obtain from solutions in different organic solvents. The high heat resistance and thermal stability of cardo polymers assured the stability of physico-mechanical and particularly dielectric properties of films up to 300^{o}C [129-134]. The fibers with high heat resistance are obtained by solution casting from cardo polyarylates and some other cardo polymers having an isotropic amorphous structure with stress of crystallinity.

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129. V. V. Korshak, S. V. Vinogradova; Polyarylaty Nauka, Moscow, 1964
130. S. V. Vinogradova and D. R. Tur, Polymer Sci. USSR., **15**, 323, 1973; Vysokomol. Soedin, A 15, 284 ,1973
131. V. V. Korshak, S. V. Vinogrdova and V. A. Pankratov, Plast. Massy, **5**, 21, 1967; C**.** A**. 67**, 54,496 ,1967
132. G. L. Slonimskii and A. A. Askadskii, Mekhanika Polimerov, **1**, 36 ,1965
133. A. A. Askadskii, Phisiko-Khimiya Polyarylatov, Khimiya, Moscow ,1968
134. T. S. Knjaseva, V. V. Korshak, M. S. Akutin. M. M. Kuleva, S. V. Vinogradova, L. A. Rodivilova, T. P. Nedo Pekina, P. M. Valesky, S. A. Morozova, and S. N. Salazkin, Plast. Masy, **12**, 37 ,1962,

The cardo polymers possess promising applications as plastic coatings, bonding materials for glass reinforces plastics, antifriction self lubricating materials, and so on [135-138]

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135. V. V. Korshak, M. S. Akutin, S. V. Vinogradova, L. A. Rodivilova, P. M. Lebedeva and S. N. Salazkin, Plast, Masy, **1**, 9 ,1962; C. A. **57**, 16849 ,1962.

136. V. V. Korshak and I. A. Gribova, ”Plastic antifriction material”, French Pat. , 1,540,136, 1980; C. A**. 71**, 13, 689, 1969.

137. V. V. Korshak, S. V. Vinogradova, et. al. USSR. 204, 574 (1976); U. S. Pat., 3, 530, 068, 1967; Ger. Pat., 1,694,458, 1967; Brit. Pat. 1,179, 400, 1967; Ita. Pat., 816, 907, 1967; Can. Pat., 826, 721, 1967; Jap.Pat., 636, 983 1967; C. A. **71**, 13689 ,1969.

138. V. V. Korshak and I. A. Gribova, Ger.Pat., 1, 956, 461 ,1969; Brit. Pat. 1, 244, 427, 1967; French Pat. 2,057, 293, 1969; Ita. Pat., 883, 944, 1969; C. A. **76,** 155, 046 ,1997.

CHAPTER – 2

SYNTHESES OF MONOMERS
AND
COPOLYESTERS

CHAPTER-2

SYNTHESES OF MONOMERS AND COPOLYESTERS

This chapter is further subdivided into two sections:

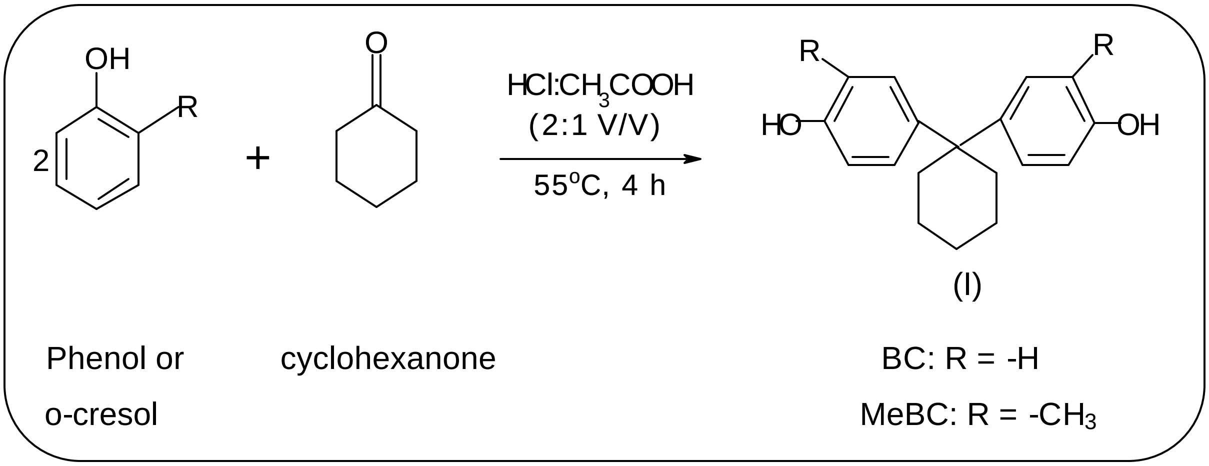
SECTION-I: Syntheses of monomers

SECTION-II: Syntheses of copolyesters

SECTION-I: SYNTHESES OF MONOMERS

This section deals with the syntheses of monomers and their purification.

(A) Synthesis of 1, 1'-bis (4-hydroxy phenyl) cyclohexane and 1, 1'-bis (3- methyl-4-hydroxy phenyl) cyclohexane



1,1'-Bis(4-hydroxy phenyl) cyclohexane and 1,1'-bis(3-methyl-4-hydroxy phenyl) cyclohexane of general structure (I), here after designated as BC and MeBC were synthesized according to reported methods [1-2] .

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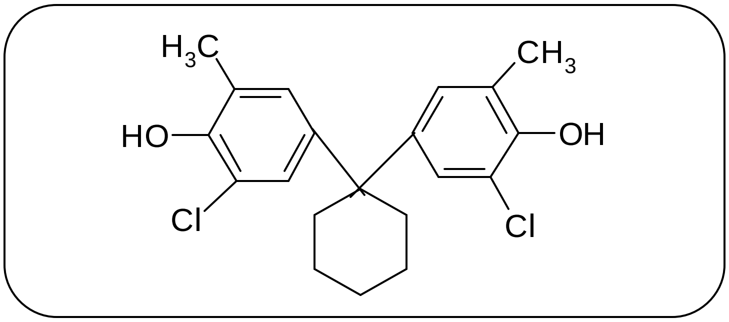
1. M. V. Rao, A. J. Rojivadia, P. H. Parsania and H. H. Parekh, "A convenient method for the preparation of bisphenols", J. Ind. Chem. Soc., **4**, 758-9, 1987
2. H. H. Garchar, H. N. Shukla and P. H. Parsania, "Kinetics of formation of 1,1'-bis(3-methyl-4-hydroxyphenyl)cyclohexane", Indian Acad. Sci., Chem. Sci. , **103**, 149-153, 1991.

Thus, cyclohexanone (0.5 mol, 49 g) was treated with phenol and o-cresol (1.0 mol, 94 g) in the presence of mixture of HCl:CH_3COOH (2:1 v/v, 100:50 ml) as a Friedel-Craft catalyst at 55°C for 4 h. The pink colored product was filtered, washed well with boiling water and treated with 2N NaOH solution. The resinous material was removed by filteration through cotton plug. The yellowish solution so obtained was acidified with dilute sulfuric acid, filtered, washed well with water and dried at 50°C. BC and MeBC were further recrystallized repeatedly from benzene and methanol water system. The process was repeated to get pure, white, shining crystals of ~81% yield of BC and 77% yield of MeBC, m.p. of BC and MeBC was 186°C.

(B) Synthesis of 1, 1'-bis (3-methyl-5-chloro-4-hydroxy phenyl) cyclohexane



(II)

ClMeBC

MeBC was chlorinated [3] by using thionyl chloride. Thus, a 0.5 mol (148 g) MeBC was suspended in 600 ml of carbon tetrachloride containing 4 g sodium sulphide as a catalyst and a 1.3 mol (95 ml) of thionyl chloride was added drop wise. The reaction mixture was refluxed for 4 h. After completion of the reaction, the excess of thionyl chloride and carbon tetrachloride were distilled off and the product was isolated from water, filtered, washed well with distilled water and dried at 50°C. ClMeBC was repeatedly recrystallized from benzene and methanol-water systems prior to their use. The yield and m.p. of ClMeBC was respectively, 70 % and 181°C.

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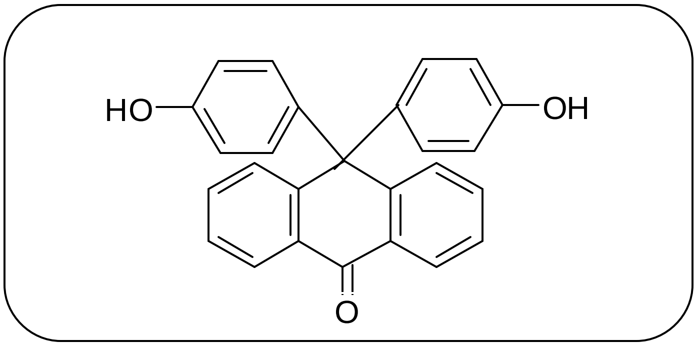
3. A. M. Serebryanyi, I. M Bilik and N. M. Mironova, "1,1'-Bis(3-chloro-4-hydroxyphenyl) cyclohexane",Metody Poluchkhim, Reactive Prep. (USSR) **20**, 35 ,1969; *C. A*. **76**, 85,493 ,1972.

(C) Synthesis of 9, 9'-Bis (4-hydroxy phenyl) anthrone-10 (BAN)



(III)

9,9'-Bis (4-hydroxy phenyl) anthrone-10 (BAN) was synthesized according to the reported method [4]. Thus, anthraquinone (1 mol) was condensed with phenol (7 mol) at 120ºC in presence of stannic chloride (1.5 mol) for 6h. Excess phenol was removed by steam distillation and product was boiled in an acetic acid to remove resinous material. The dark brown colored product was filtered, washed well with boiling water and dried at 50ºC.

Crude BAN (light gray) was dissolved in 2N NaOH solution and filtered through cotton plug. The yellowish solution so obtained was acidified with dilute HCl, filtered, washed well with water and dried. BAN was further recrystallized repeatedly from dioxane-water system to get pure, white shining crystals of yield ~ 80 % and m.p. was 324 º C.

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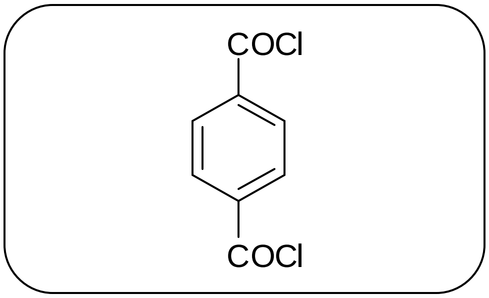
4. S. V. Vinogradova, S. N. Salazkin, L. A. Beridge, A. I. Mzhel'skii, A. A. Askadski, G. L. Slonimskii, and V. V. Korshak, "Polyarylates from 9,9'-bis-(4-hydroxyphenyl)-anthrone-10" ,Polym. Sci . USSR; **11**, No.1-3, 27, 1969.

(D) Synthesis of terephthaloyl chloride (TC).



(IV)

Terephthaloyl chloride (TC) was synthesized from terephthalic acid and thionyl chloride [5].

A mixture of terephthalic acid (100 g), thionyl chloride (500 g) and 2 ml pyridine was refluxed for 12 h. The excess of thionyl chloride was distilled off and TC was recrystallized from n-hexane to get fine white, shining crystals. The yield and m.p. of TC were 85% and 81^0-82^0C, respectively.

Ethylene glycol (EG), propylene glycol (PG), 1,4-butane diol (BD), 1,6-hexane diol (HD) and polyethylene glycol (PEG-400) were used as received.

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5. E.L. Wittbeker and P.W. Morgan, J.Polym. Sci , **60**, 28 ,1959.

SECTION-II: Syntheses of copolyesters

Polycondensation is a reversible reaction, this means that two processes take place simultaneously namely formation of product and interaction of the condensation product with low molecular weight byproduct such as H_2O, HCl, ROH, etc.

Molecular weight of the polymers depends on the reactivity of the initial compound [6]. In order to get high molecular weight polymer, it is essential to remove the byproduct from the reaction zone and stoichiometric must be maintained. An excess of one of the reactants always results in the formation of low molecular weight polymer.

Wittbeker and Morgan [7] showed that interfacial poly condensation is a better technique than that of melt polymerization. In melt polymerization, the polymerization is generally carried out well above 200^{o}C and further this technique is limited to intermediates and polymers those are stable under several conditions, while interfacial polycondensation is a rapid technique for the preparation of high molecular weight polymers at room temperature and below room temperature.

Interfacial polymerization is a term used to describe condensation polymerization and it takes place at the interphase of the two immiscible liquid phases. Usually one of the liquid phases is water containing acid acceptor such as NaOH or Na_2CO_3 and other phase is an organic solvent, generally one of the reactant i.e., dichloride or diacid chloride is dissolved in an organic solvent, while other reactant i.e., diamine, diol, etc. is dissolved in water. When two liquids containing monomers come in contact with each other, polymerization takes place at the interphase of the two liquid phases.

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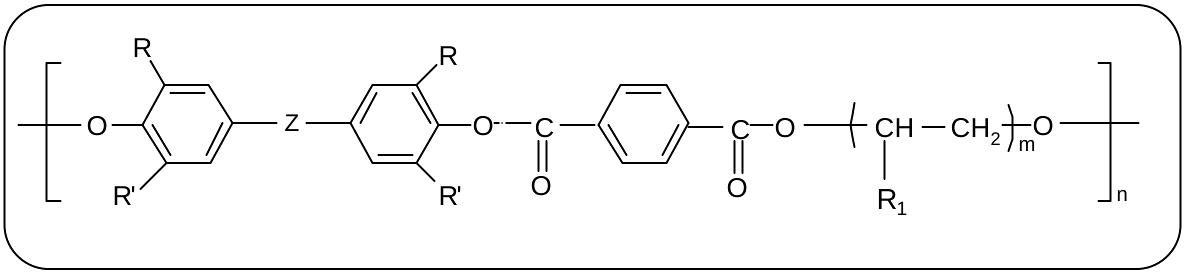
6. V. V. Korshak, V. A. Sergeev, V. K. Shitikov, A. A. Severov, V. F. Durlutsky, and S. G. Djeltakova, “Phenol-aldehyde resins”, Avt. Svudet, U.S.S.R. **172**, 489, 1962; Bull. Izobr., 13, **70** ,1965; **C. A. 63**, 16, 564 ,1965
7. E. L. Wittbeker and P. W. Morgan, J. Polym. Sci., **60**, 289, 1959.

Thus, the polymer film formed at the interphase is continuously removed and the byproduct is generally water soluble and removed from the reaction sphere. The rate of polymerization can be increased by vigorous agitation. With proper selection of reagents and concentration, it is possible to polymerize entire polymer reaction mixture in few minutes.

Copolyester synthesis

Into a 250 ml three neck flask equipped with a high speed mechanical stirrer and a thermometer, 0.005 mol (MeBC / ClMeBC / BAN: EG / PG / BD / HD – 50:50 / 75:25 / 25:75 %) or 0.0025 mol (0.945 g) BAN: 0.0025 mol (1 g) PEG-400 and 0.0125 mol (0.5 g) NaOH were dissolved in 50 ml of distilled water and the solution was cooled to 0^oC. A 50 mg cetyl trimethyl ammonium bromide (CTAB) was added and the solution was stirred vigorously for about 15min. To this solution, a 0.005 mol (1.015 g) terephthaloyl chloride (TC) in 12.5 ml chloroform was added drop wise through a dropping funnel over 10 min. The emulsion was vigorously stirred for 2 h at 0^oC. The organic layer was run into a large excess of methanol to precipitate the copolyester. The separated copolyester was filtered, washed well with water and finally with methanol and dried at 50^oC. The copolyesters were further purified thrice by dissolving in chloroform and precipitating in methanol. The yields were 81-96%.



[MeBC : EG : TC]

MET : m=1, R= CH_3 , R'=H, R_1=H and Z=  [50 : 50 : 100]

MET-1 : m=1, R= CH_3 , R'=H, R_1=H and Z=  [75 : 25 : 100]

MET-2 : m=1, R= CH_3 , R'=H, R_1=H and Z=  [25 : 75 : 100]

[MeBC : PG : TC]

MPT : m=1, R= CH_3 , R'=H, R_1= CH_3 and Z=  [50 : 50 : 100]

MPT-1 : m=1, R= CH_3 , R'=H, R_1= CH_3 and Z=  [75 : 25 : 100]

MPT-2 : m=1, R= CH_3 , R'=H, R_1= CH_3 and Z=  [25 : 75 : 100]

[MeBC : BD : TC]

MBT : m=2, R= CH_3 , R'=H, R_1= H and Z=  [50 : 50 : 100]

MBT-1 : m=2, R= CH_3 , R'=H, R_1= H and Z=  [75 : 25 : 100]

MBT-2 : m=2, R= CH_3 , R'=H, R_1= H and Z=  [25 : 75 : 100]

[MeBC : HD : TC]

MHT : m=3, R= CH_3 , R'=H, R_1= H and Z=  [50 : 50 : 100]

MHT-1 : m=3, R= CH_3 , R'=H, R_1= H and Z=  [75 : 25 : 100]

MHT-2 : m=3, R= CH_3 , R'=H, R_1= H and Z=  [25 : 75 : 100]

[ClMeBC : EG : TC]

ClMET : m=1, $R= CH_3$, R’=Cl, R_1= H and Z=  [50 : 50 : 100]

ClMET-1 : m=1, $R= CH_3$, R’=Cl, R_1= H and Z=  [75 : 25 : 100]

ClMET-2 : m=1, $R= CH_3$, R’=Cl, R_1= H and Z=  [25 : 75 : 100]

[ClMeBC: PG: TC]

ClMPT : m=1, $R= CH_3$, R’=Cl, R_1= CH_3 and Z=  [50 : 50 : 100]

ClMPT-1 : m=1, $R= CH_3$, R’=Cl, R_1= CH_3 and Z=  [75 : 25 : 100]

ClMPT -2 : m=1, $R= CH_3$, R’=Cl, R_1= CH_3 and Z=  [25 : 75 : 100]

[ClMeBC : BD : TC]

ClMBT : m=2, $R= CH_3$, R’=Cl, R_1= H and Z=  [50 : 50 : 100]

ClMBT-1 : m=2, $R= CH_3$, R’=Cl, R_1= H and Z=  [75 : 25 : 100]

ClMBT -2 : m=2, $R= CH_3$, R’=Cl, R_1= H and Z=  [25 : 75 : 100]

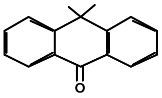
[ClMeBC : HD : TC]

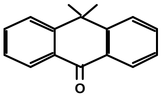
ClMHT : m=3, $R= CH_3$, R’=Cl, R_1= H and Z=  [50 : 50 :100]

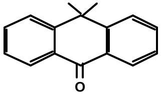
ClMHT-1 : m=3, $R= CH_3$, R’=Cl, R_1= H and Z=  [75 : 25 :100]

ClMHT -2 : m=3, $R= CH_3$, R’=Cl, R_1= H and Z=  [25 :75 :100]

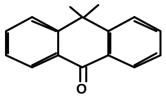
[BAN : EG : TC]

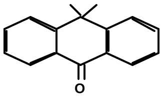
BANET : m=1, $R=R'=R_1=H$ and Z =  [50 : 50 : 100]

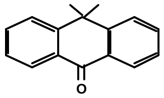
BANET-1: m=1, $R=R'=R_1$ =H and Z=  [75 : 25 : 100]

BANET-2: m=1,$R=R'=R_1$ =H and Z=  [25 : 75 : 100]

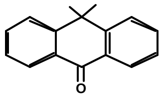
[BAN : PG : TC]

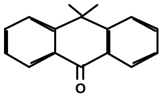
BANPT : m=1, $R=R'=H,R_1=CH_3$ and Z =  [50 : 50 : 100]

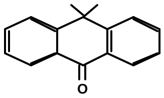
BANPT-1 : m=1, $R=R'=H,R_1=CH_3$ and Z =  [75 : 25 : 100]

BANPT-2 : m=1, $R=R'=H,R_1=CH_3$ and Z =  [25 : 75 : 100]

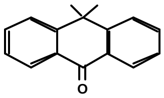
[BAN : BD : TC]

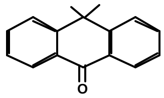
BANBT : m=2, $R=R'=R_1$=H and Z =  [50 : 50 : 100]

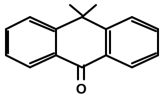
BANBT-1: m=2,$R=R'=R_1$ =H and Z=  [75 : 25 : 100]

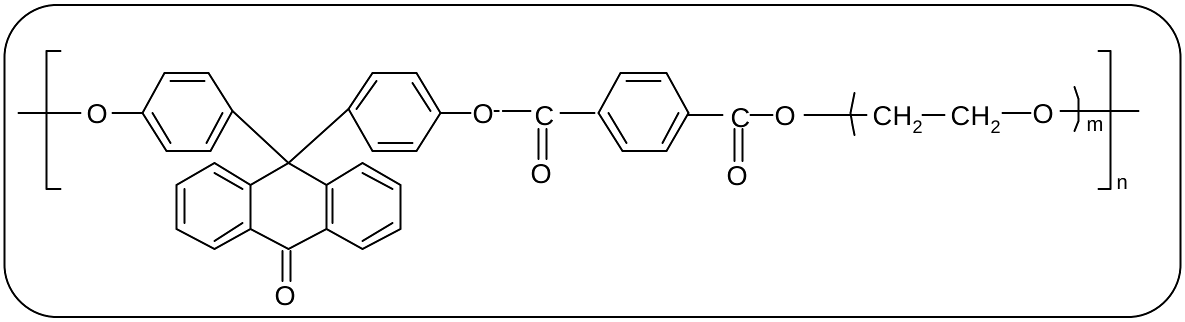
BANBT-2: m=2,$R=R'=R_1$ =H and Z=  [25 : 75 : 100]

[BAN : HD : TC]

BANHT : m=3, $R=R'=R_1$=H and Z =  [50 : 50 : 100]

BANHT-1: m=3,$R=R'=R_1$ =H and Z=  [75 : 25 : 100]

BANHT-2: m=3,$R=R'=R_1$ =H and Z=  [25 : 75 : 100]



BPEGT

CHAPTER – 3

CHARACTERIZATION

OF

COPOLYESTERS

CHAPTER- 3

CHARACTERIZATION OF COPOLYESTERS

This chapter of the thesis describes the characterization of copolyesters and it is further subdivided into seven sections:

SECTION-I: Solubility of copolyesters

SECTION-II: Spectral characterization of copolyesters

SECTION-III: Preparation of copolyester films

SECTION-IV: Density measurements

SECTION-V: Viscosity measurements

SECTION-VI: Hydrolytic stability of copolyesters

SECTION-VII: Microbial activity of copolyesters

SECTION 1: SOLUBILITY OF COPOLYESTERS

The solubility consideration is of prime importance [1-3] in solution processing during the casting of films, manufacturing of fibers and adhesive materials and also during the use of polymers under conditions, which expose them to attack by potential solvents either in industry or in the household applications.

The solubility of liquids and gases in polymer strongly depends on crystallinity. Crystallinity decreases the solubility of polymers markedly, since the process of solution involves overcoming the heat and entropy factors associated with crystallization as well as those of the intermolecular interactions in the amorphous regions. Properties related to solubility, such as the cloud point of the dilute solutions are often functions of crystallinity and relatively independent of molecular weight.

When we introduce the polar groups among the polymer chain, solubility of that polymer decreases, since strong polymer-polymer bonds usually develop. The situation is complicated however, by factors such as the arrangement and bulkiness of the groups, which in turn influence crystallinity. The solubility of a polymer may improve or grow worse with increasing temperature. In this same temperature range some polymers will dissolve better when heated, while others when cooled, in the same solvent. Solubility relation in polymer systems are more complex than those among low molecular weight compounds because of the size, molecular weight difference, viscosity difference between the polymer, and solvent molecules and the possible presence of a crystalline phase.

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1. J. H. Hildebrand, R. L. Scott, “The Solubility of Non-electrolytes” 3rd Ed. Reinhold, New York, 1950.
2. F. W. Billmeyer, “Textbook of Polymer Science” 4th Ed., John Willey and Sons., New York, 1994.
3. P. J. Flory. “Principles of Polymer Chemistry” Cornell University Press, Ithaca, New York, 1962.

Dissolution of a polymer is a slow process and occurring in two stages. First, solvent is slowly imbibed into the polymer to produce a swollen gel. In the second stage, the gels gradually disintegrate into a true solution. Only the second stage is materially speed up by agitation. If the polymer is cross linked by primary valence bonds or strong hydrogen bonds or is highly crystalline, only swelling may take place.

Solubility test

In order to test the solubility of a given polymer, approximately 50 mg of polymer sample was placed in a series of test tubes containing about 5ml of solvents and kept them aside for sometime. Gradual disintegration of swollen gel indicated the formation of true solution. The solubility data for copolyesters are reported in Table-3.1,from which it is clear that copolyesters of MeBC and ClMeBC are only soluble in chloroform, 1,2-dichloroethane and dichloromethane while copolyesters of BAN are found soluble in common solvents like chloroform, 1,2-dichloroethane, dichloromethane, DMF, DMSO, THF, etc.

Table-3.1: The solubility of copolyesters in different solvents at room temperature.

Solvent	Copolyesters					
	MET	MET-1	MET-2	MPT	MPT-1	MPT-2
Chloroform	S	S	S	S	S	S
1,2 - Dichloroethane	S	S	S	S	S	S
Dichloromethane	S	S	S	S	S	S
1,4 – Dioxane	PS	PS	PS	PS	PS	PS
N,N-Dimethylformamide	PS	PS	PS	PS	PS	PS
Dimethylsulfoxide	PS	PS	PS	PS	PS	PS
Chlorobenzene	IS	IS	IS	IS	IS	IS
Tetrahydrofuran	PS	PS	PS	PS	PS	PS
Cyclo hexanone	IS	IS	IS	IS	IS	IS
Acetone	IS	IS	IS	IS	IS	IS
Benzene	IS	IS	IS	IS	IS	IS
Toluene	IS	IS	IS	IS	IS	IS
Nitrobenzene	IS	IS	IS	IS	IS	IS
Methanol	IS	IS	IS	IS	IS	IS
Isopropyl alcohol	IS	IS	IS	IS	IS	IS
n-Propyl alcohol	IS	IS	IS	IS	IS	IS
n-Butanol	IS	IS	IS	IS	IS	IS
Ethanol	IS	IS	IS	IS	IS	IS
Diethyl ether	IS	IS	IS	IS	IS	IS
Carbon tetrachloride	IS	IS	IS	IS	IS	IS
Acetophenone	IS	IS	IS	IS	IS	IS

S=Soluble, IS=Insoluble, PS= Partially soluble

Solvent	Copolyesters						
	MBT	MBT-1	MBT-2	MHT	MHT-1	MHT-2	BPEGT
Chloroform	S	S	S	S	S	S	S
1,2 - Dichloroethane	S	S	S	S	S	S	S
Dichloromethane	S	S	S	S	S	S	S
1,4 – Dioxane	PS	PS	PS	PS	PS	PS	S
N,N-Dimethylformamide	PS	PS	PS	PS	PS	PS	S
Dimethylsulfoxide	PS	PS	PS	PS	PS	PS	S
Chlorobenzene	IS	IS	IS	IS	IS	IS	IS
Tetrahydrofuran	PS	PS	PS	PS	PS	PS	S
Cyclo hexanone	IS	IS	IS	IS	IS	IS	IS
Acetone	IS	IS	IS	IS	IS	IS	IS
Benzene	IS	IS	IS	IS	IS	IS	IS
Toluene	IS	IS	IS	IS	IS	IS	IS
Nitrobenzene	IS	IS	IS	IS	IS	IS	IS
Methanol	IS	IS	IS	IS	IS	IS	IS
Isopropyl alcohol	IS	IS	IS	IS	IS	IS	IS
n-Propyl alcohol	IS	IS	IS	IS	IS	IS	IS
n-Butanol	IS	IS	IS	IS	IS	IS	IS
Ethanol	IS	IS	IS	IS	IS	IS	IS
Diethyl ether	IS	IS	IS	IS	IS	IS	IS
Carbon tetrachloride	IS	IS	IS	IS	IS	IS	IS
Acetophenone	IS	IS	IS	IS	IS	IS	IS

S=Soluble, IS=Insoluble, PS= Partially soluble

Solvent	Copolyesters					
	CIMET	**CIMET-1**	**CIMET-2**	**CIMPT**	**CIMPT-1**	**CIMPT-2**
Chloroform	S	S	S	S	S	S
1,2 - Dichloroethane	S	S	S	S	S	S
Dichloromethane	S	S	S	S	S	S
1,4 – Dioxane	PS	PS	PS	PS	PS	PS
N,N-Dimethylformamide	PS	PS	PS	PS	PS	PS
Dimethylsulfoxide	PS	PS	PS	PS	PS	PS
Chlorobenzene	IS	IS	IS	IS	IS	IS
Tetrahydrofuran	PS	PS	PS	PS	PS	PS
Cyclo hexanone	IS	IS	IS	IS	IS	IS
Acetone	IS	IS	IS	IS	IS	IS
Benzene	IS	IS	IS	IS	IS	IS
Toluene	IS	IS	IS	IS	IS	IS
Nitrobenzene	IS	IS	IS	IS	IS	IS
Methanol	IS	IS	IS	IS	IS	IS
Isopropyl alcohol	IS	IS	IS	IS	IS	IS
n-Propyl alcohol	IS	IS	IS	IS	IS	IS
n-Butanol	IS	IS	IS	IS	IS	IS
Ethanol	IS	IS	IS	IS	IS	IS
Diethyl ether	IS	IS	IS	IS	IS	IS
Carbon tetrachloride	IS	IS	IS	IS	IS	IS
Acetophenone	IS	IS	IS	IS	IS	IS

S=Soluble, IS=Insoluble, PS= Partially soluble

Solvent	Copolyesters					
	CIMBT	**CIMBT-1**	**CIMBT-2**	**CIMHT**	**CIMHT-1**	**CIMHT-2**
Chloroform	S	S	S	S	S	S
1,2 - Dichloroethane	S	S	S	S	S	S
Dichloromethane	S	S	S	S	S	S
1,4 – Dioxane	PS	PS	PS	PS	PS	PS
N,N-Dimethylformamide	PS	PS	PS	PS	PS	PS
Dimethylsulfoxide	PS	PS	PS	PS	PS	PS
Chlorobenzene	IS	IS	IS	IS	IS	IS
Tetrahydrofuran	PS	PS	PS	PS	PS	PS
Cyclo hexanone	IS	IS	IS	IS	IS	IS
Acetone	IS	IS	IS	IS	IS	IS
Benzene	IS	IS	IS	IS	IS	IS
Toluene	IS	IS	IS	IS	IS	IS
Nitrobenzene	IS	IS	IS	IS	IS	IS
Methanol	IS	IS	IS	IS	IS	IS
Isopropyl alcohol	IS	IS	IS	IS	IS	IS
n-Propyl alcohol	IS	IS	IS	IS	IS	IS
n-Butanol	IS	IS	IS	IS	IS	IS
Ethanol	IS	IS	IS	IS	IS	IS
Diethyl ether	IS	IS	IS	IS	IS	IS
Carbon tetrachloride	IS	IS	IS	IS	IS	IS
Acetophenone	IS	IS	IS	IS	IS	IS

S=Soluble, IS=Insoluble, PS= Partially soluble

Solvent	Copolyesters					
	BANET	**BANET-1**	**BANET-2**	**BANPT**	**BANPT-1**	**BANPT-2**
Chloroform	S	S	S	S	S	S
1,2- Dichloroethane	S	S	S	S	S	S
Dichloromethane	S	S	S	S	S	S
1,4 – Dioxane	S	S	S	S	S	S
N,N-Dimethylformamide	S	S	S	S	S	S
Dimethylsulfoxide	S	S	S	S	S	S
Chlorobenzene	IS	IS	IS	IS	IS	IS
Tetrahydrofuran	S	S	S	S	S	S
Cyclo hexanone	IS	IS	IS	IS	IS	IS
Acetone	IS	IS	IS	IS	IS	IS
Benzene	IS	IS	IS	IS	IS	IS
Toluene	IS	IS	IS	IS	IS	IS
Nitrobenzene	IS	IS	IS	IS	IS	IS
Methanol	IS	IS	IS	IS	IS	IS
Isopropyl alcohol	IS	IS	IS	IS	IS	IS
n-Propyl alcohol	IS	IS	IS	IS	IS	IS
n-Butanol	IS	IS	IS	IS	IS	IS
Ethanol	IS	IS	IS	IS	IS	IS
Diethyl ether	IS	IS	IS	IS	IS	IS
Carbon tetrachloride	IS	IS	IS	IS	IS	IS
Acetophenone	IS	IS	IS	IS	IS	IS

S=Soluble, IS=Insoluble, PS= Partially soluble

Solvent	**Copolyesters**					
	BANBT	**BANBT-1**	**BANBT-2**	**BANHT**	**BANHT-1**	**BANHT-2**
Chloroform	S	S	S	S	S	S
1,2-Dichloroethane	S	S	S	S	S	S
Dichloromethane	S	S	S	S	S	S
1,4 – Dioxane	S	S	S	S	S	S
N,N-Dimethylformamide	S	S	S	S	S	S
Dimethylsulfoxide	S	S	S	S	S	S
Chlorobenzene	IS	IS	IS	IS	IS	IS
Tetrahydrofuran	S	S	S	S	S	S
Cyclo hexanone	IS	IS	IS	IS	IS	IS
Acetone	IS	IS	IS	IS	IS	IS
Benzene	IS	IS	IS	IS	IS	IS
Toluene	IS	IS	IS	IS	IS	IS
Nitrobenzene	IS	IS	IS	IS	IS	IS
Methanol	IS	IS	IS	IS	IS	IS
Isopropyl alcohol	IS	IS	IS	IS	IS	IS
n-Propyl alcohol	IS	IS	IS	IS	IS	IS
n-Butanol	IS	IS	IS	IS	IS	IS
Ethanol	IS	IS	IS	IS	IS	IS
Diethyl ether	IS	IS	IS	IS	IS	IS
Carbon tetrachloride	IS	IS	IS	IS	IS	IS
Acetophenone	IS	IS	IS	IS	IS	IS

S=Soluble, IS=Insoluble, PS= Partially soluble

SECTION-2: SPECTRAL CHARACTERIZATION OF COPOLYESTERS

This section includes IR and NMR spectral characterization of copolyesters

[A] IR SPECTRAL CHARACTERIZATION

IR spectroscopy is an excellent technique for the qualitative analysis because except for optical isomers, the spectrum of compound is unique. Information about the structure of a molecule could frequently be obtained from its absorption spectrum. An infrared spectrum is obtained by passing infrared radiation through a sample. A detector generates a plot of % transmittance of radiation versus the wave number or wavelength of the radiation transmitted. At 100% transmittance, all the energy of radiation passes through the molecule. At lower values of % transmittance, some of the energy is being absorbed by the compound. Each spike in the infrared (IR) spectrum represents absorption of energy. These spikes are called absorption bands.

Electromagnetic radiation with wave numbers from 4000 to 400 cm^{-1} has just the right energy to correspond to stretching and bending vibrations in molecules. Electromagnetic radiation with this energy is known as infrared radiation because it is just below the “red region” of visible light. (Infra is Latin word for “below”).

The intensity of an absorption band depends on the size of dipole moment change associated with the vibration. In other words, depends on polarity of the vibrating bond. Intensity of the absorption bond also depends on number of bonds responsible for the absorption. The concentration of the sample used to obtain an IR spectrum also affects the intensity of absorption bands. Concentrated samples have greater wave numbers and therefore more intense absorption bands.

The IR spectra (films) of copolyesters were scanned on a Shimadzu-8400 FTIR spectrometer over the frequency range from 4000-400 cm^{-1}. The IR spectra of copolyesters are shown in Figs. 3.1 to 3.6. The characteristic IR absorption frequencies (cm^{-1}) are reported in Table-3.2.

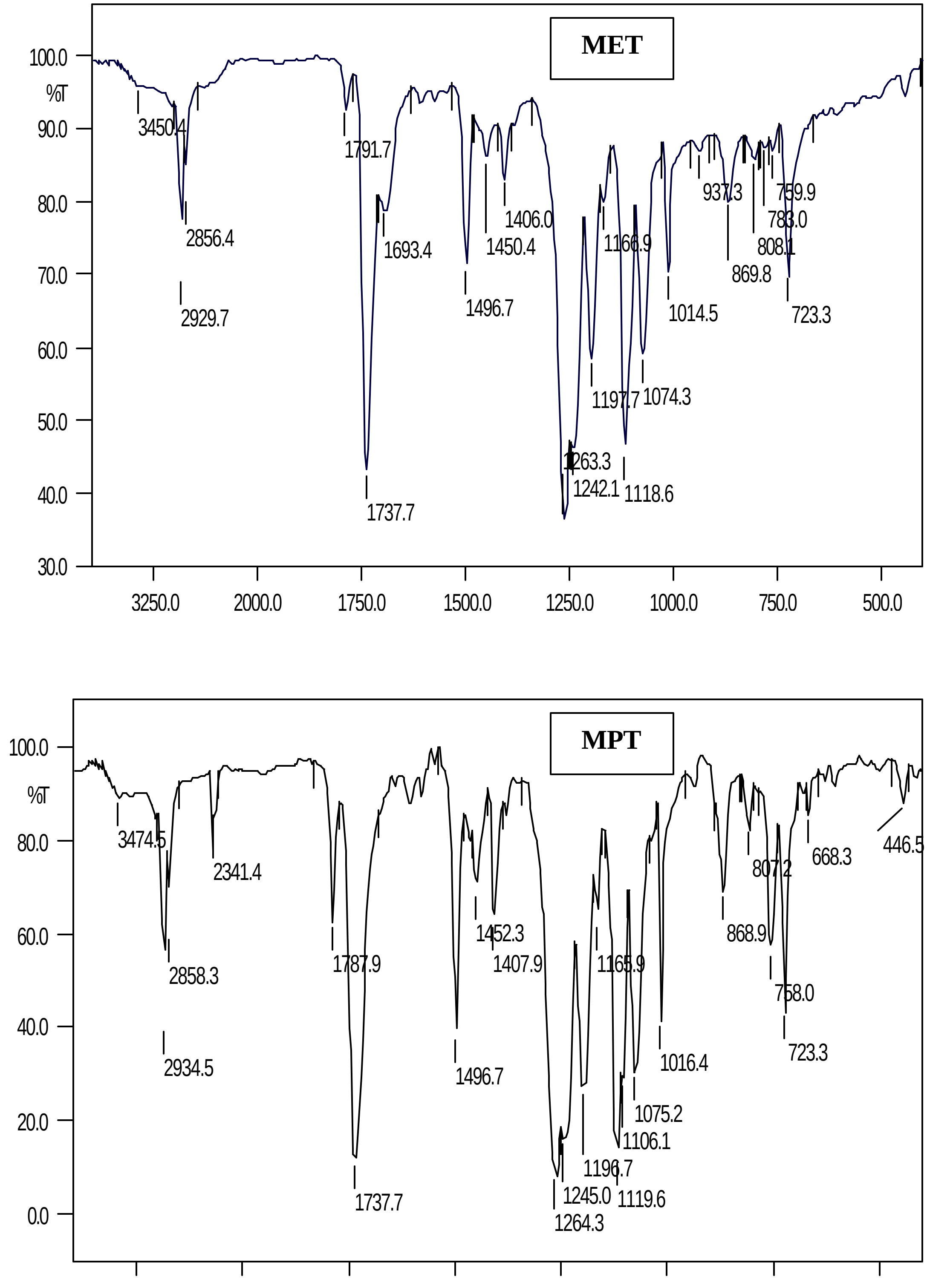

Fig.- 3.1: IR spectra of MET and MPT

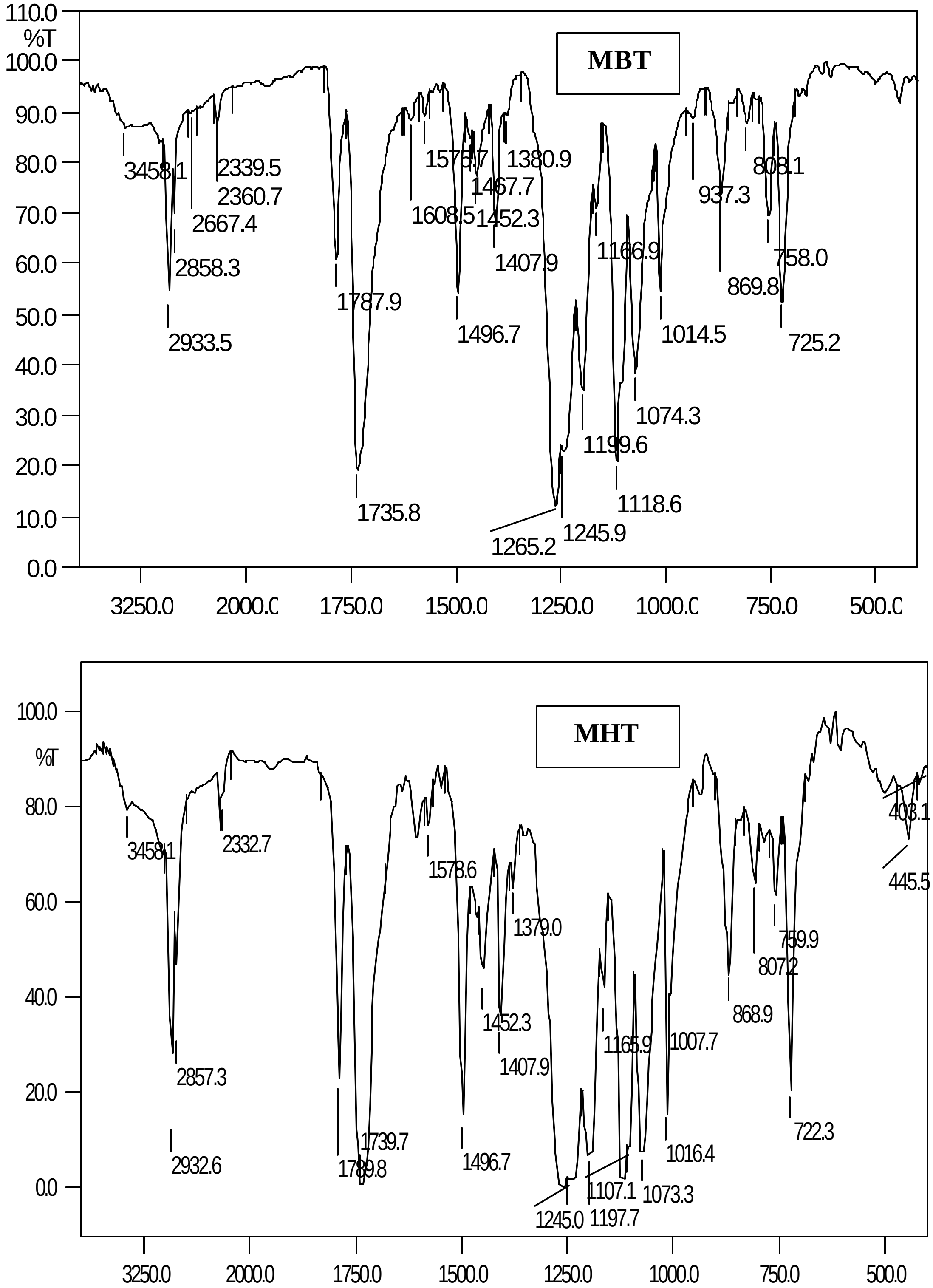

Fig.- 3.2: IR spectra of MBT and MHT

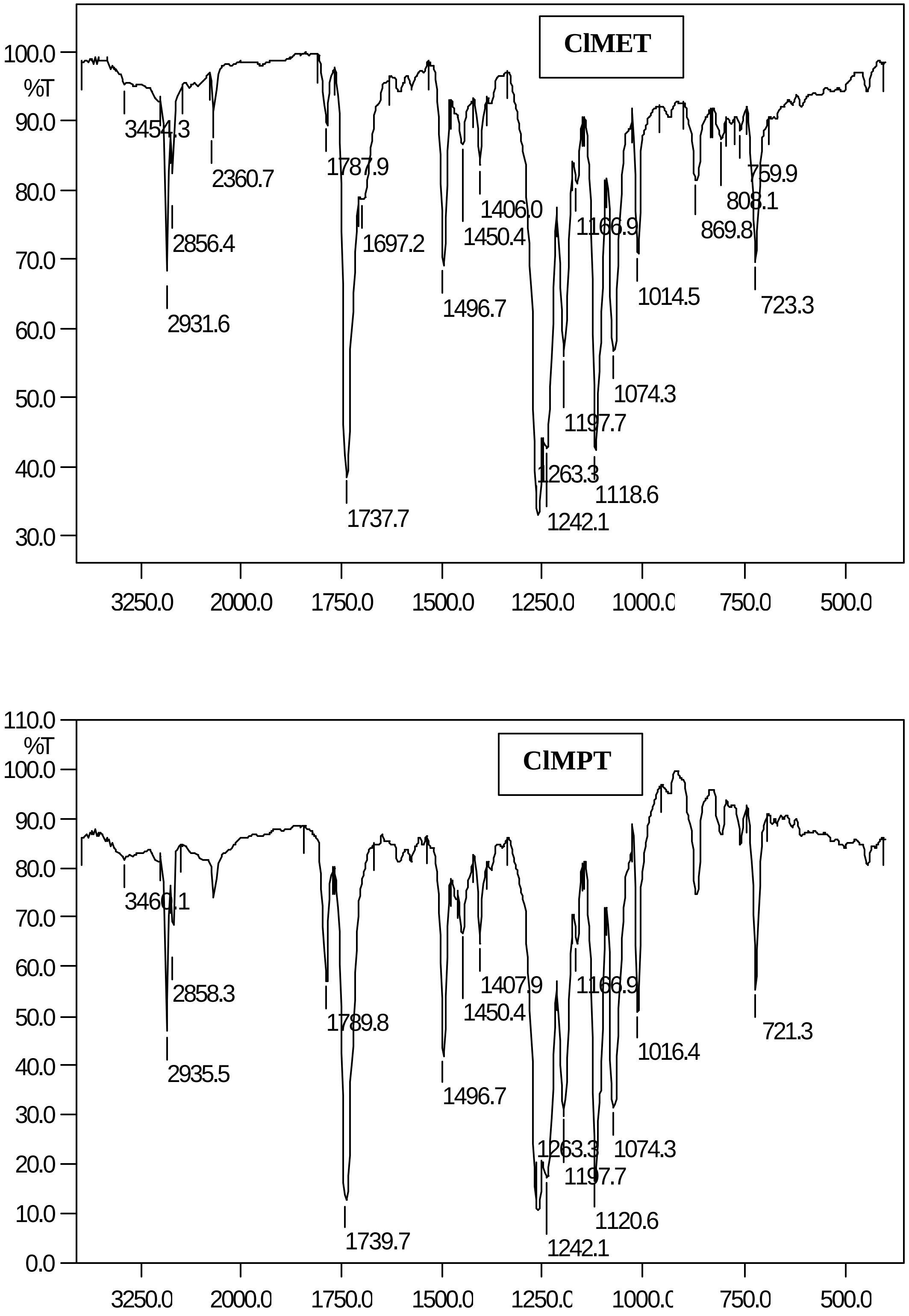

Fig.- 3.3: IR spectra of ClMET and ClMPT

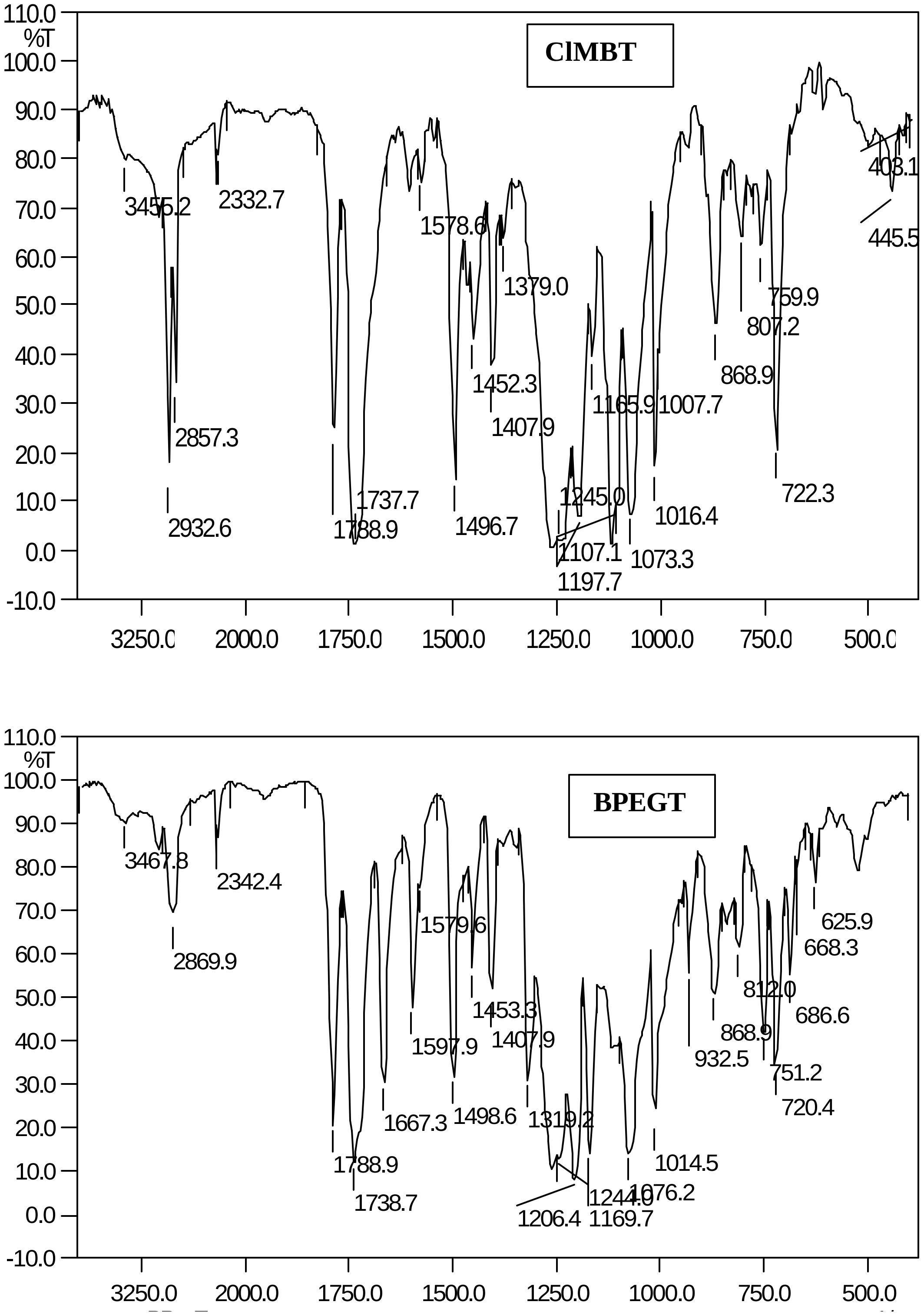

Fig.- 3.4: IR spectra of ClMBT and BPEGT

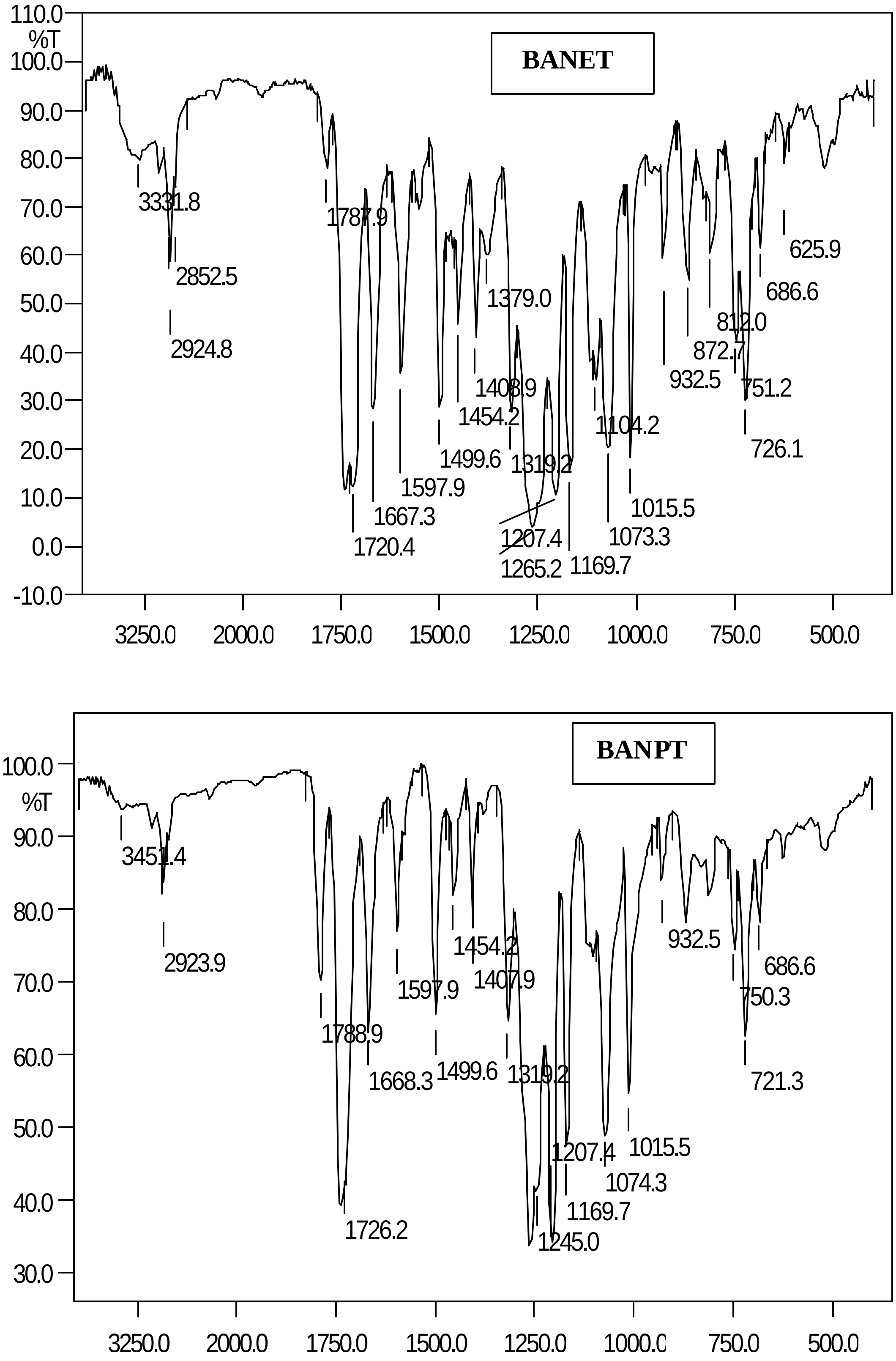

Fig. 3.5: IR spectra of BANET and BANPT

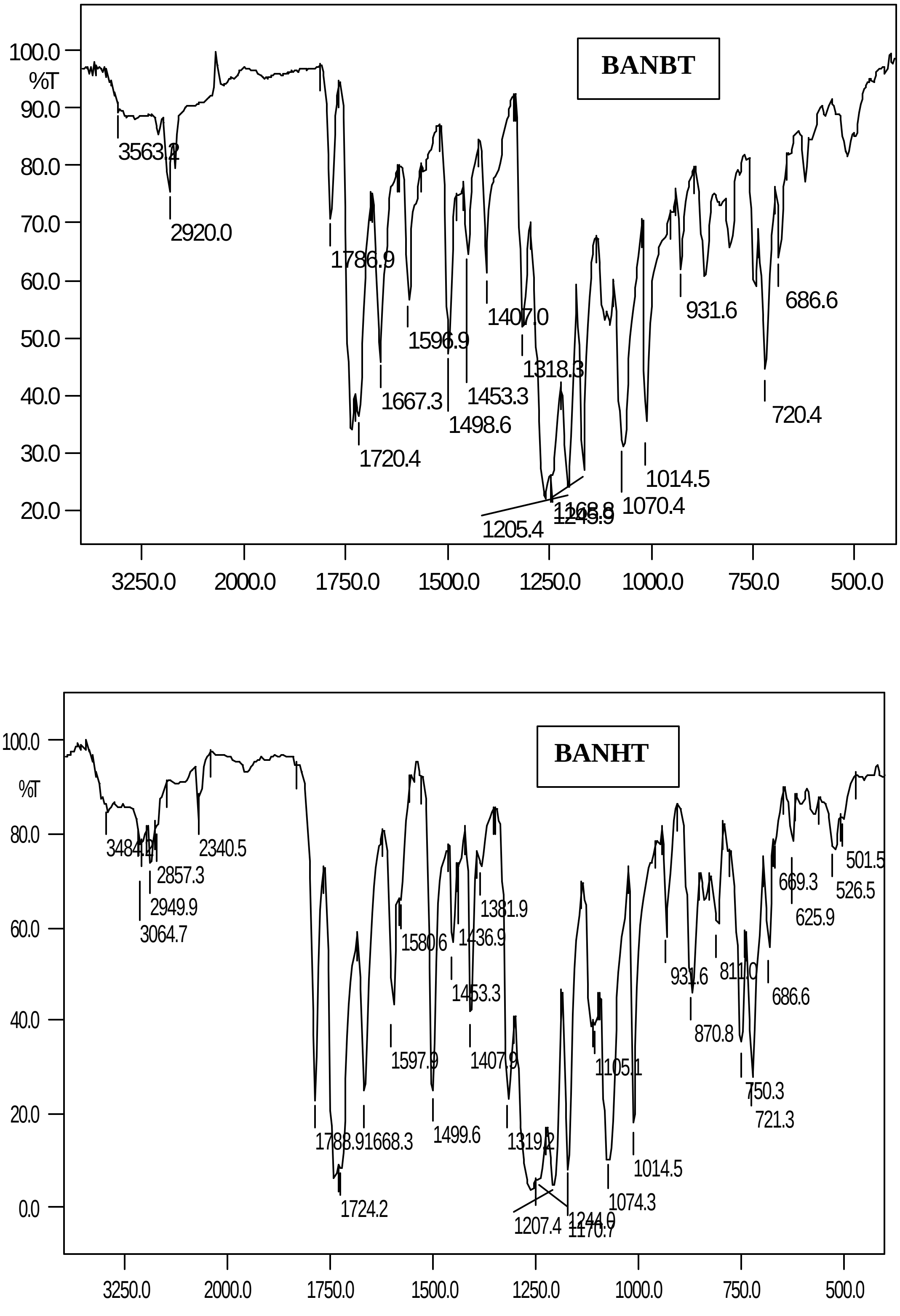

Fig.- 3.6: IR spectra of BANBT and BANHT

Table-3.2: The characteristic IR absorption bands (cm^{-1}) of copolyesters

Types	Group Vibration mode	Observed IR Frequencies, (cm^{-1})				Expected Frequencies (cm^{-1})
		MET	MPT	MBT	MHT	
Alkane	C-H (str.) ?$_{as}$	2929.7	2934.5	2933.5	2932.6	2975-2950
	?$_{s}$	2856.4	2858.3	2858.3	2857.3	2880-2860
	C-H (def), -CH_3	1450.4	1452.3	1452.3	1452.3	1470-1435
	C-H (def), -CH_2-	1496.7	1496.7	1496.7	1496.7	1485-1445
	CH_2(rocking)	723.3	723.3	725.2	722.3	~720
-CH_2 -	C-H (str.) ?$_{as}$	2929.7	2934.5	2933.5	2932.6	2940-2915
	?$_{s}$	2856.4	2858.3	2858.3	2857.3	2870-2845
	Scissoring	1450.4	1452.3	1452.3	1452.3	1480-1440
	Twistting & Wagging	1242.1	1245.0	1245.9	1245.0	~1250
	Skeletal CH_2 4 or>	759.9	758.0	758.0	759.9	750-720
Ar-OH	O-H def.	1406.0	1407.9	1407.9	1407.9	1410-1310
	C- O (str.)	1197.7	1196.7	1199.6	1197.7	1230-1140
Ar-COOH	O-H (str.)	3450.4	3474.5	3458.1	3458.1	3550-3400
	C- O (str.)	1263.3	1264.3	1265.2	1265.0	1320-1210
	O-H def.	1450.4	1452.3	1452.3	1452.3	1440-1395

Types	Group Vibration mode	Observed IR Frequencies, (cm^{-1})				Expected Frequencies (cm^{-1})
		MET	MPT	MBT	MHT	
Aromatic	C=C (str.)	1406.0	1407.9	1407.9	1407.9	1606±6,1579±6, 1409±8 (1,4 sub.)
		1496.7	1496.7	1496.7	1496.7	1616±8,1577±8, 1510±8,1456±1 (1,2,4 sub.)
	C-H (i.p.d)	1118.6	1119.6	1118.6	1107.1	1258±11, 1175±6,1117±7, 1073±5 (1,4 sub)
	C-H (i.p.d)	1014.5	1016.4	1014.5	1016.4	1225-1175,1175-1125,1070-1000 (1,2,4 sub)
	C-H (o.o.p.d)	808.1	807.2	808.1	807.2	817±15 (1,4 sub)
	C-H (o.o.p.d)	869.8	868.9	869.8	868.9	900-860,860-800(1,2,4 sub)
Ester	C= O (str.)	1737.7 1791.7	1737.7 1787.9	1735.8 1787.9	1739.7 1789.8	1780-1710
	C- O (str.)	1242.1 1263.3	1245.0 1264.3	1245.9 1265.2	1245.0 1260.0	1300-1250

Types	**Group Vibration mode**	**Observed IR Frequencies, (cm^{-1})**			**Expected Frequencies (cm^{-1})**
		ClMET	ClMPT	ClMBT	
Alkane	C-H (str.) ?$_{as}$	2931.6	2935.5	2932.6	2975-2950
	?$_{s}$	2856.4	2858.3	2857.3	2880-2860
	C-H (def), -CH$_3$-	1450.4	1450.4	1452.3	1470-1435
	C-H (def) , -CH$_2$-	1496.7	1496.7	1496.7	1485-1445
	CH$_2$(rocking)	723.3	721.3	722.3	~720
-CH$_2$ -	C-H (str.) ?$_{as}$	2931.6	2935.5	2932.6	2940-2915
	?$_{s}$	2856.4	2858.3	2857.3	2870-2845
	Scissoring	1450.4	1450.4	1452.3	1480-1440
	Twistting & Wagging	1242.1	1242.1	1245.0	~1250
	Skeletal CH$_2$ 4 or>	759.9	758.09	759.9	750-720
Ar-OH	O-H def.	1406.0	1407.9	1407.9	1410-1310
	C- O (str.)	1197.7	1197.7	1197.7	1230-1140
Ar-COOH	O-H (str.)	3454.3	3460.1	3455.2	3550-3500
	C- O (str.)	1263.3	1263.3	1263.4	1320-1210
	O-H def.	1450.4	1450.4	1452.3	1440-1395

Types	**Group Vibration mode**	**Observed IR Frequencies, (cm^{-1})**			**Expected Frequencies (cm^{-1})**
		ClMET	ClMPT	ClMBT	
Aromatic	C=C (str.)	1406.0	1407.9	1407.9	1606±6,1579±6,1520 -1480,1409±8 (1,4 sub.)
		1496.7	1496.7	1496.7	1616±8, 1577±8, 1510±8, 1456±1 (1,2,4 sub.)
	C-H (i.p.d)	1118.6	1166.9	1165.9	1258±11, 1175±6,1117±7, 1073±5 (1,4 sub)
	C-H (i.p.d)	1014.5	1016.4	1016.4	1225-1175,1175-1125,1070-1000 (1,2,4 sub)
	C-H (o.o.p.d)	808.1	807.4	807.2	817±15 (1,4 sub)
	C-H (o.o.p.d)	869.8	868.4	868.9	900-860,860-800(1,2,4 sub)
Ester	C= O (str.)	1737.7 1787.9	1739.7 1789.8	1737.7 1788.9	1780-1710
	C- O (str.)	1242.1 1263.3	1242.1 1263.3	1245.0 1264.1	1300-1250
Halogen	C-Cl (str.)	723.3	721.3	722.3	800-600

Types	Group Vibration mode	Observed IR Frequencies, (cm^{-1})					Expected Frequencies (cm^{-1})
		BANET	BANPT	BANBT	BANHT	BPEGT	
Alkane	C-H (str.) ?$_{as}$ -CH_3	2924.8	2923.9	2920.0	2924.9	2869.9	2975-2950
	C-H (def) ?$_{as,}$ -CH_3	1454.2	1454.2	1453.3	1453.3	1454.2	1470-1435
	C-H (def) ?$_{as,}$ -CH_2-	1499.6	1499.6	1498.6	1499.6	1498.6	1485-1445
	-CH_2 - (rocking)	726.1	721.3	720.4	721.3	720.4	~720
Ar-OH	O-H def.	1408.9	1407.9	1407.0	1407.9	1407.9	1410-1310
	C- O (str.)	1169.7	1169.7	1168.8	1170.7	1169.7	1230-1140
Ar-COOH	O-H (str.)	3331.8	3451.4	3563.2	3484.2	3467.8	3550-3500
	C- O (str.)	1265.2	1266.1	1267.3	1319.2	1244.0	1320-1210
	O-H def.	1454.2	1454.2	1453.3	1453.3	1453.3	1440-1395
Aromatic	C=C (str.)	1408.9	1407.9	1407.0	1407.9	1407.9	1579±6, 1480, 1409±8 (1,4 sub.)
		1499.6 1597.9	1499.6 1597.9	1498.6 1596.9	1499.6 1597.9	1498.6 1597.9	
	C-H (i.p.d)	1169.7	1169.7	1168.9	1170.7	1169.7	1258±11, 1175±6, 1117±7, 1073±5 (1,4 sub)
	C-H (o.o.p.d)	812.0	811.9	811.4	811.0	812.0	817±15 (1,4 sub)

Types	**Group Vibration mode**	**Observed IR Frequencies, (cm^{-1})**					**Expected Frequencies (cm^{-1})**
		BANET	BANPT	BANBT	BANHT	BPEGT	
Ester	C= O (str.)	1720.4 1787.9	1726.2 1788.9	1720.4 1786.9	1724.2 1788.9	1738.7 1788.9	1780-1710
	C- O (str.)	1265.2 1207.4	1245.0 1207.4	1249.9 1205.4	1244.0 1207.4	1244.0 1206.4	1300-1250
Ketone	C= O (str.)	1667.3	1668.3	1667.3	1668.3	1667.3	1685-1665

[B] NMR SPECTRAL CHARACTERIZATION

Some nuclei spin about their axes in a manner to that electrons spin. In the presence of an externally applied magnetic field, a spinning nucleus can only assume a limited number of stable orientations. Nuclear magnetic resonance occurs when a spinning nucleus in a lower energetic orientation in a magnetic field absorbs sufficient electromagnetic radiation to be excited to a higher energetic orientation. The excitation energy varies with the type and environment of the nucleus. NMR spectroscopy can be used for the quantitative chemical analysis [4-8]. NMR spectroscopy consists of measuring the energy that is required to change a spinning nucleus from a stable orientation to a less stable orientation in the magnetic field. Different spinning nuclei at different frequencies in the magnetic field absorb different frequencies of radiation to change their orientations. The frequencies at which absorption occurs can be used for qualitative analysis. The decrease in intensity of incident radiation owing to absorption during a particular transition is related to the different spinning nuclei at different frequencies in the magnetic field absorb different frequencies of radiation to change their orientations. The frequencies at which absorption occur can be used for qualitative analysis. The decrease in intensity of incident radiation owing to absorption during a particular transition is related to the number of nuclei in the sample that undergo the transition and can be used for quantitative analysis.

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NMR spectrometer was invented in 1945 by Falix Bloch (Stanford University) and Edward Purcell. They shared the Nobel Prize (1952) in Physics for their work.

The estimation of copolymer composition is of paramount importance for tailor making copolymers with the required physico-chemical properties. For quantitative copolymer composition, UV, IR and NMR spectroscopic techniques are well established [9-13]. NMR technique is more convenient for the quantitative estimation of copolymer composition as compared to other spectroscopic techniques.

The NMR spectra of polymers were scanned on a Bruker FTNMR (300MHz) spectrometer by using $CDCl_3$ as a solvent and TMS as an internal standard. NMR spectra of copolyesters are shown in Figs. 3.7 to 3.12. The chemical shifts are reported in Table-3.3. The signal due to residual chloroform is merged with aromatic protons at about 7.27 ppm. The integrated areas are found in excellent agreement with observed one within experimental errors involved in determining integrated peak areas. In compounds with identical para substituents, whatever their electronegativity, the benzenoid protons display a singlet due to symmetry reasons. TC moiety displayed a singlet in all copolyesters.

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The methyl groups do not strongly influence the electro density of the ring or the amount of shielding felt by any of the substituents on the ring. Often the chemical shift differences induced by substituents are large enough to give superficially first order spectra for benzene derivatives having both electro withdrawing and donating groups. It is interesting to note that the protons bonded to ester linkage displayed in the up field with increase in the alkyl chain length. The types of protons and peaks are assigned in corresponding spectrum.

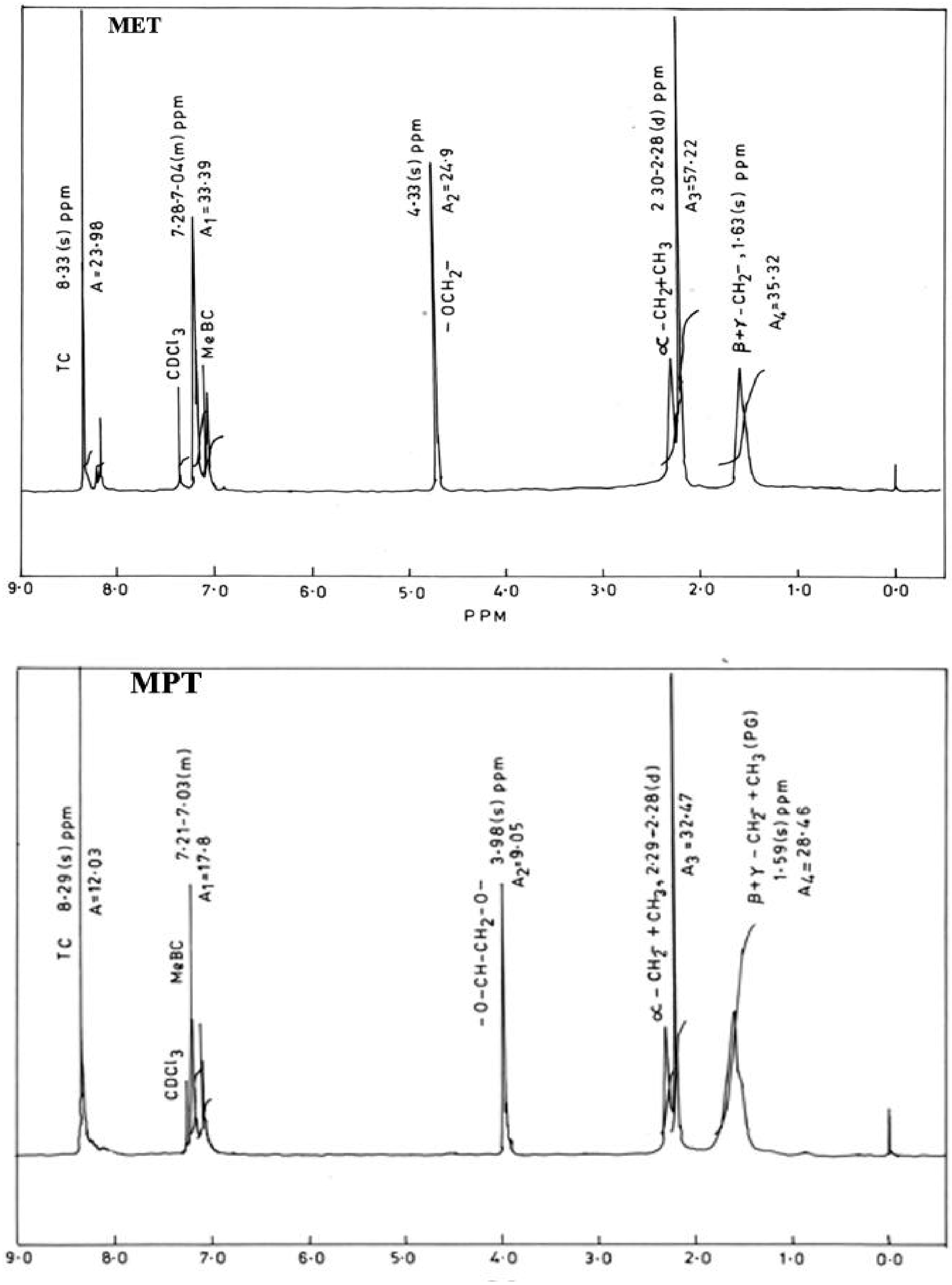


Fig.-3.7: NMR (300MHZ) spectra of MET and MPT

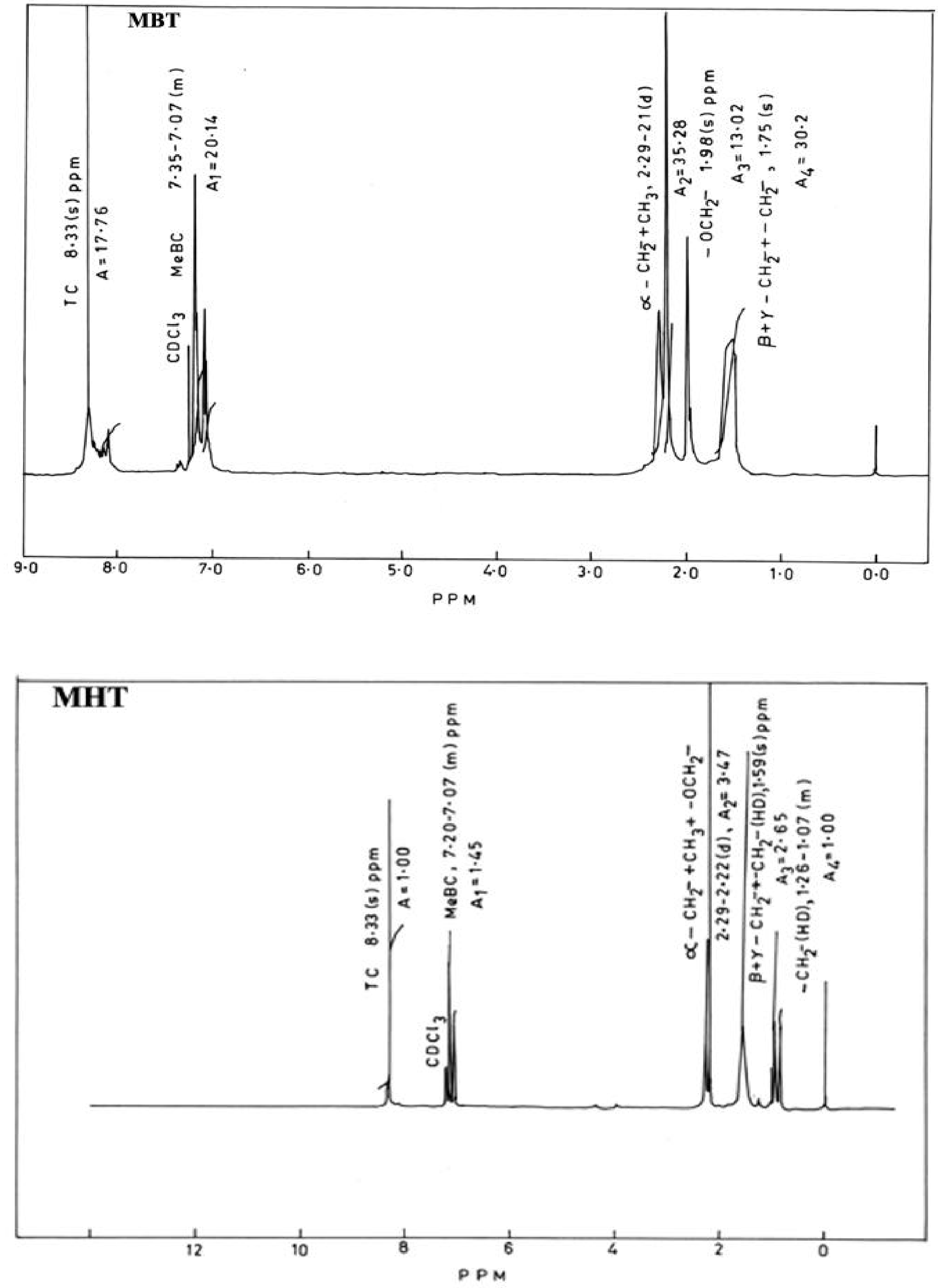


Fig.-3.8: NMR (300MHZ) spectra of MBT and MHT

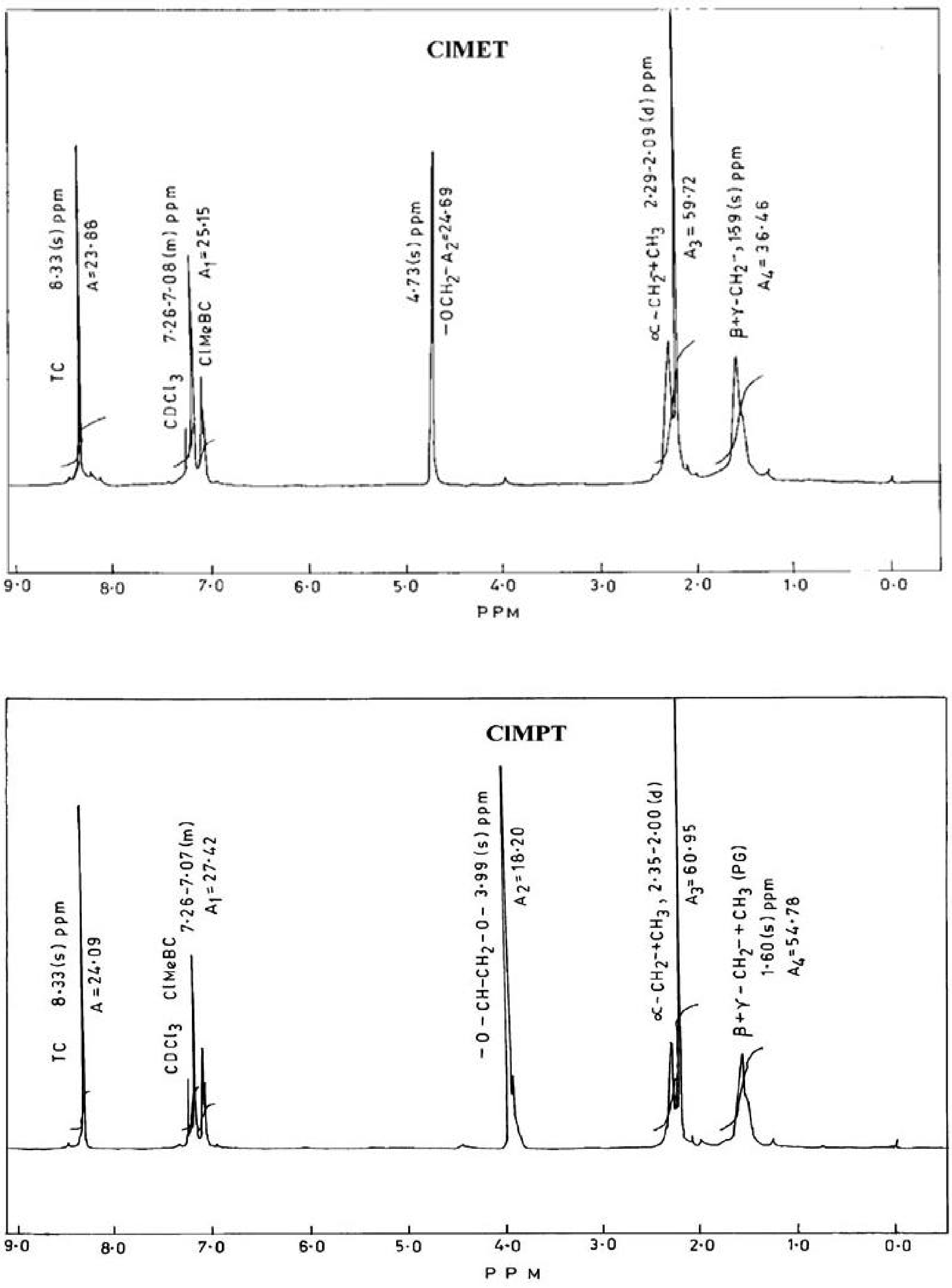
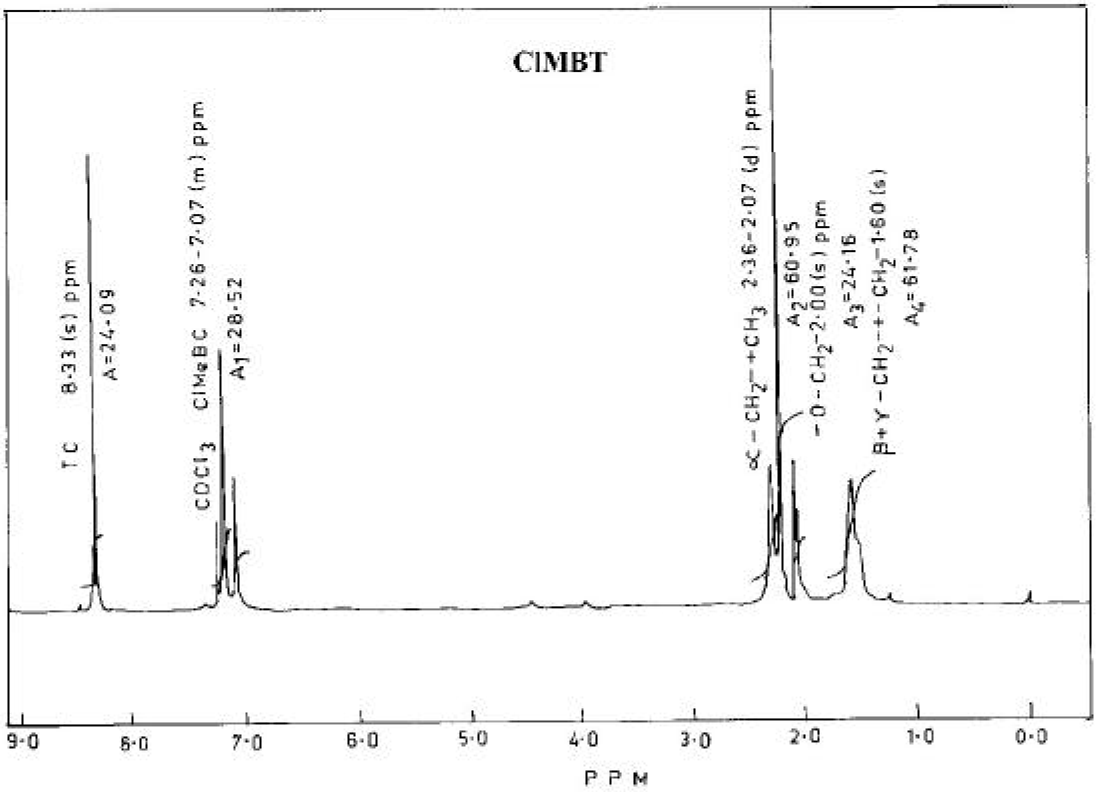


Fig.-3.9: NMR (300MHZ) spectra of ClMET and ClMPT



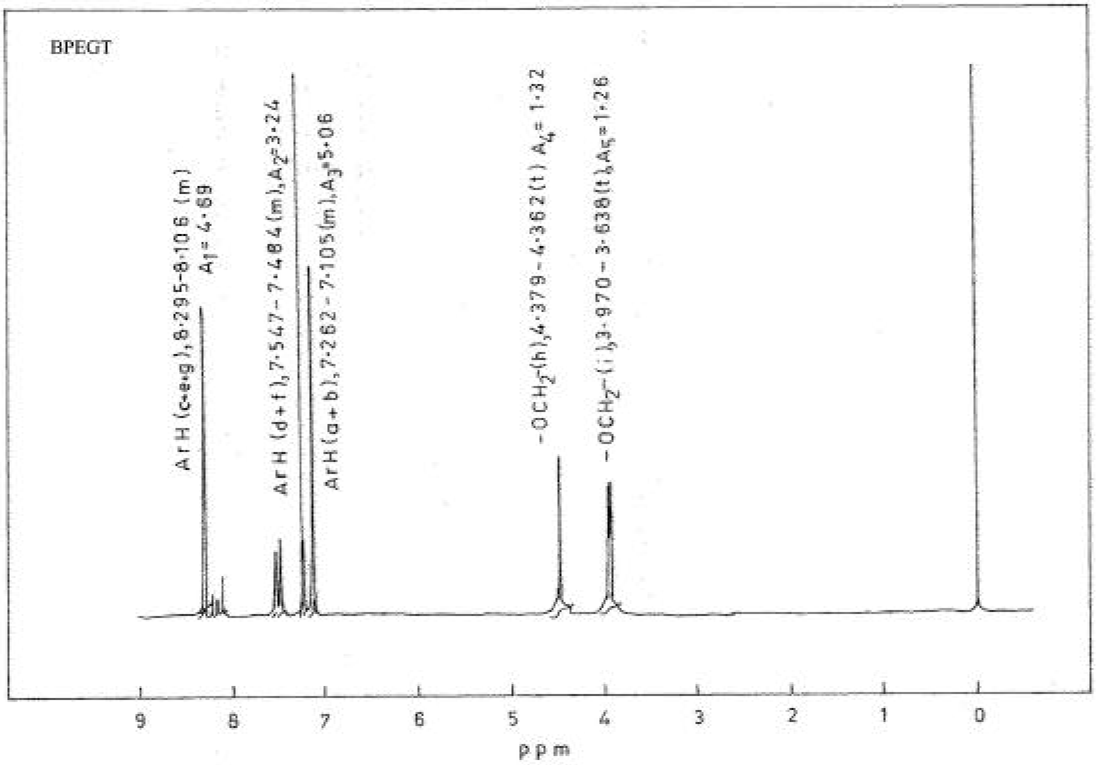


Fig.-3.11: NMR (300MHZ) spectra of ClMBT and BPEGT

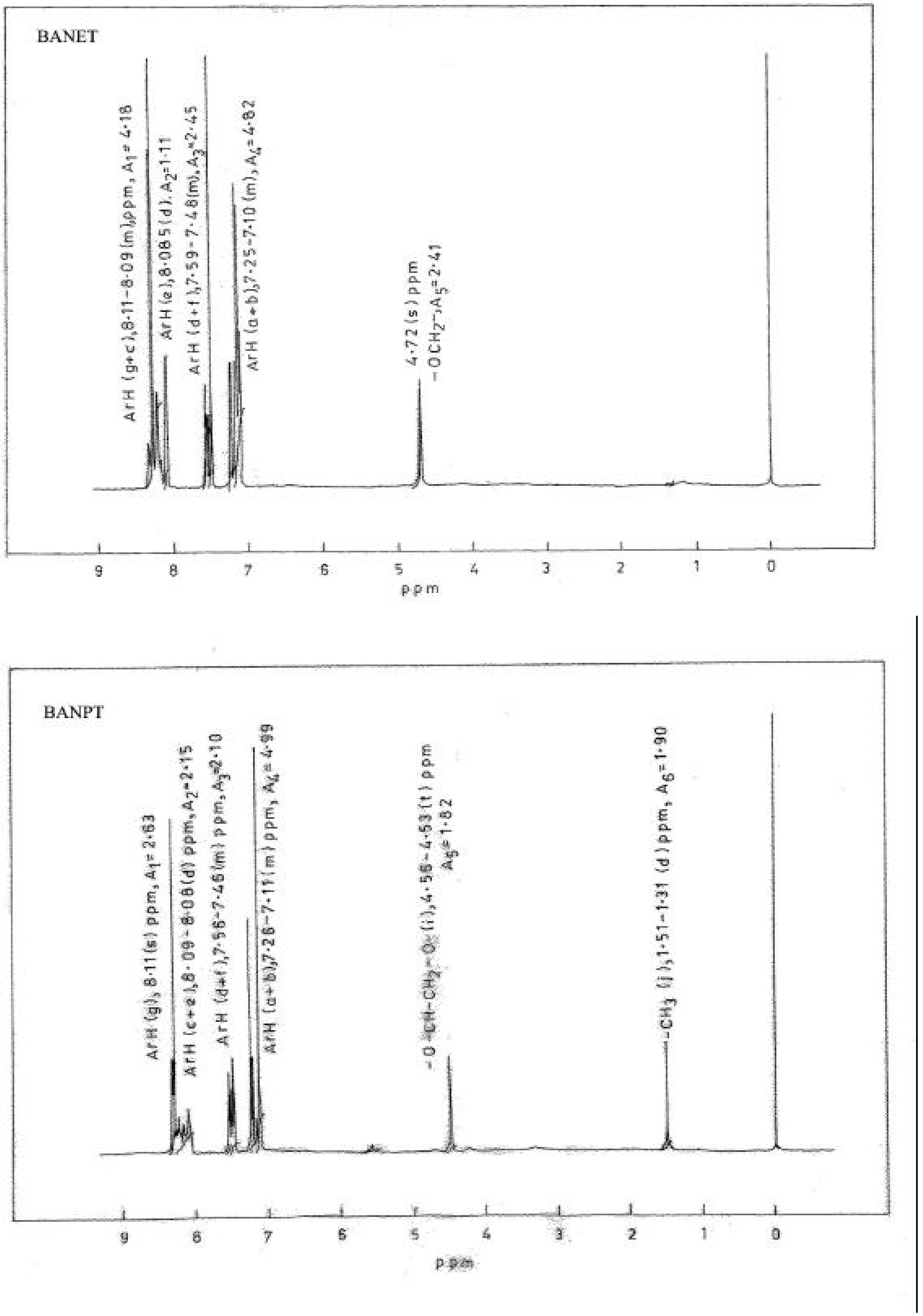


Fig.-3.12: NMR (300MHZ) spectra of BANET and BANPT

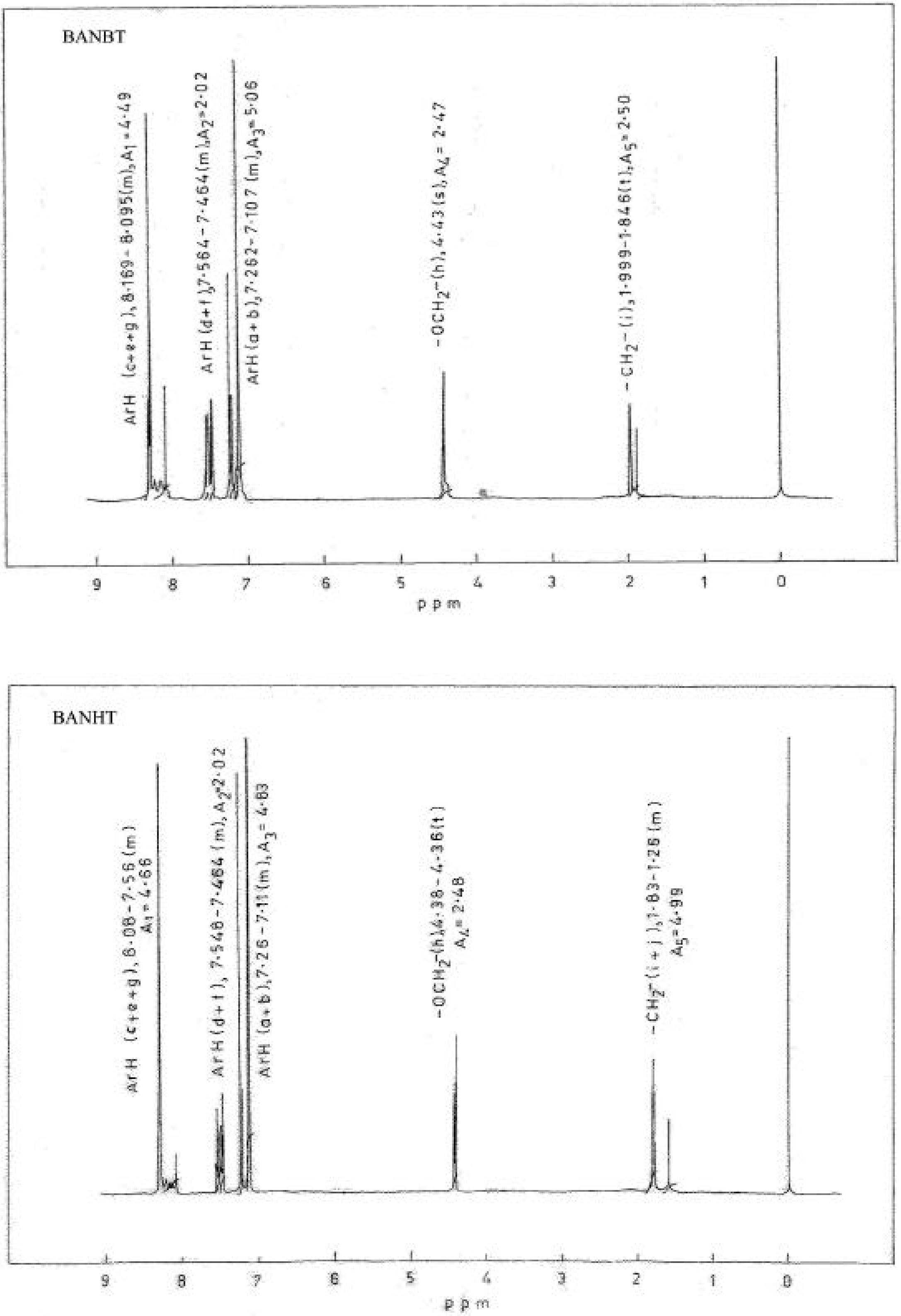
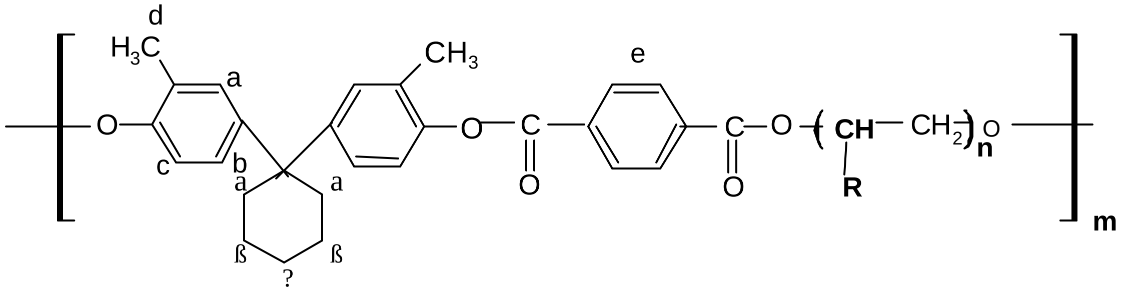


FIG. 3.13 NMR (300MHZ) spectra of BANBT and BANHT

Table-3.3: NMR chemical shifts of Copolyesters



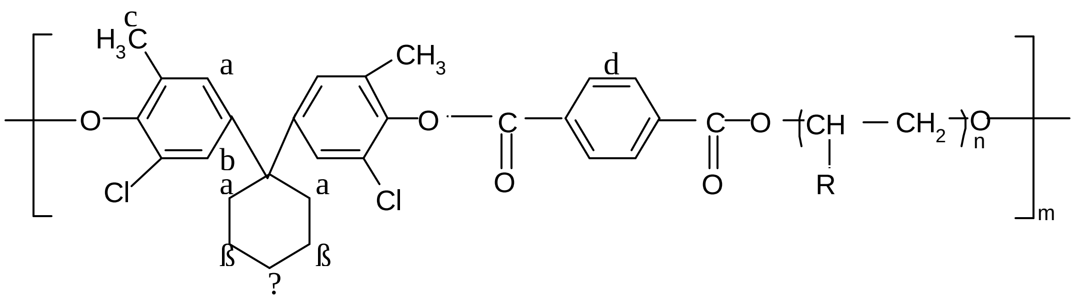
MET: n=1 and R=H

MBT: n=2 and R=H

MPT: n=1 and R=CH_3

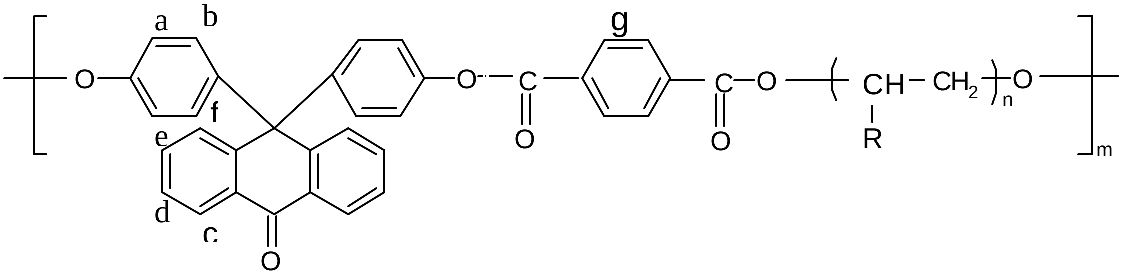
MHT: n=3 and R=H

Sample	NMR chemical shifts, ppm
MET f **-CH_2-CH_2-**	1.630 [6H, s, (ß + ?) -CH_2-], 2.296-2.279 [10H, d, (a) -CH_2- + (d) -CH_3] 4.328-4.300 [4H, s, (f) –OCH_2-] 7.277-7.047 [6H,m, (a+b+c) Ar-H] 8.330 [4H, s, (e) Ar-H]
MPT f g **-CH-CH_2-** **I** **CH_3** h	1.593 [9H, s, (ß + ?) -CH_2- + (h)-CH_3] 2.290-2.276 [10H, d, (a) -CH_2- + (d) -CH_3] 3.984 [3H, s, (f + g) –OCH-CH_2-O-] 7.207-7.034 [6H,m, (a+b+c) Ar-H] 8.287 [4H, s, (e) Ar-H]
MBT f g **-CH_2-CH_2-CH_2-CH_2-**	1.748 [10H, s, (ß + ?) -CH_2- + (g)-CH_2-] 1.976 [4H, s, (f) –OCH_2-] 2.291-2.217 [10H, d, (a) -CH_2- + (d) -CH_3] 7.351-7.259 [6H,m, (a+b+c) Ar-H] 8.331 [4H, s, (e) Ar-H]
MHT f g h **-CH_2-CH_2-CH_2-CH_2-** **CH_2- CH_2-**	1.26-1.07 [4H, m, (h) -CH_2-] 1.59 [10H, s, (ß + ?) -CH_2- + (g)-CH_2-] 2.29-2.22 [14H, d, (a) -CH_2- + (d) -CH_3 + (f) –OCH_2-] 7.20-7.07 [6H,m, (a+b+c) Ar-H] 8.33 [4H, s, (e) Ar-H]



ClMET: R = H and n=1, **ClMPT**: R=CH_3 and n=1, **ClMBT**: R= H and n=2

Sample	**NMR chemical shifts, ppm**
ClMET e **$-CH_2-CH_2-$**	1.593 [6H, s, (ß + ?) -CH2-], 2.293-2.090 [10H, d, (a) -CH2-+ (c) -CH3] 4.728 [4H, s , (e) –OCH2-] 7.257-7.076 [4H,m, (a+b) Ar-H] 8.332 [4H, s, (d) Ar-H]
ClMPT e f **$-CH-CH_2-$** **I** **CH_3** g	1.595 [9H, s, (ß + ?) -CH_2- + (g)-CH_3] 2.357-2.002 [10H, d, (a) -CH_2- + (c) -CH_3] 3.985-3.978 [3H, s, (e + f) –OCH-CH_2-O-] 7.207-7.034 [4H,m, (a+b) Ar-H] 8.334 [4H, s, (d) Ar-H]
ClMBT e f **$-CH_2-CH_2-CH_2-CH_2-$**	1.595 [10H, s, (ß + ?) -CH_2- + (f)-CH_2-] 2.357-2.079 [14H, d, (a) -CH_2- + (c) -CH_3 + (e) -OCH_2-] 7.256-7.076 [4H,m, (a+b) Ar-H] 8.332 [4H, s, (d) Ar-H]

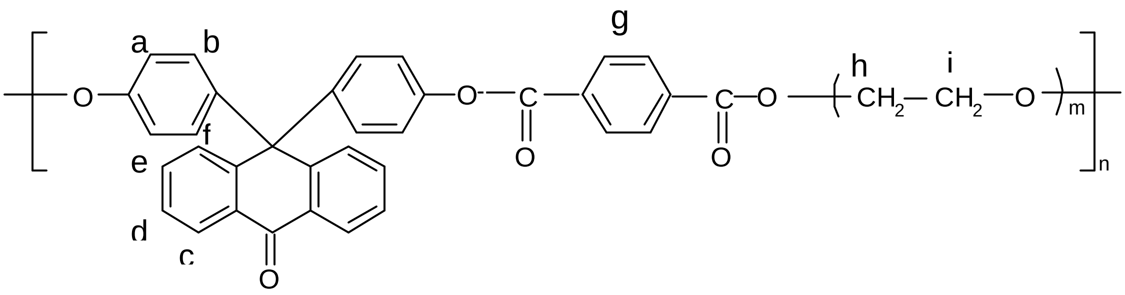


BANET: n=1 and R=H **BANBT:** n=2 and R=H

BANPT: n=1 and R=CH_3 **BANHT:** n=3 and R=H

Sample	**NMR chemical shifts, ppm**
BANET h **-CH_2-CH_2-**	4.721 [4H, s, (h) –OCH_2-] 7.250-7.104 [8H,m, (a+b) Ar-H] 7.594-7.480 [4H,m, (d+f) Ar-H] 8.085 [2H, d, (e) Ar-H] 8.105-8.093 [6H,m, (g+c) Ar-H]
BANPT h i **-CH-CH_2-** **I** **CH_3** J	1.507-1.313 [3H, d, (j) -CH_3] 4.559-4.531 [3H, s, (h + i) –OCH-CH_2-O-] 7.262-7.107 [8H,m, (a+b) Ar-H] 7.563-7.464 [4H,m, (d+f) Ar-H] 8.088-8.076 [4H,d, (c+e) Ar-H] 8.105 [4H, s, (g) Ar-H]
BANBT h i **-CH_2-CH_2-CH_2-CH_2-**	1.999-1.845 [4H, d, (i) -CH_2-] 4.437-4.394 [4H, s, (h) –OCH_2-] 7.262-7.107 [8H,d, (a+b) Ar-H] 7.564-7.464 [4H,m, (d+f) Ar-H] 8.169-8.095 [8H, m, (g+c+e) Ar-H]

BANHT h i j **-CH_2-CH_2-CH_2-CH_2-CH_2- CH_2-**	1.829-1.256 [8H, m, (i+j) -CH_2-] 4.379-4.362 [4H, t, (h) –OCH_2-] 7.261-7.105 [8H,m, (a+b) Ar-H] 7.5648-7.464 [4H,d, (d+f) Ar-H] 8.083-7.564 [8H, m, (g+c+e) Ar-H]



BPEGT

BPEGT	3.970-3.638 [2H, t, (i) –OCH_2-] 4.379-4.362 [2H, t, (h) –OCH_2-] 7.262-7.105 [8H,m, (a+b) Ar-H] 7.547-7.464 [4H,m, (d+f) Ar-H] 8.295-8.106 [8H, m, (g+c+e) Ar-H]

Copolymer composition for MET to MHT:

An attempt has been made to evaluate copolyester compositions according to following relationships:

$$\text{Composition} = \frac{\text{Peak areas due to diol protons}}{\text{Peak areas due to MeBC protons}} \quad \ldots 3.1$$

For MET:

$$\text{Composition} = \frac{A_2}{A_1 + A_3 + A_4}$$

$$= \frac{24.9}{125.93}$$

$$\cong 0.2$$

For MPT:

$$\text{Composition} = \frac{A_2 + \frac{1}{3}A_4}{A_1 + A_3 + \frac{2}{3}A_4}$$

$$= \frac{18.54}{69.24}$$

$$\cong 0.27$$

For MBT:

$$\text{Composition} = \frac{A_3 + \frac{2}{5}A_4}{A_1 + A_2 + \frac{3}{5}A_4}$$

$$= \frac{25.1}{73.54}$$

$$\approx 0.34$$

For MHT:

$$\text{Composition} = \frac{\frac{2}{7}A_2 + \frac{2}{5}A_3 + A_4}{A_1 + \frac{5}{7}A_2 + \frac{3}{5}A_3}$$

$$= \frac{3.05}{5.52} \approx 0.55$$

Copolymer composition for ClMET to ClMBT:

$$\text{Composition} = \frac{\text{Peak areas due to diol protons}}{\text{Peak areas due to ClMeBC protons}} \qquad ...3.2$$

For ClMET:

$$\text{Composition} = \frac{A_2}{A_1 + A_3 + A_4}$$

$$= \frac{24.69}{121.33} = 0.20$$

For ClMPT:

$$\text{Composition} = \frac{A_2 + \frac{1}{3}A_4}{A_1 + A_3 + \frac{2}{3}A_4}$$

$$= \frac{36.46}{124.89} = 0.29$$

For ClMBT:

$$\text{Composition} = \frac{A_3 + \frac{2}{5}A_4}{A_1 + A_2 + \frac{3}{5}A_4}$$

$$= \frac{48.86}{126.54} = 0.39$$

Copolymer composition for BANET to BPEGT:

$$\text{Composition} \;=.\; \frac{\text{Peak areas due to diol protons}}{\text{Peak areas due to BAN protons}} \qquad \text{...3.3}$$

For BANET: Composition

$$= \frac{A_5}{\frac{1}{3}A_1 + A_2 + A_3 + A_4}$$

$$= \frac{2.41}{9.77} \approx 0.25$$

For BANPT: Composition

$$= \frac{A_5 + A_6}{A_2 + A_3 + A_4}$$

$$= \frac{3.72}{9.24} \approx 0.40$$

For BANBT: Composition

$$= \frac{A_4 + A_5}{\frac{1}{2}A_1 + A_2 + A_3}$$

$$= \frac{4.97}{9.325} \approx 0.53$$

For BANHT: Composition

$$= \frac{A_4 + A_5}{\frac{1}{2}A_1 + A_2 + A_3}$$

$$= \frac{7.47}{9.75} \approx 0.77$$

For BPEGT: Composition

$$= \frac{A_4 + A_5}{\frac{1}{2}A_1 + A_2 + A_3}$$

$$= \frac{2.58}{10.65} \approx 0.24$$

The composition determined according to equations 3.1 to 3.3 are reported in Table-3.4. The experimental and feed compositions are in good agreement. Slight disagreement is due to unreliable measured peak areas because of peak broadening.

Table-3.4: Copolymer compositions

Coopolymer	**$A_{Aliphatic\ Diol}$**	**$A_{MeBC/ClMeBC/BAN}$**	**$A_{Aliphatic\ Diol}$ / $A_{MeBC/ClMeBC/BAN}$**	
			Experimental	**Expected**
MET	24.90	125.93	0.20	0.18
MPT	18.54	69.24	0.27	0.27
MBT	25.10	73.54	0.34	0.36
MHT	3.05	5.52	0.55	0.55
ClMET	24.69	121.33	0.20	0.20
ClMPT	36.46	124.89	0.29	0.30
ClMBT	48.86	126.54	0.39	0.40
BANET	2.41	9.77	0.25	0.25
BANPT	3.72	9.24	0.40	0.38
BANBT	4.97	9.33	0.53	0.50
BANHT	7.47	9.75	0.77	0.75
BPEGT	2.58	10.65	0.24	0.25

SECTION – 3: PREPERATION OF POLYMER FILMS

Films, including photographic film and cellophane are made by spreading a solution of the polymer on to an extremely smooth surface in the form of a large polished wheel or occasionally, a metal belt or band. After the solvent has evaporated (or in the case of cellophane, the polymer has coagulated) the film is stripped from the casting surface.

Tough and transparent films of polymers were cast from concentrated chloroform solutions (3%) on a leveled glass plate. The rate of evaporation of chloroform was kept slow by covering the glass plate. The films were dried under vacuum at 80^{o} C until the entrapped solvent molecules have been removed completely as indicated by constant weight. The polymer films were analyzed for their mechanical and electrical properties, density measurements by floatation method and chemical resistance.

SECTION – 4: DENSITY MEASUREMENTS

A vast majority of polymers are constituted from a small number of different atoms and it is possible to calculate the intrinsic volumes of polymer repeat units from the atomic radii and bond lengths. The density, specific volume and molecular mass are useful in evaluation of various thermodynamic properties of the sample as well as polymer materials [14-18]. These data are most useful for the average distance between macromolecular chains and the extent of crystallinity in polymers.

Theoretical calculations of the density by floatation method

The density of the polymer can be calculated from the knowledge of the structural aspects. According to Slonimskii et al. [19] the density of polymer may be expressed as:

$$r = \frac{KM}{N_A \sum \Delta Vi} \qquad \text{....} \quad \mathbf{3.4}$$

Where K is the packing coefficient, M is the molecular weight of the repeating unit of the polymer, S?Vi is the intrinsic volume of the polymer repeat unit and N_A is the Avogadro's number

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15. C. Tanford, "Physical Chemistry of Macromolecules", John Willey and Sons, Inc. New York, 1961.
16. V. R. Gowariker, N. V. Vishvanathan and J. Sreedhar, "Polymer Science", Willey Eastern Ltd. ,1986
17. T.M.Aminabhavi and P.Munk,Macromolecules, 6, 1186, 1979.
18. Holiday and W.A.Ghlomeswalker,J Appl.Polym.Sci.,16,139, 1972.
19. G. L. Slonimskii, A. A. Askadskii and A. I. Kitaigorodkii, Polym. Sci. USSR, **A-12 (3)** ,556, 1970.

According to Slonimskii et. al [19] the values of S?Vi can be calculated from the knowledge of the volume increments ?Vi of the atoms and groups of atoms. The packing coefficient K is the ratio of the intrinsic volume to the true volume and it can be calculated from the experimental density of the polymer.

$$K = V_{int} / V_{true} = N_A S ? Vi / (M/?) \qquad \ldots \mathbf{3.5}$$

Slonimskii et. al [19] have calculated packing coefficient of seventy polymers of widely different chemical and physical structure for both addition and condensation polymers. They have reported the average value of K 0.681 and 0.695 for both bulk and film samples, respectively. Theoretical densities of copolyesters are not determined due to uncertain repeat unit molecular weights.

EXPERIMENTAL

Densities of copolyester films were determined by floatation method by using CCl_4-n-hexane system at 30^oC. In six different stoppered test tubes, a small piece of film and about 5ml of CCl_4 were placed and n-hexane was added drop wise with shaking till the polymer film remained suspended halfway in each test tube. The composition of the two solvents was adjusted in such a way that the film just remained suspended throughout. The densities of the mixtures were determined after 24h by the usual method. The average of six measurements along with the standard deviation is reported in Table-3.5.

According to equation 3.5 the density depends upon M and S?Vi and independent of intermolecular interactions. The formation of any organic molecule or repeat unit of a polymer involves replacement of H-atom by other elements. The polar group changes intrinsic volume and weight, and the ratio of these two quantities, is very important in deciding the density of a given polymer. Again it is clear from eqn. 3.5 that the density is directly proportional to M and inversely proportional to S?Vi.

From Table 3.5, it is clear that the density has decreased with increase in the alkyl chain length of diol in the copolymer chains, indicating increase in the chain flexibility, Upon comparing densities of halogenated copolyesters with unhalogenated copolyesters of the same type revealed that halogenated copolyesters possess somewhat high densities confirming compact packing as compared to unhalogenated copolyesters. The compact molecular packing is due to strong molecular interactions in the solid state. As Cl is an electronegative group, which attracts electro positive groups resulting in more compact structure of polymers.

Table-3.5: The densities of copolyesters determined by floatation method at 35 °C

Copolyester	r **, g cm^{-3}**	**Copolyester**	r **, g cm^{-3}**
MET	1.2697±0.0004	ClMET	1.2775±0.0017
MET-1	1.2701±0.0001	ClMET-1	1.2812±0.0012
MET-2	1.2609±0.0002	ClMET-2	1.2731±0.0011
MPT	1.1984±0.0010	ClMPT	1.2192±0.0017
MPT-1	1.2015±0.0012	ClMPT-1	1.2302±0.0012
MPT-2	1.1905±0.0005	ClMPT-2	1.2097±0.0015
MBT	1.1011±0.0002	ClMBT	1.1392±0.0004
MBT-1	1.1107±0.0004	ClMBT-1	1.1485±0.0005
MBT-2	1.1010±0.0003	ClMBT-2	1.1302±0.0002
MHT	1.2389±0.0004	ClMHT	1.1234±0.0005
MHT-1	1.2471±0.0012	ClMHT-1	1.1371±0.0003
MHT-2	1.2280±0.0005	ClMHT-2	1.1182±0.0004
BANET	1.3015±0.0016	BANBT	1.2706±0.0003
BANET -1	1.3125±0.0012	BANBT -1	1.2811±0.0001
BANET -2	1.2945±0.0011	BANBT -2	1.2655±0.0001
BANPT	1.2842±0.0012	BANHT	1.2442±0.0023
BANPT -1	1.2951±0.0017	BANHT -1	1.2581±0.0012
BANPT -2	1.2802±0.0011	BANHT -2	1.2401±0.0005
BPEGT	1.3192±0.0004		

SECTION – 5: VISCOSITY MEASUREMENTS

Viscosity measurement is the simplest and the most widely used technique for determining molecular weights [20]. The International Union of Pure and Applied Chemistry have recommended names for various designations [21]. These are given in parentheses after the more common names. The IUPAC made these recommendations to avoid inconsistencies in the old terminology arising from some designations being called 'viscosity' although not having units of viscosity. Despite the fact that the recommendations were made a number of years ago, the old terminology is still most commonly used in the polymer literature. Viscosity of polymers varies from thousands (for polymers having a relatively low molecular mass) to 10^{13} poise (at glass transition temperature).

The viscosity measurements were carried out with an Ubbelohde [22] suspended level viscometer in which the solution could be diluted within the viscometer for which kinetic energy and other corrections are less than 1% of the intrinsic viscosity and are neglected.

The viscosity measurements were carried out at three different temperatures: 30^0, 35^0 and 40^0 C in 1,2–dichloroethane (DCE) and chloroform (CF) by using an Ubbelohde suspended level viscometer.

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21. International Union of Pure and Applied Chemistry, J. Polymer Sci, **8**, 257, 1952.
22. L. Ubbelohde, Ins. Pet. London, **19**, 376, 1933.

EXPERIMENTAL

Preparation of solutions

The required amounts of polymers were weighed accurately in 10 ml volumetric flasks and an adequate quantity of appropriate solvent was added in each flask. The flasks were kept aside for sometime. During this period, the samples swelled and dissolved completely. The solutions were diluted up to the mark and filtered through G-3 sintered glass funnel before viscosity measurements.

Viscometer was washed with chromic acid, distilled water, acetone and then dried in an oven at 50^o C. The viscometer was clamped in a thermostat and a measured quantity of solvent or solution was taken into the viscometer and was allowed to attain the temperature of the bath. The flow time for the liquid between the two marks of the viscometer bulb was measured accurately at least three times by means of a racer stop watch and the average values not exceeding ±0.1 second were considered. The solution inside the viscometer was diluted by adding known quantity (2 ml) of solvent. The solution was thoroughly mixed by blowing a slow stream of air through it. The viscometer capillary bulb was rinsed with dilute solution by sucking the solution and allowed it to drain in the viscometer reservoir. Flow times for this liquid were measured accurately. The same procedure was followed for the successive dilutions.

From the knowledge of solution flow time (t) and solvent flow time (t_o) at a given temperature for a given solvent, the relative viscosity ($?_r$) and specific viscosity ($?_{sp}$) were determined according to eqns. 3.6 and 3.7, respectively:

$$h_r = t/t_0 \qquad \textbf{…3.6}$$

$$h_{sp} = (h - h_0)/h_0 = h_r - 1 = (t - t_o)/t_o \qquad \textbf{…3.7}$$

The intrinsic viscosity [?], can be determined from the joint application of reduced viscosity (?$_{sp}$/C) and inherent viscosity (ln?$_{r}$/C) data according to Huggin’s [23] and Kraemer’s [24] relationships:

$$h_{sp}/C = [h] + k'[h]^2 C \qquad \textbf{Huggin's Eqn.} \qquad \textbf{…3.8}$$

$$\ln h_r/C = [h] - k''[h]^2 C \qquad \textbf{Kraemer's Eqn.} \qquad \textbf{…3.9}$$

Generally k’ + k” = 0.5 for most polymers.

RESULTS AND DISCUSSION

The characterization of molecular interactions in solutions by viscosity is an important tool. It is a direct measure of hydrodynamic volume of molecules. The values of [?] and k’ for polymers in different solvents at different temperatures : 30, 35 and 40^{0}C were determined according to Eqn. 3.8 and they are reported in Table- 3.6. The plots of ?$_{sp}$/C against C for copolyesters in CF and DCE at different temperatures are shown in Figs.-3.13 to 3.28.

The viscosity of a polymer solution depends on its molecular weight, temperature, and concentration, nature of solvent and on its thermodynamic affinity for a polymer. The viscosity of dilute solutions is greatly affected by the molecular weight and molecular shape of the dissolved polymer. Intrinsic viscosity [?] and the slope of ?$_{sp}$/C vs C line depend on the nature of a solvent and this is due to the fact that the polymer coil swells differently in different solvents and therefore has different sizes. For flexible polymers, high values of k’ are the characteristics of the poor solvents and this is not observed in polymers with rigid chains and strong specific interactions. High value of k’ indicates poor nature of a solvent.

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24. E. O. Kraemer, Ind.Eng.Chem., **30**, 1200, 1938.

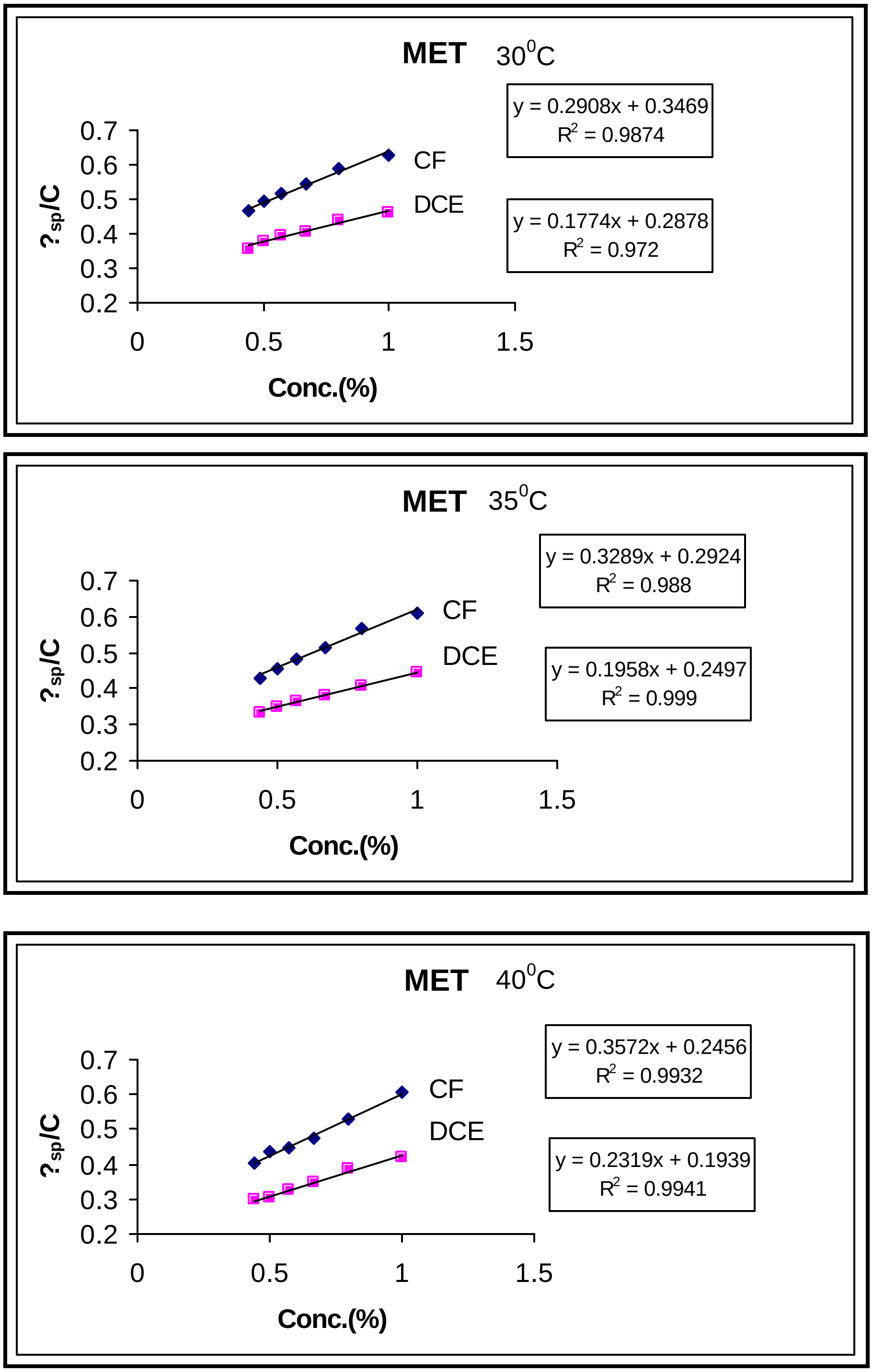


Fig.-3.13 : The plots of ?$_{sp}$/C against C for copolyester (MET) in CF and DCE at 30^{o}C , 35^{o}C and 40^{o}C.

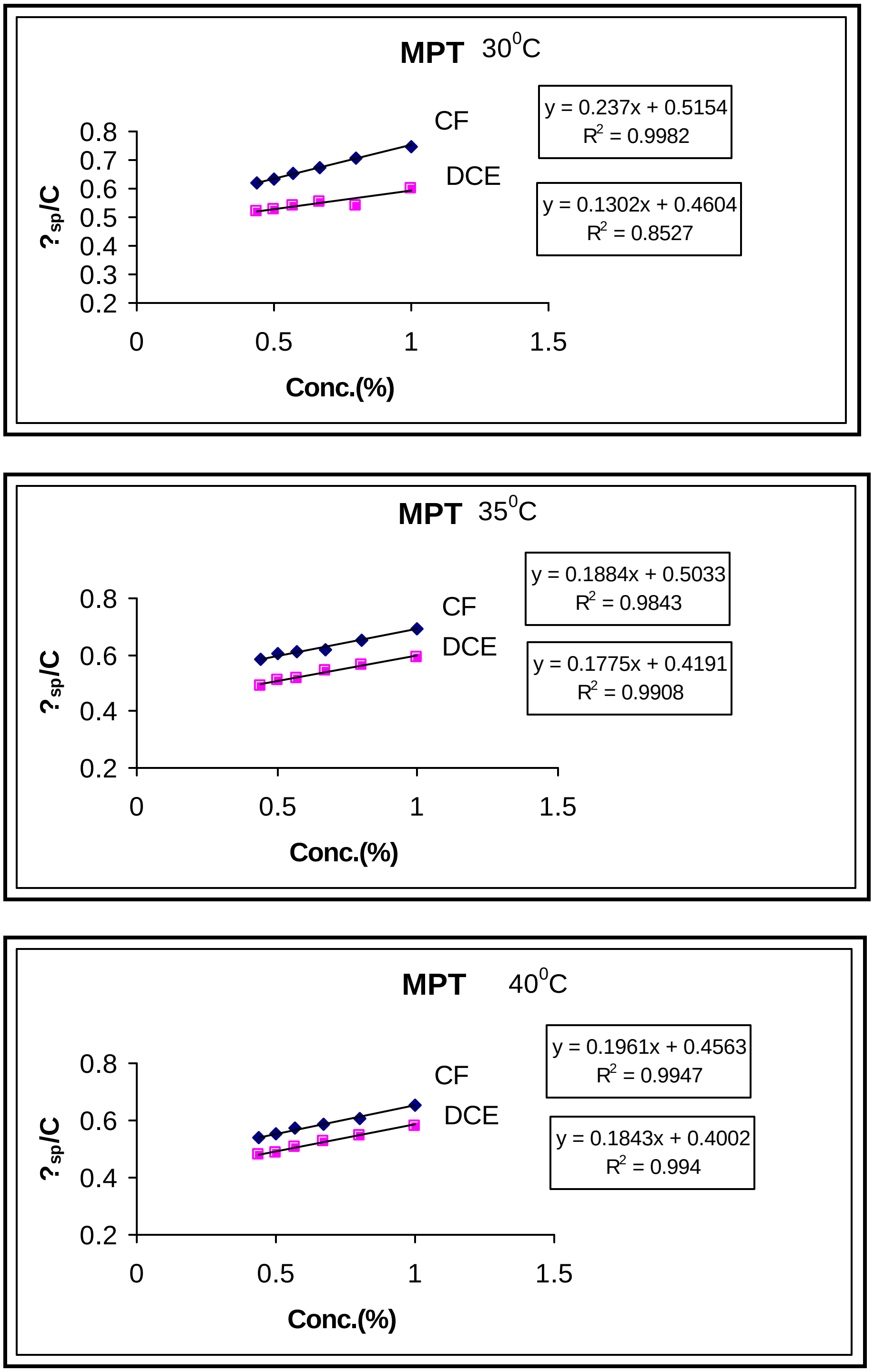


Fig.-3.14 : The plots of ?$_{sp}$/C against C for copolyester (MPT) in CF and DCE at 30°C , 35°C and 40°C.

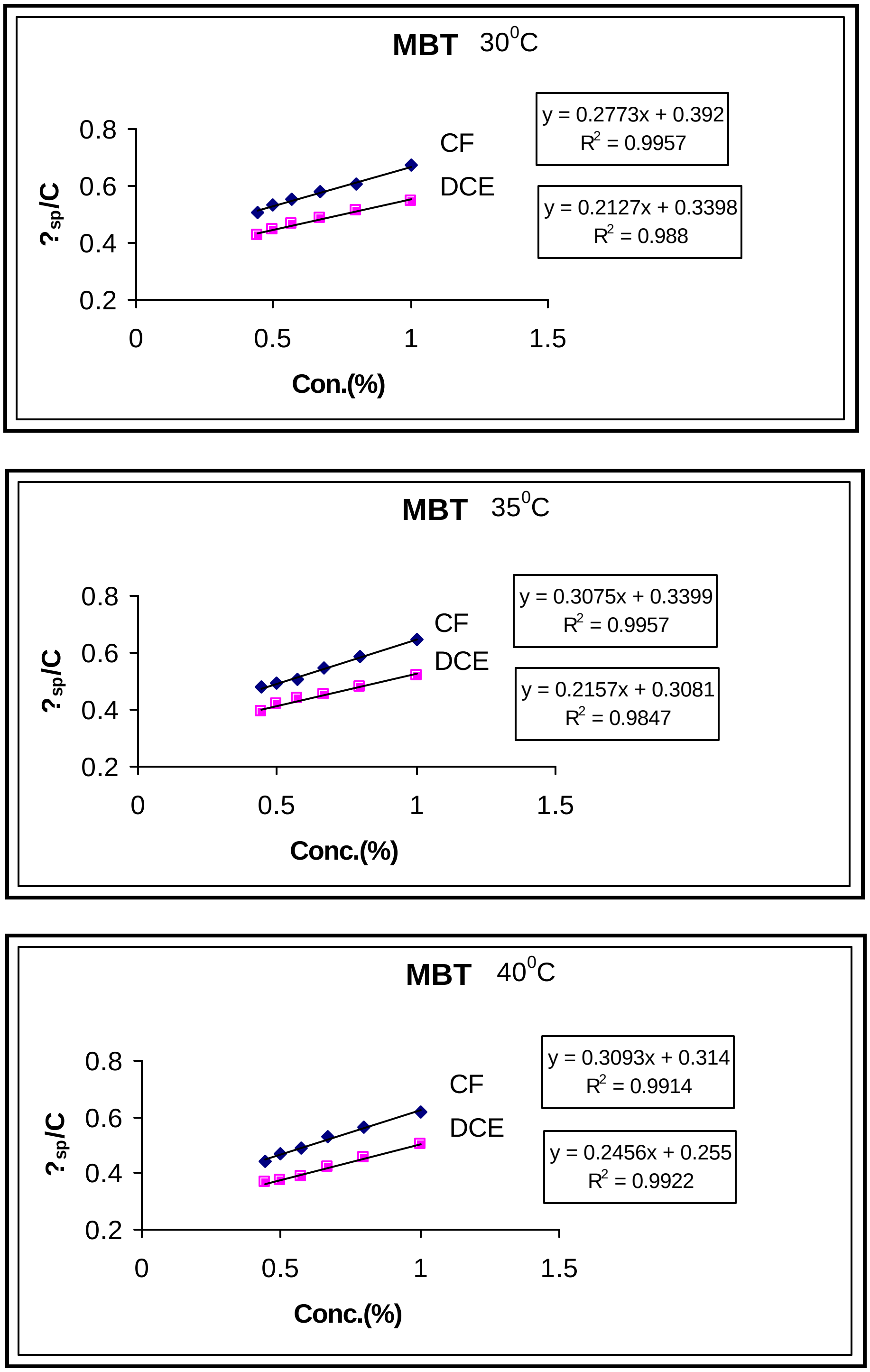


Fig.-3.15 : The plots of ?$_{sp}$/C against C for copolyester (MBT) in CF and DCE at 30^{o}C , 35^{o}C and 40^{o}C.

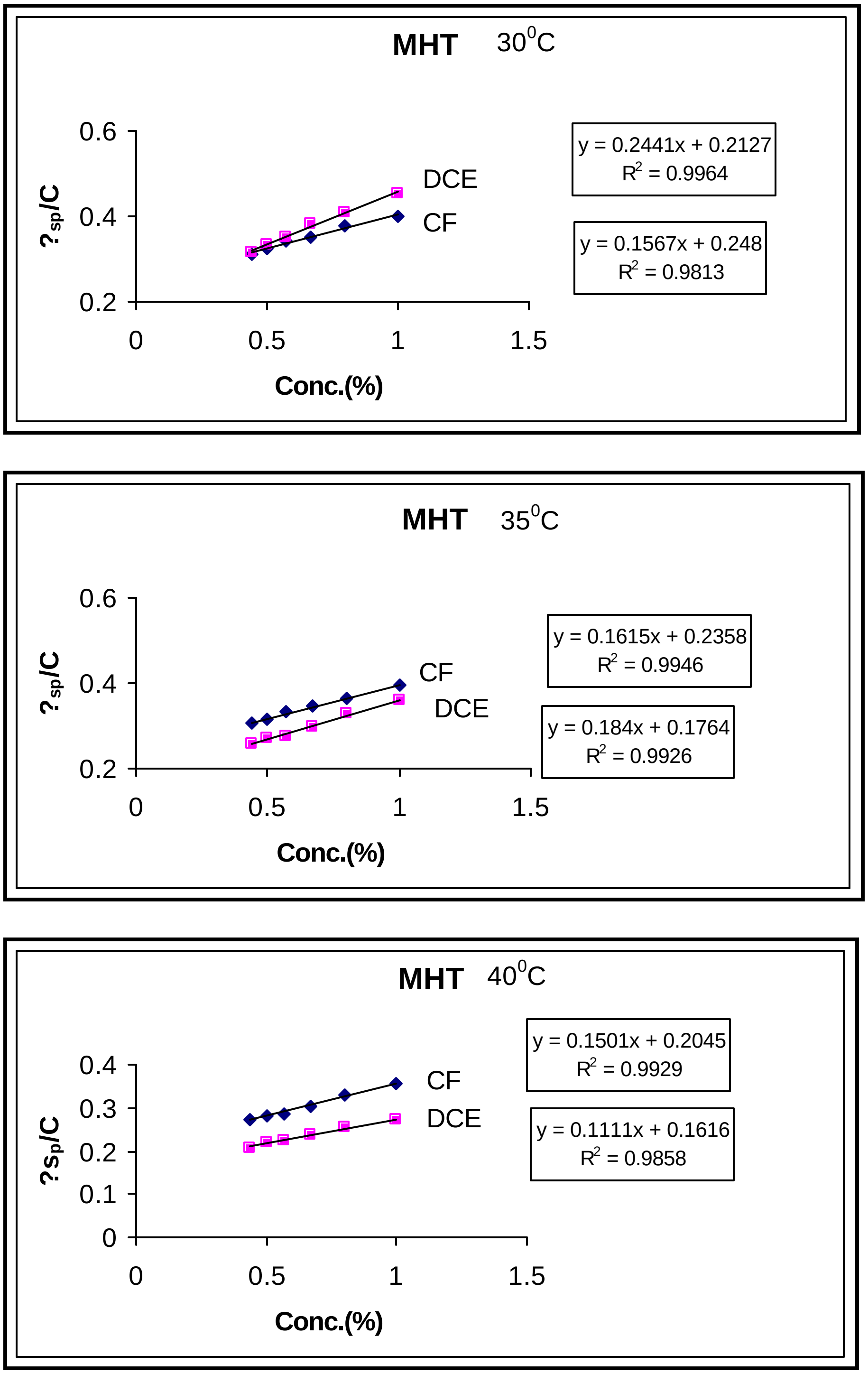


Fig.-3.16: The plots of $?_{sp}$/C against C for copolyester (MHT) in CF and DCE at 30°C , 35°C and 40°C.

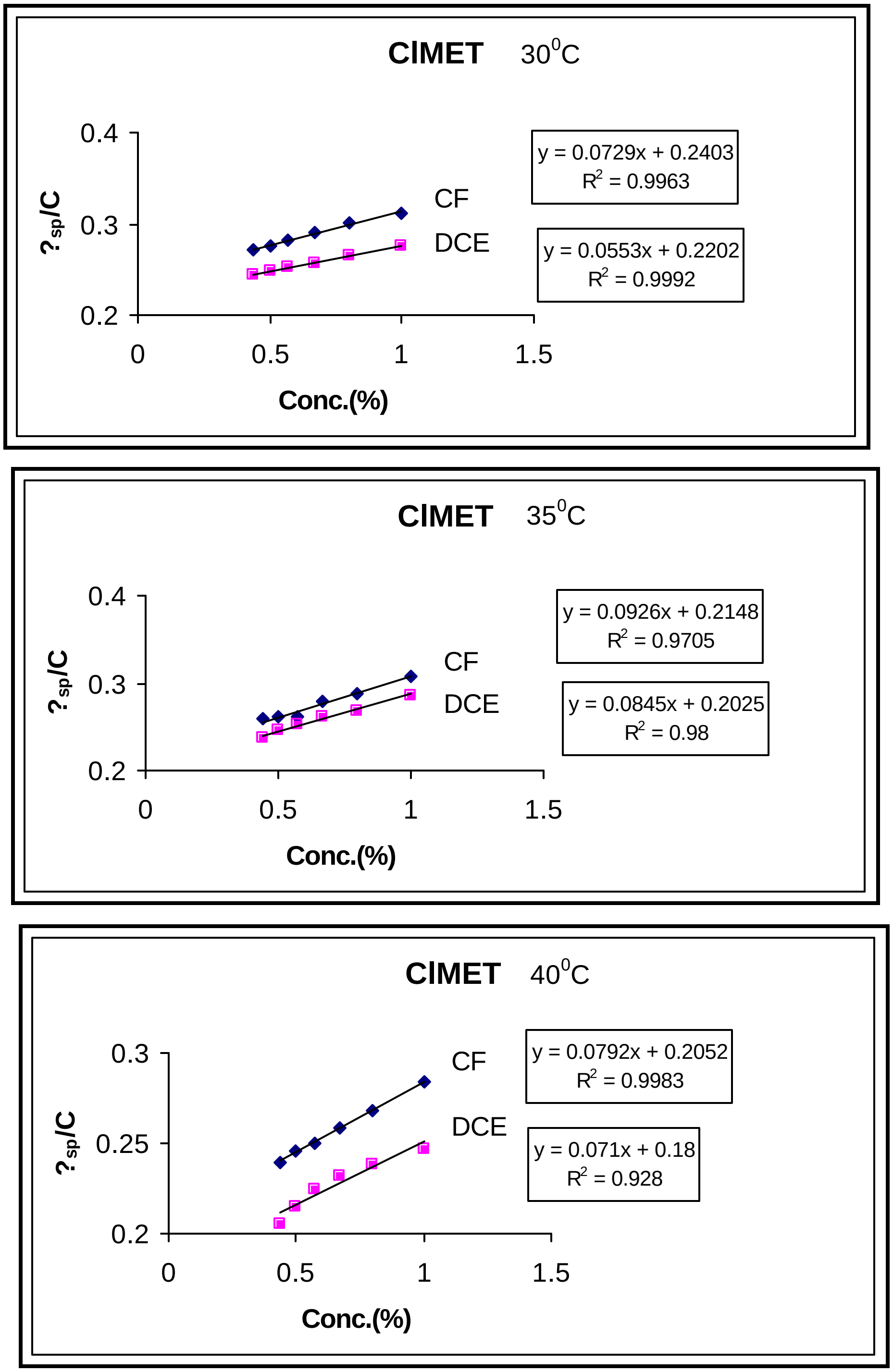


Fig.- 3.17 : The plots of ?$_{sp}$/C against C for copolyester (ClMET) in CF and DCE at 30^{o}C , 35^{o}C and 40^{o}C.

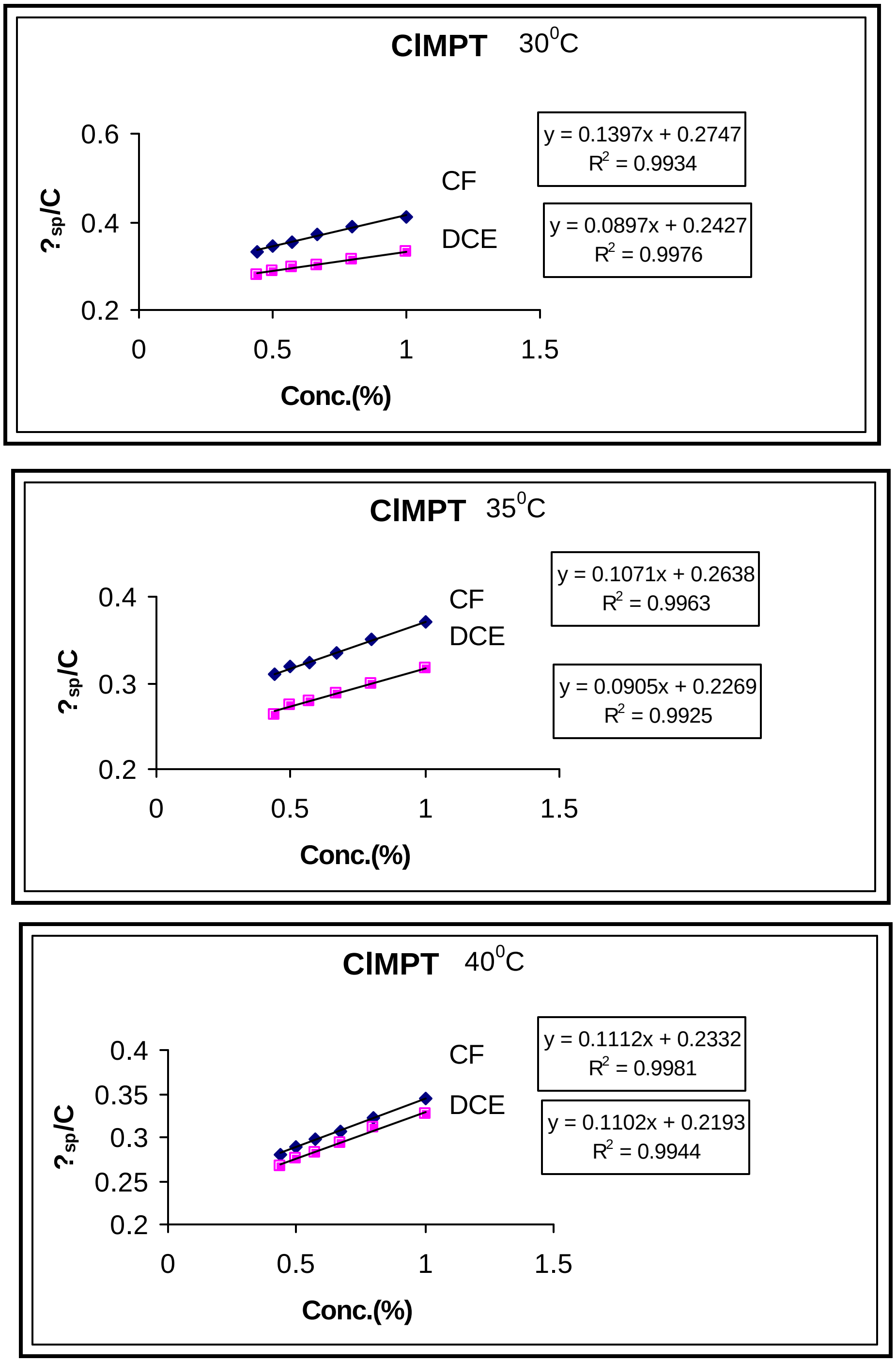


Fig.- 3.18 : **The plots of ?$_{sp}$/C against C for copolyester (ClMPT) in CF and DCE at 30^{o}C , 35^{o}C and 40^{o}C.**

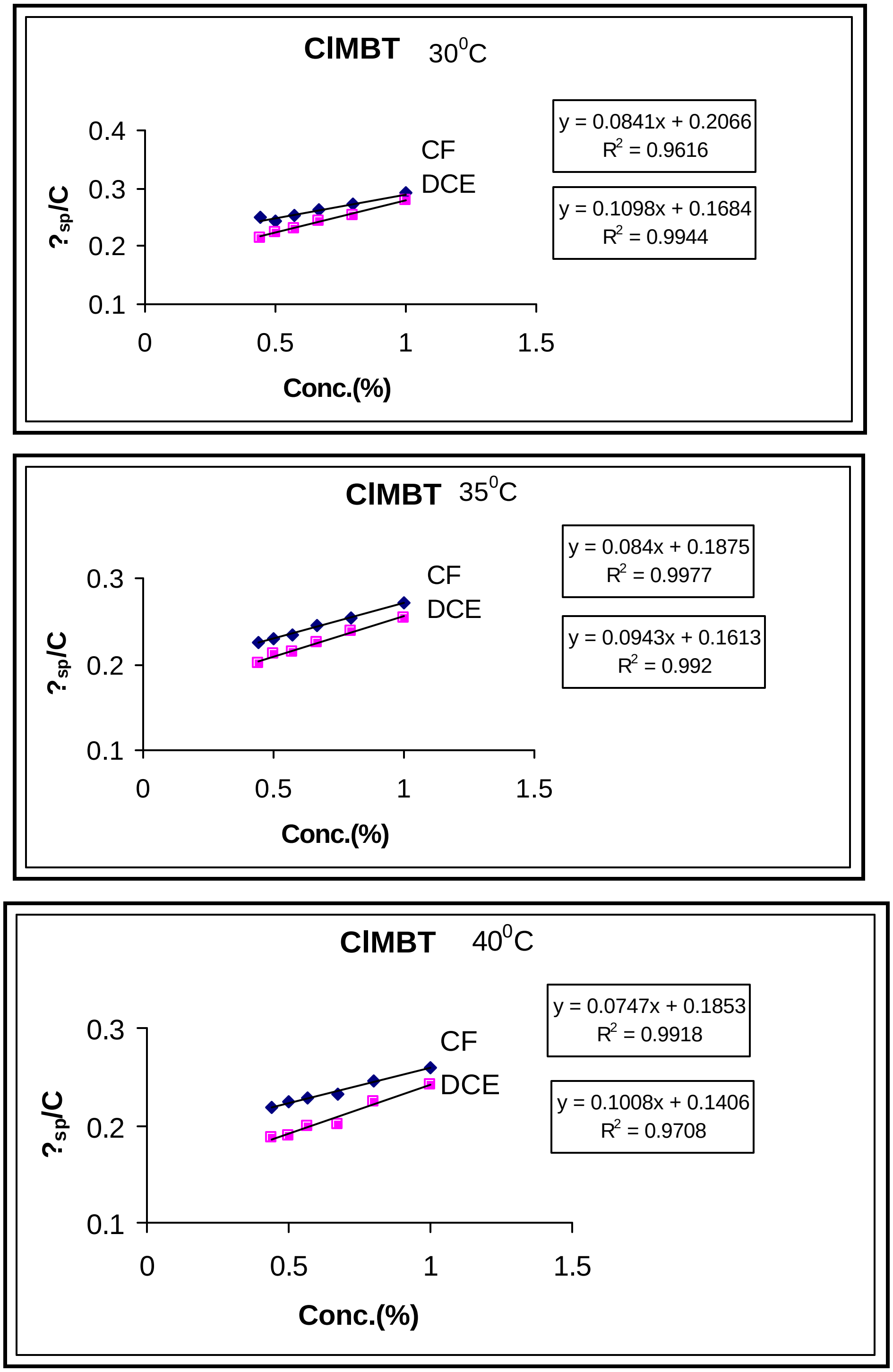


Fig.- 3.19 : The plots of ?$_{sp}$/C against C for copolyester (ClMBT) in CF and DCE at 30^{o}C , 35^{o}C and 40^{o}C.

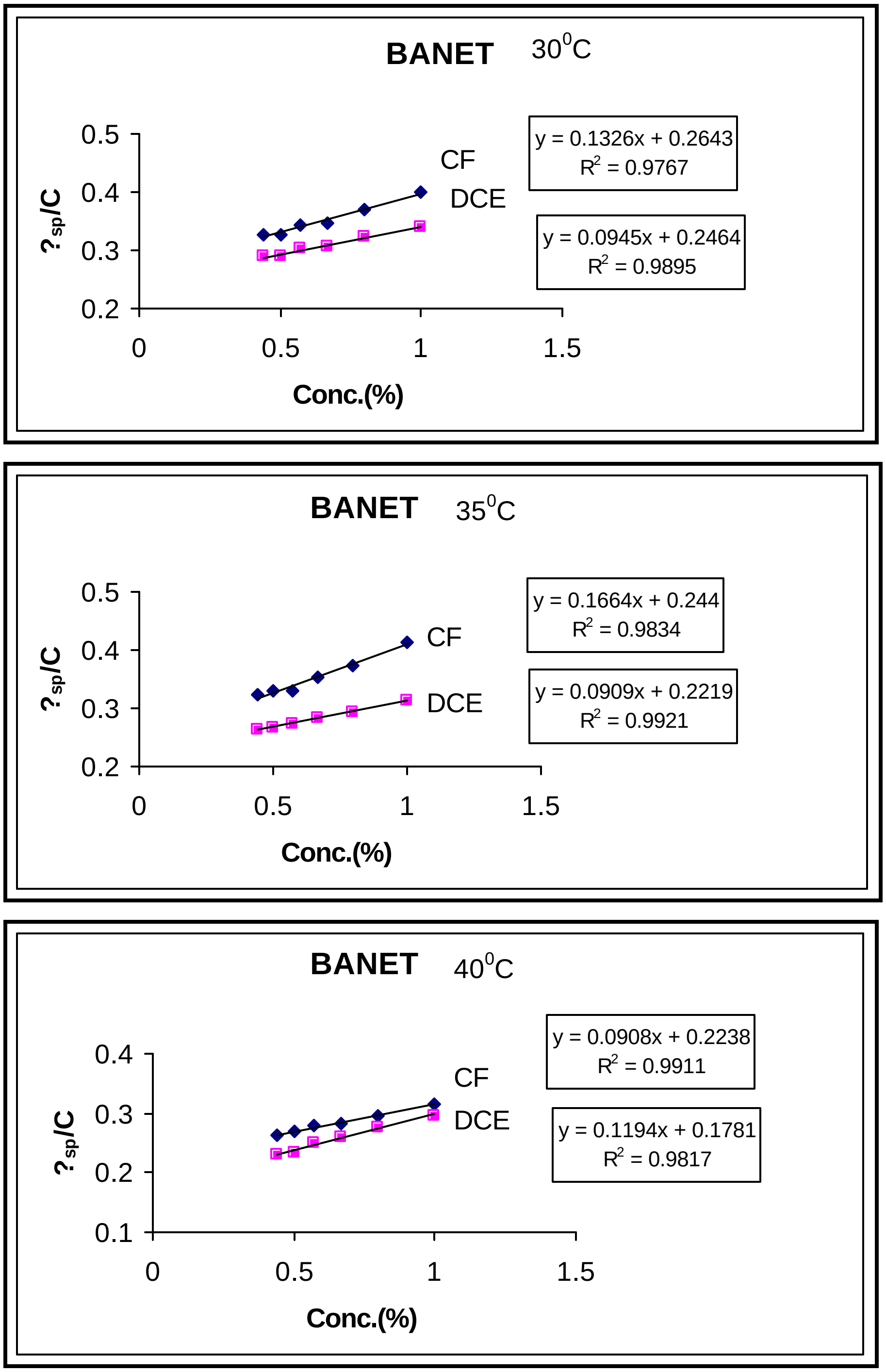


Fig.- 3.20 : The plots of ?$_{sp}$/C against C for copolyester (BANET) in CF and DCE at 30^{o}C , 35^{o}C and 40^{o}C.

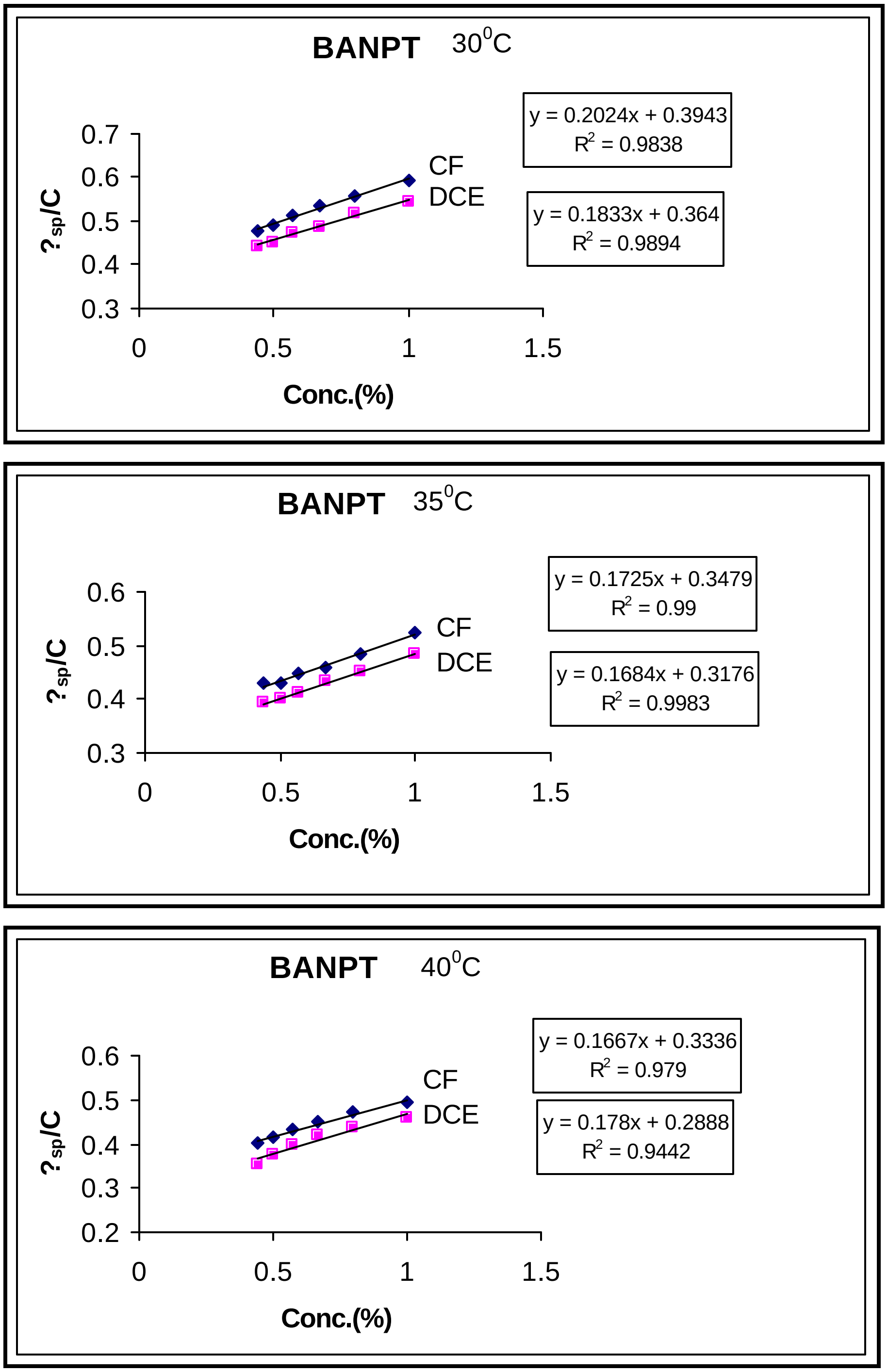


Fig.- 3.21 : The plots of $?_{sp}$/C against C for copolyester (BANPT) in CF and DCE at 30^{o}C , 35^{o}C and 40^{o}C.

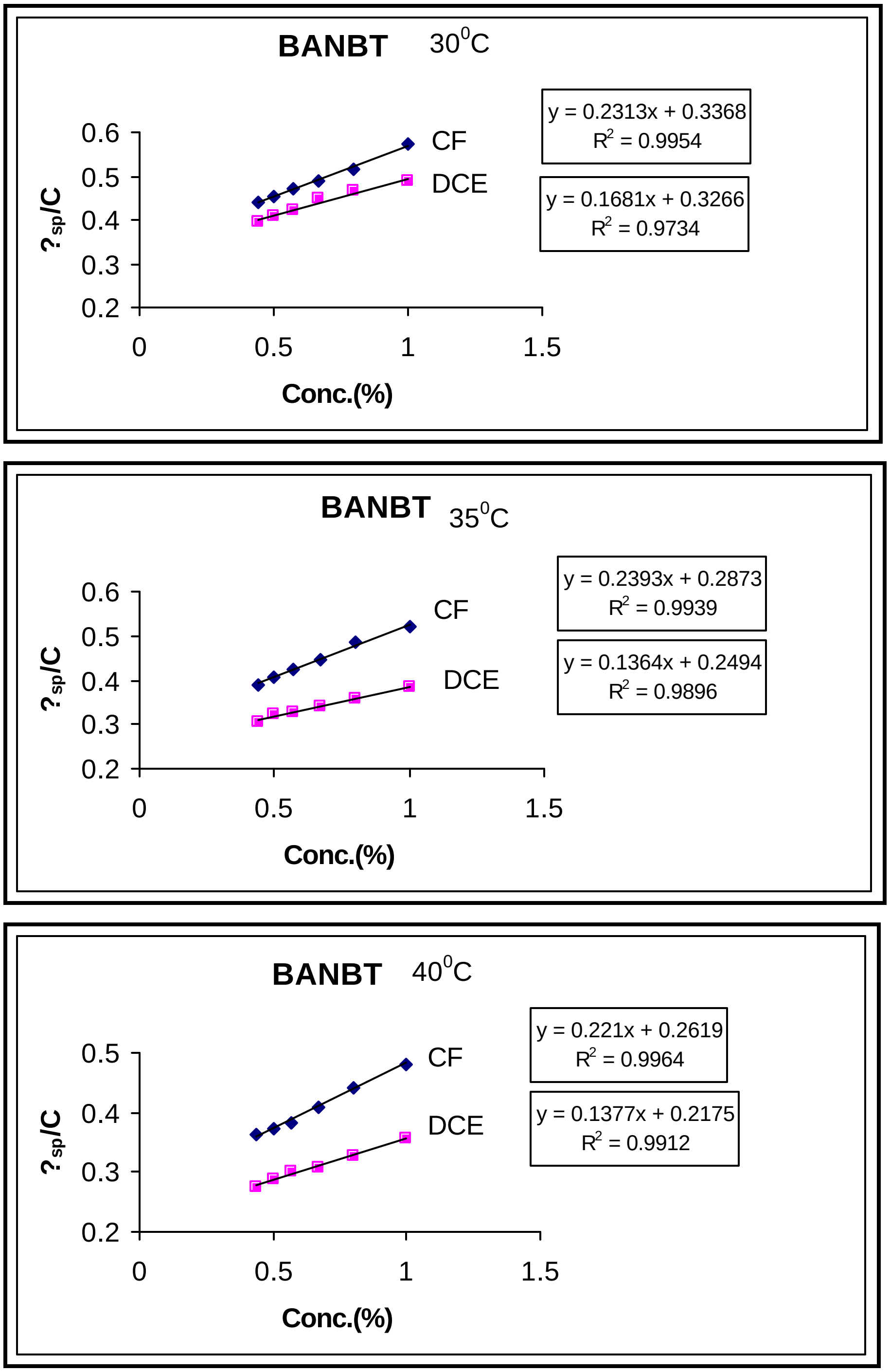


Fig.- 3.22 : The plots of ?$_{sp}$/C against C for copolyester (BANBT) in CF and DCE at 30^{o}C , 35^{o}C and 40^{o}C.

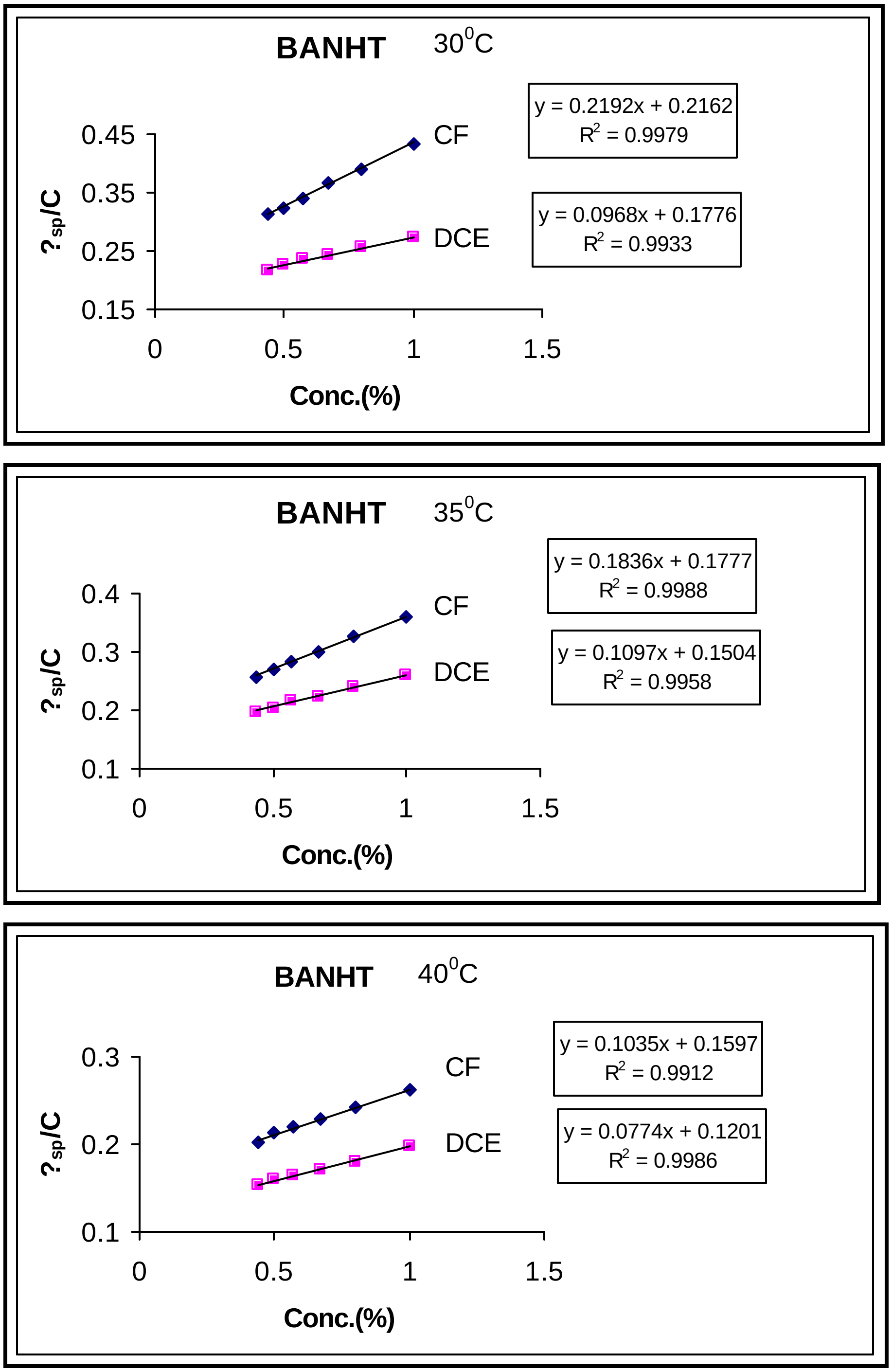


Fig.- 3.23 : The plots of ?$_{sp}$/C against C for copolyester (BANHT) in CF and DCE at 30^{o}C , 35^{o}C and 40^{o}C.

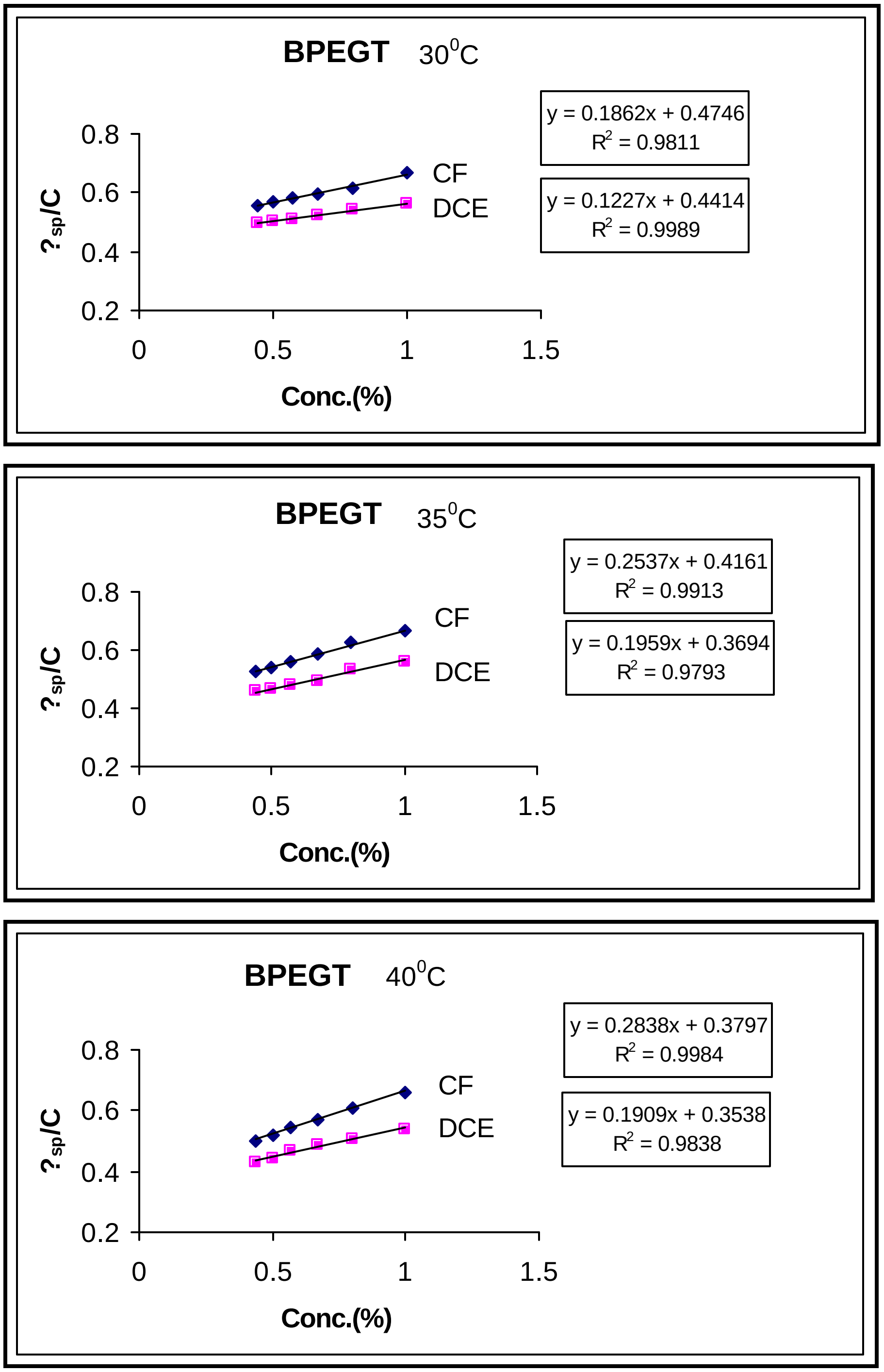


Fig.- 3.24 : The plots of $?_{sp}$/C against C for copolyester (BPEGT) in CF and DCE at 30^{o}C , 35^{o}C and 40^{o}C.

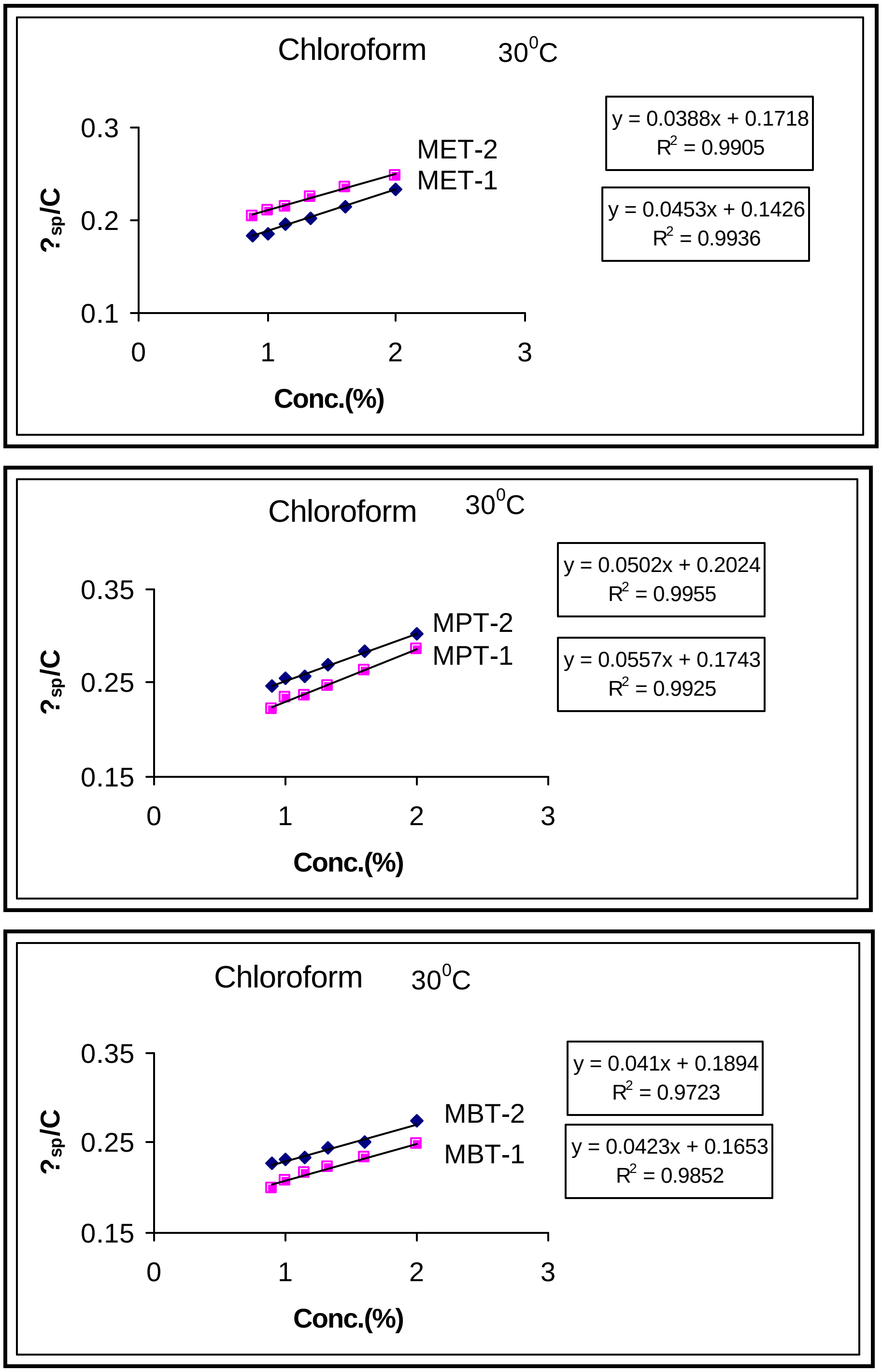
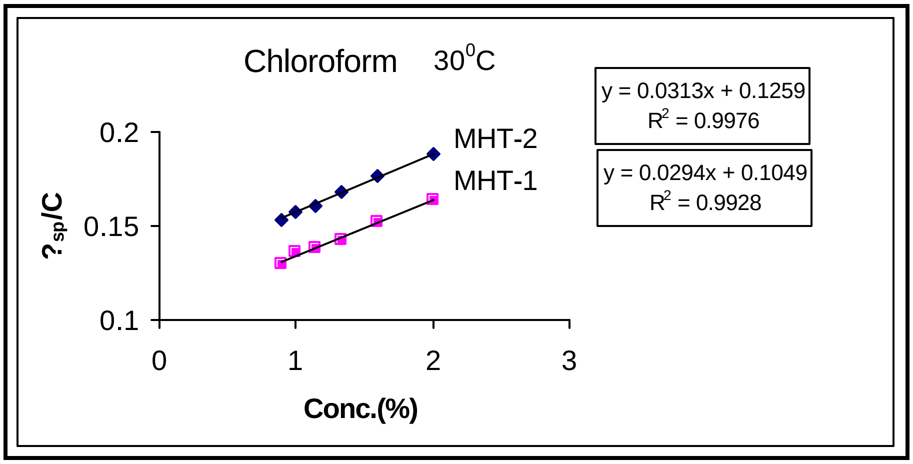
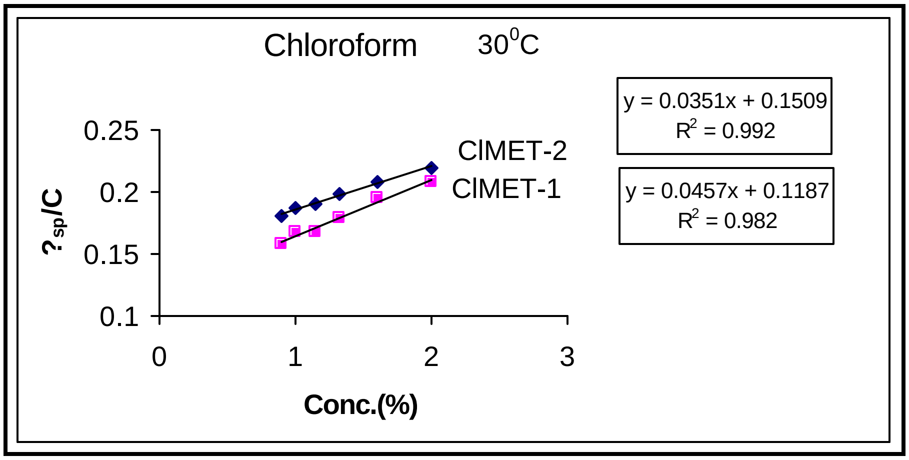


Fig.- 3.25 : The plots of $?_{sp}$/C against C for copolyesters (MET-1,MET-2, MPT-2, MPT-2, MBT-1 and MBT-2) in CF at 30^{o}C.





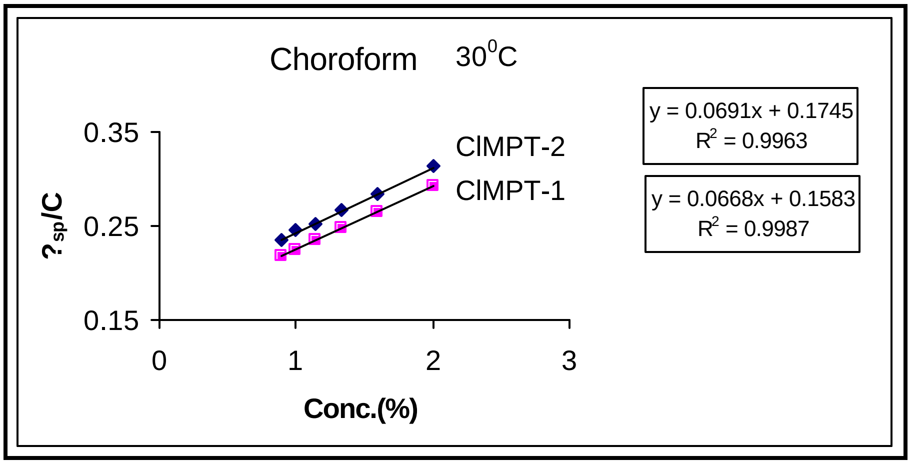


Fig.- 3.26 : The plots of $?_{sp}$/C against C for copolyesters (MHT-1,MHT-2, ClMET-1, ClMET-2, ClMPT-1 and ClMPT-2) in CF at 30°C.

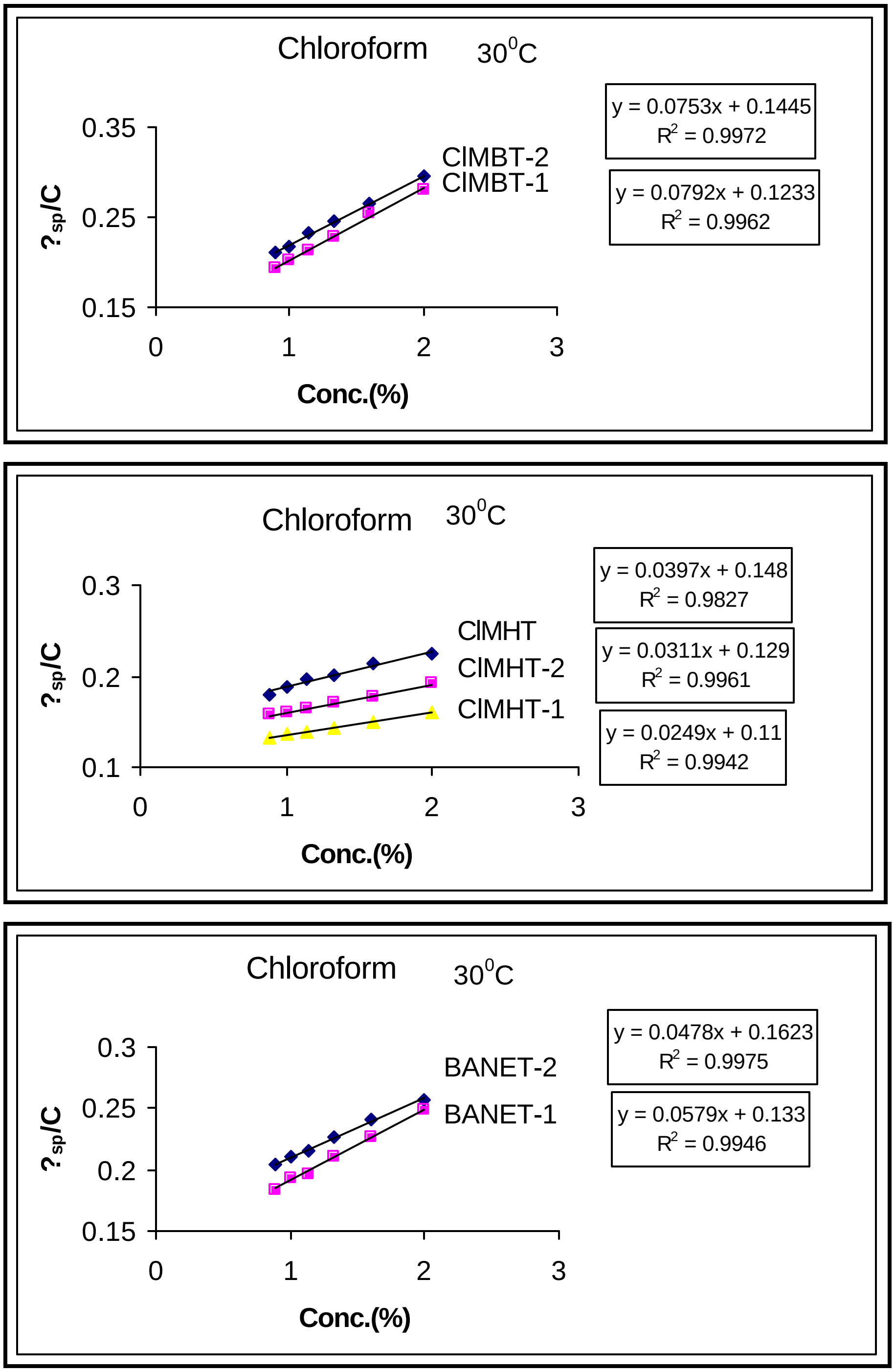


Fig.- 3.27 : The plots of ?$_{sp}$/C against C for copolyesters (ClMBT-1,ClMBT-2, ClMHT,ClMHT-1,ClMHT-2,BANET-1 and BANET-2) in CF at 30^{o}C.

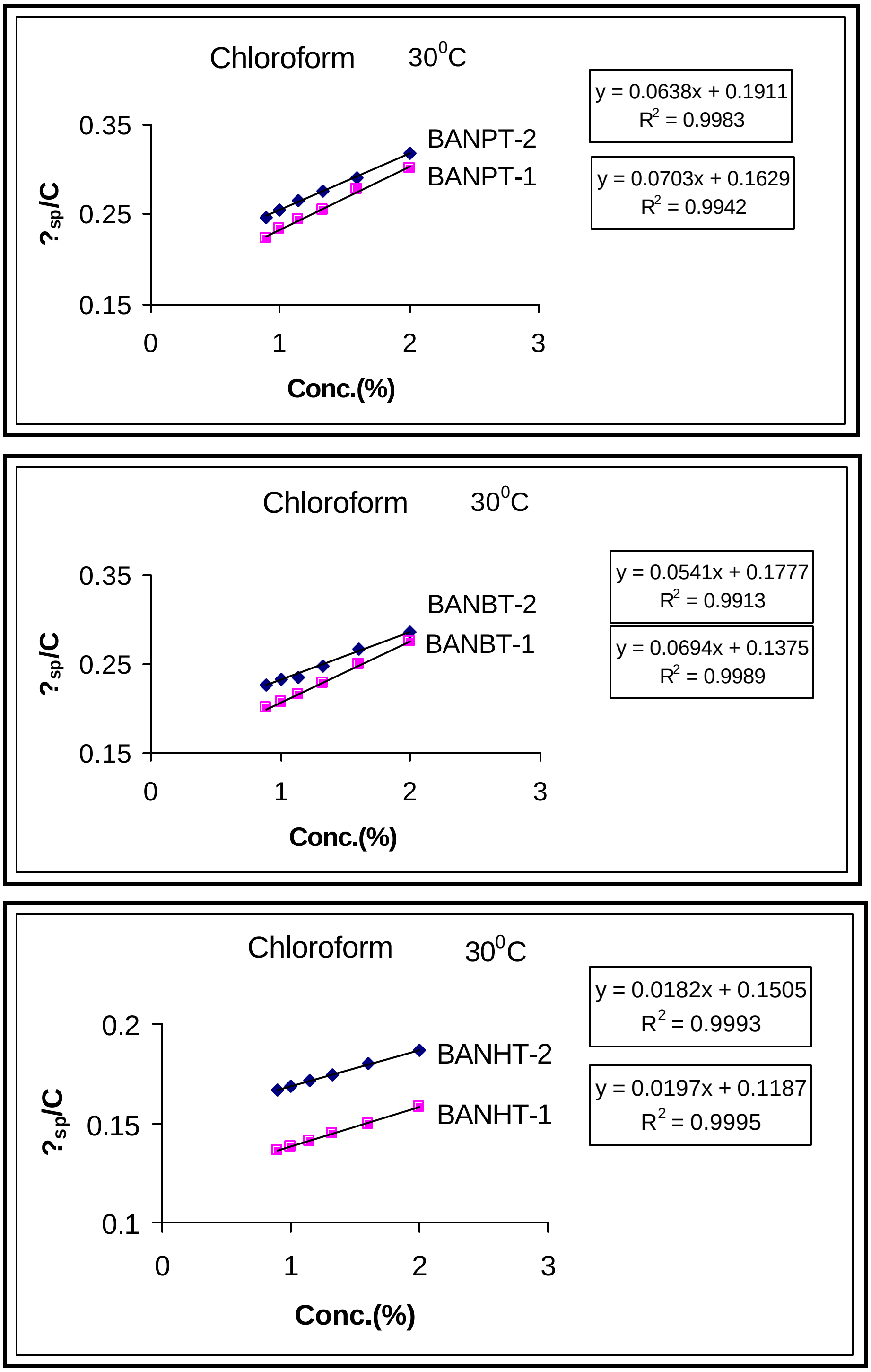


Fig.- 3.28: The plots of ?$_{sp}$/C against C for copolyesters (BANPT-1, BANET-2, BANBT-1, BANBT-2, BANHT-1and BANHT-2) in CF at 30^{o}C.

Table-3.6: The intrinsic viscosities and Huggins constant of polymers in different solvents and different temperatures.

Copolyester	**DCE**			**CF**		
	[h]	**k**	g	**[h]**	**k**	g
	30ºC					
MET	0.29	2.10	0.972	0.35	2.37	0.987
MPT	0.46	0.61	0.852	0.52	0.88	0.998
MBT	0.34	1.84	0.988	0.39	1.82	0.996
MHT	0.21	5.53	0.996	0.25	2.51	0.981
ClMET	0.22	1.14	0.999	0.24	1.27	0.996
ClMPT	0.24	1.56	0.998	0.28	1.78	0.998
ClMBT	0.17	3.87	0.994	0.21	1.91	0.962
ClMHT	-	-	-	0.15	1.81	0.983
BANET	0.25	1.51	0.989	0.26	1.90	0.978
BANPT	0.36	1.41	0.989	0.39	1.33	0.984
BANBT	0.33	1.54	0.973	0.34	2.00	0.995
BANHT	0.18	2.99	0.993	0.22	4.52	0.998
BPEGT	0.44	0.63	0.999	0.48	0.81	0.981
	35ºC					
MET	0.25	3.13	0.999	0.29	3.91	0.998
MPT	0.42	1.02	0.991	0.50	0.75	0.984
MBT	0.32	2.10	0.985	0.34	2.66	0.996
MHT	0.18	5.67	0.998	0.24	2.80	0.994
ClMET	0.20	2.11	0.980	0.22	1.91	0.971
ClMPT	0.23	1.71	0.996	0.26	1.58	0.996
ClMBT	0.16	3.62	0.992	0.19	2.33	0.998
BANET	0.22	1.88	0.992	0.24	2.89	0.983
BANPT	0.32	1.64	0.998	0.34	1.40	0.990
BANBT	0.25	2.18	0.989	0.29	2.84	0.994
BANHT	0.15	4.87	0.996	0.18	5.66	0.999
BPEGT	0.37	1.43	0.979	0.41	1.43	0.991
	40ºC					
MET	0.19	6.47	0.992	0.25	5.71	0.993
MPT	0.40	1.15	0.994	0.46	0.87	0.990
MBT	0.26	3.63	0.992	0.31	3.22	0.991
MHT	0.16	4.34	0.986	0.21	3.40	0.993
ClMET	0.18	2.44	0.928	0.21	1.80	0.998
ClMPT	0.22	2.28	0.995	0.23	2.10	0.998
ClMBT	0.14	5.09	0.971	0.18	2.31	0.992
BANET	0.18	3.68	0.981	0.22	1.88	0.991
BANPT	0.29	2.63	0.996	0.33	1.53	0.979
BANBT	0.22	2.84	0.991	0.26	3.27	0.996
BANHT	0.12	5.37	0.999	0.16	4.04	0.991
BPEGT	0.35	1.55	0.984	0.38	1.97	0.998

Copolyester	CF			Copolyester	CF		
	[h]	**k**	g		**[h]**	**k**	g
MET-1	0.14	2.41	0.994	ClMBT-1	0.12	5.50	0.996
MET-2	0.17	1.38	0.989	ClMBT-2	0.15	3.35	0.997
MPT-1	0.18	1.60	0.987	ClMHT-1	0.11	2.06	0.994
MPT-2	0.20	1.18	0.994	ClMHT-2	0.13	1.84	0.996
MBT-1	0.17	1.55	0.985	BANET-1	0.13	3.43	0.995
MBT-2	0.19	1.14	0.972	BANET-2	0.16	1.88	0.998
MHT-1	0.11	2.13	0.977	BANPT-1	0.16	2.75	0.994
MHT-2	0.13	1.67	0.988	BANPT-2	0.19	1.18	0.998
ClMET-1	0.11	3.54	0.982	BANBT-1	0.14	3.54	0.998
ClMET-2	0.15	1.54	0.992	BANBT-2	0.18	1.67	0.991
ClMPT-1	0.16	2.61	0.998	BANHT-1	0.12	1.37	0.999
ClMPT-2	0.18	2.13	0.996	BANHT-2	0.15	0.81	0.999

From Table-3.5, it is clear that the [?] has decreased with increasing alkyl chain length in the copolymer chains and hence decrease in reactivity of the diols. Methyl pendant group in aliphatic diol (PG) resulted in improvement in molecular weight to a small extent and [?] is slightly greater in chloroform system and it is decreased with temperature. A little temperature effect on [?] indicated flexible nature of the copolyesters. The increase of k’ with increase of temperature indicated increase of molecular interactions in the solutions. Both [?] and k’ depend upon temperature, structure of the polymer, nature of the solvent, polydispersity, etc.

SECTION-6: HYDROLYTIC STABILITY

Nonmetallic materials including textiles, wood, paper, plastics, elastomers, coatings, leather and ceramics are more widely used than metals. The nonmetallic materials are also subject to deterioration. The resistance of glass, cellulose and many organic polymers is related to the proportion of crystalline and amorphous region.

The chemical stability of a plastic is evaluated by change in the mass, linear dimensions and mechanical properties of material in the state of stress free state and also by the tendency to splitting in the stress-strain state after the samples has been exposed to reagents for a definite length of time [25, 26].

Test specification such as procedure of conditioning a specimen for testing purpose, concentration of reagents, time and temperature of testing, apparatus and instrument should be described in more detail for chemical resistance.

The recommended reagents for testing chemical resistance of plastics are reported in Table-3.7. Other reagents used for testing plastics for chemical resistance are oleic acid, methanol, acetone, 1,2-dichloroethane, carbon tetrachloride, heptane, benzene, toluene, aniline, mineral oil, transformer oil, olive oil, kerosene, gasoline, terpentine, 1%soap solution and other substances. The chemical resistance of material can be determined by change in mass, change in linear dimensions and by change in mechanical properties. A brief description of each method is described in Table 3.7.

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25. R. B. Seymour, “Treatise on Analytical Chemistry”- Interscience publication, New York, Vol III, pp 341-391

26. O.M. Kazarnovasky, B.M. Tareev, I. O. Forsilova and L. I. Lyuimov, “Testing of Electrical insulating materials” Mir Publishers , Moscow 1982.

Table-3.7: Recommended reagents and their concentrations for chemical resistance of plastics

Reagent	**Conc., %**
Sulfuric acid (1.84 g/cc)	3,30,100
Nitric acid (1.42g/cc)	10,40,100
Hydrochloric acid (1.91g/cc)	10,100
Chromic acid	40
Acetic acid	5,100
Citric acid	10
Sodium hydroxide	1,10,60
Sodium chloride	3,10
Sodium hypochlorite	10
Sodium carbonate	2,20
Ammonium hydroxide	-
Hydrogen peroxide	3,30
Ethyl alcohol	50,96
Phenol	5

(1) Chemical resistance by change in mass method

According to this method the change in the mass of a test specimen after exposure of a chosen reagent at temperature of 20°, 40°, 60°, and 100°C is determined. The test duration is dependent on the time required for plastic specimen to attain sorption, equilibrium or to loose stability in the test medium. The specimens are weighed after 12, 24, 36, 48, 96 and 128h and then every seven days. The specimen that has passed the test may either loose or gain in mass. The chemical resistance of the material is determined by averaging the changing in mass of several specimens.

The test specimen for molded or extruded plastics is in the form of a disc (50mm in diameter and 3mm in thickness). The specimens are cut from laminated or sheet plastics, the end faces of the laminated specimens are coated with same binder as used in the production of material in question. In case of rod samples, a length of rod should be 50mm and diameter should be < 50 mm.

A reagent is taken in amount of 8 ml per cm^2 surface area of plastic sample free from extractable substance and it is 20 ml per cm^2 surface area of an extractable plastics sample.

After loading the specimen in the bath, the reagent is mixed or stirred at least once in a day. After every seven days specimens are removed from the reagents once at a time, washed, wiped, dry and weighed. A percentage increase or decrease in the mass of a specimen is determined according to Eqn. 3.10

$$?M = [(M_2 - M_1)/M_1] \text{ X}100 \quad \textbf{... 3.10}$$

Where ?M is the change in the weight, M_1 and M_2 are the weights of the specimen before and after immersion in the given reagent.

(2) Chemical resistance by change in linear dimensions

The method is based on change in linear dimensions of specimen after prolong exposure to a reagent. The form, size and no. of specimens and the quantity of reagent must remain same as in the change in the mass method.

Before testing the thickness of central portion of the disc and two mutually perpendicular diameters of each specimen are measured after every seven days, the specimens are taken out from the bath, washed, wiped with a cloth and checked for the dimensions at the same place. A change in any of the linear dimensions in percent is determined according to following Eqn. 3.11.

$$?l= (l_2-l_1/l_1)\ X100 \qquad \textbf{... 3.11}$$

Where, l_1 and l_2 are linear dimensions of the specimens before and after immersion in the reagent.

(3) Chemical resistance by change in mechanical properties

This method is based on the stability of mechanical properties of plastics under prolonged exposure to reagent. The form, dimensions and number of specimens for plastic materials are chosen in compliance with the standard. After exposure to a reagent, the specimens are washed, wiped and tested for one or two most important characteristics such as tensile strength, flexural strength, impact strength, hardness, %elongation at break and mechanical stress in bending that causes a deflection equal to1.5 fold thickness of specimen. The relative change in mechanical properties may serve as a basis for dividing plastics into three groups as shown in Table-3.8.

Table -3.8: Stability characteristic of plastics on exposure to reagents

Type of plastics	**Relative change in mechanical stability characteristics, %**	
	Strength properties	**Deformation**
Thermoplastics	0-10 10.1-20 over 20	0-10……….Good 10.1-20….Adequate over 20……..Poor
Thermosets	0-15 15.1-25 over 25	-………..Good -………..Adequate -………..Poor

In present investigation the hydrolytic stability of copolyester films were determined by the change in weight method [25, 26]. For this purpose preweighed polymer films were immersed in pure water and 10% each of aqueous solutions of hydrochloric acid, sulfuric acid, nitric acid, sodium hydroxide, potassium hydroxide and sodium chloride at room temperature. After one day, one week and one month the polymer films were taken out, washed, wiped, dried and weighed and reimmersed .The change in weight of film was evaluated according to equation 3.11. The percentage weight loss or gain after one day, one week and one month were determined and is reported in Table-3.9.

From Table-3.9, it is clear that copolymers possess excellent hydrolytic stability in acids, alkalis and salt solutions investigated under stated experimental conditions. Chemical degradation and cracking or blistering can cause high moisture uptake while, slight change in weight loss or gain due to surface degradation, leaching of small molecules or solvation of ions with polar groups present in the polymer chain.

Table- 3.9: Chemical resistance of copolyesters by change in weight method at room temperature

Solution, %	% Weight change								
	After 24h	After one week	After one month	After 24h	After one week	After one month	After 24h	After one week	After one month
	MET			MPT			MBT		
HNO_3	3.2	4.1	3.6	-4.0	-3.2	-2.8	4.9	4.2	5.6
H_2SO_4	1.8	2.6	3.5	-3.9	-6.5	-4.3	-2.5	-3.1	-4.6
HCl	3.5	2.7	3.5	-5.3	-2.7	0.0	1.1	2.9	4.0
KOH	3.5	5.7	2.8	-1.3	-3.0	0.0	-3.9	2.6	3.9
NaOH	1.7	1.7	2.9	-3.5	0.4	0.0	-2.3	3.8	5.3
NaCl	3.9	2.6	1.9	-2.1	7.8	-0.1	4.0	2.4	5.6
H_20	4.1	4.8	3.8	0.9	3.9	0.0	0.7	1.4	2.8
	ClMET			ClMPT			ClMBT		
HNO_3	-0.93	-2.50	-3.13	-0.75	-2.10	-2.76	-1.26	-2.51	-3.01
H_2SO_4	-1.34	-3.02	-2.68	-0.53	-1.86	-2.65	-0.75	-1.74	-3.23
HCl	-1.43	-2.85	-2.85	-0.77	-2.30	-3.07	-1.71	-2.56	-2.85
KOH	1.33	2.66	2.33	0.84	1.95	2.86	0.86	2.29	3.15
NaOH	1.69	1.69	2.37	0.86	2.28	3.71	1.25	2.25	2.75
NaCl	1.32	1.98	2.98	0.59	1.78	2.96	1.01	2.53	3.03
H_20	-2.15	-1.79	-1.43	-0.52	-1.31	-2.36	-1.28	-1.03	-2.56
	BANET			BANPT			BANBT		
HNO_3	-0.67	-2.42	-3.39	-0.31	-2.22	-3.82	-0.31	-2.50	-3.33
H_2SO_4	-0.64	-2.24	-2.88	-0.30	-1.85	-3.08	-0.63	-1.89	-3.79
HCl	-0.66	-2.33	-3.98	-0.64	-2.26	-4.19	-0.64	-2.24	-4.17
KOH	0.33	2.67	4.01	1.00	2.35	3.35	0.65	2.90	4.19
NaOH	0.32	2.29	3.60	0.62	1.56	3.02	0.61	2.15	3.08
NaCl	0.64	2.52	4.18	0.66	2.00	4.01	0.98	2.95	3.61
H_20	-0.95	-2.85	-4.13	-0.31	-1.24	-4.03	-0.64	-3.21	-4.18
	BANHT			BPEGT					
HNO_3	-0.68	-2.41	-4.13	-0.64	-1.93	-3.22			
H_2SO_4	-0.71	-2.84	-3.91	-0.67	-1.67	-3.34			
HCl	-0.35	-2.43	-3.47	-0.98	-2.29	-3.28			
KOH	0.37	2.96	3.70	0.63	2.22	4.12			
NaOH	0.66	3.00	3.33	0.33	2.33	4.00			
NaCl	0.34	2.01	4.02	0.97	1.94	3.24			
H_20	-0.66	-2.66	-4.13	-0.63	-2.21	-3.47			

SECTION-7: ANTI BACTERIAL ACTIVITY OF POLYMERS

Polymer materials possess some unique characteristics, which exert a profound influence on biological activities [27, 28] in number of cases. The nature, molecular weight, molecular weight distribution of polymers, degree of cross linking, stereo configuration, etc. have significant role on biological activities.

EXPERIMENTAL

In order to grow different microorganisms, the nutrient agar media was prepared according to reported method [29, 30].

Peptone (bacteriological)	0.5
Meat extract	0.5
Sodium chloride	0.5
Agar	0.5
Distilled water	100 ml

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27. M.Ghosh, Polymer Mater. Sci. Engg., ACS. **55**, 755, 1986
28. M.Ghosh, J.Polym. Mater, **6**, 81, 1989
29. A.L.Bary, “The Antimicrobic Susceptibility Test, Principles and Practices.” Illus Lea and Febiger, Philadelphia, pp 180-193, 1976
30. R.Chuickshank, J.P.Duigd, D.P.Marmom and R.H.A.Swain, “Medical Microbiology” Churchill- Livingstone, Edinburgh, London. Vol 2,1975.

The ingredients were mixed together and heated on a low flame till fully dissolved. The pH of the media was adjusted to 7.5. The media was cooled to $50^{O}C$ and was poured in 15ml lots in sterilized petri dishes and allowed to harden. Surface seeding of the hardened plates was done with different microorganisms namely Escherichia coli, Bacillus megaterium, Proteus vulgaris, Staphylococcus aureus, Aspergillus niger. The plates were incubated at $37^{o}C$ for 24h. Sterile cups were punched and loaded with 0.1ml (50µg) of each sample solution and DMF control. The plates were further incubated for 24h at $37^{o}C$ and zones of inhibition of the bacterial growth were measured in diameter (mm). A comparative zone of inhibition for standard drugs and polymer samples are reported in Table-3.10. From the Table-3.14, it is clear that copolyesters show mild antibacterial and antifungal activities as compared to standard drugs like amoxicillin, ampicillin, norfloxacin and oxacin. The moderate fungal activity might be due to phenolic (-OH) and -Cl end groups.

Table-3.10: A comparative zones of inhibition for standard and polymers against different microorganisms

Sample	Zone of inhibition, mm				
	E.coli	B.mega	P.vulgaris	S. aureus	A. niger
MET	8	10	11	9	10
MPT	9	8	9	12	12
MBT	9	11	8	13	9
MHT	10	9	12	11	11
ClMET	12	11	13	10	9
ClMPT	11	10	9	10	11
ClMBT	9	8	10	11	9
Amoxicillin S_1	17	19	22	22	18
Ampicillin S_2	15	21	19	23	20
Norfloxacin S_3	22	20	21	24	19
Oxacin S_4	19	18	20	24	18

.

CHAPTER – 4

THERMO-MECHANICAL

AND

ELECTRICAL PROPERTIES

OF

COPOLYESTERS

CHAPTER-4

THERMO – MECHANICAL AND ELECTRICAL PROPERTIES OF CARDO COPOLY ESTERS

This chapter of the thesis describes thermo-mechanical and electrical studies of copolyesters and is further subdivided into two sections:

SECTION-1: THERMAL PROPERTIES OF COPOLYESTERS

SECTION-2: MECHANICAL AND ELECTRICAL PROPERTIES OF COPOLYESTERS

SECTION-1: THERMAL PROPERTIES OF COPOLYESTERS

Thermal analysis of polymers is of great importance especially for the study of degradation kinetics, degradation mechanism, bond strength, thermal stability and molecular architecture. It is also useful in designing materials for high temperature applications and for the identification purposes as well as processability. A major driving force for the growth and interest in the thermally stable polymers is attributable to their extensive applications such as space exploration, terrestrial transportation, modern communication, energy saving, environmental protection, public health, microbiology, medicine, aeronautics and in supersonic applications. Considerable research work has been undertaken [1] on thermally stable polymers.

Increased emphasis on occupational safety and consumer protection has generated significant interest in analytical methods to evaluate safe processing, storage, shipping and safety conditions for a wide variety of materials. Thermal techniques particularly differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA) have been proven useful for evaluating kinetic parameters of various reactions and materials [2-4]. These kinetic parameters provide usefulness of the potentially unstable nature of materials. TGA provides qualitative and semi quantitative rapid comparison about thermal stability and degradation finger print patterns of polymers [5].

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1. R. T. Conley,"Thermal Stability of Polymers", Marcell Dekker, New York, 1973.
2. H. J. Borchardt and F. J. Daniels, J.Am.Chem.Soc. **79** , 41, 1957.
3. T. Ozawa, J. Therm. Anal., **2**, 301, 1970.
4. H. E. Kissinger, J. Research Natl. Bur. Standards, **57**, 217, 1956; C. A.,**51,** 3258, 1957
5. L. Reich, D. W. Levi, Macromolecular Reviews. New York: Wiley-Interscience, **1,** 173, 1968.

Studies on thermal behavior of polymers are of paramount importance from both scientific and practical point of views [6]. Scientific studies help to reveal the molecular structure such as the sequence and arrangement of repeating units and side groups in the polymers as well as the nature of the chain ends and of the cross links between chains. The kinetics of degradation is very useful in determining the strength of various bonds in polymer structure [7].

Thermal studies throw light on molecular architecture of polymers such as degree of polymerization, orientation, crystal perfection, percentage crystallinity, the extent of chain branching, strength of various bonds holding together polymer molecules, on the kinetic of depolymerization, on the effects of time, temperature, pressure, etc. and on the rates and products of degradation.

For any given application, it is likely that one or a few physical and or chemical properties will be most important. A few that often encountered are structural integrity, tensile strength, viscosity, weight loss and susceptibility to oxidation. Thermal stability of high polymers is of prime importance in the fabrication processes and their uses at high temperatures. Thermal behavior of polymers provides much useful information about their specific uses. Still [8] has reviewed the problems associated with applications of thermal methods to polymers.

On practical side, thermal analysis of polymers not only explains the behavior of polymers under conditions of high temperatures but also help in selecting the right kind of material for the specific uses where high temperatures are encountered. It also suggests the design and synthesis of new materials for specific requirements in polymer technology such as high temperature resistant synthetic and natural fibers, transportation industries, electrical and electronic instruments, appliances, etc.

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6. J. W. Bain and G. F. Kay, Trans Roy. Soc. Can., **18**, 269, 1924; C.A. **19**, 893, 1925
7. H. C. Anderson, J.Appl.Polym.Sci., **6**, 484, 1962.
8. R. H. Still , British Polym. J. **11**, 101, 1979.

Effect of various operating parameters

1. Atmosphere

The atmosphere associated with any thermal analyses, which composed of gases that are introduced from outside and those are evolved from the samples. The presence or absence of such gases may have a strong influence on the results. These gases may react with the sample or with each other, and change the reaction mechanism or product composition. Inert atmosphere and vacuum will influence the decomposition processes as well. In vacuum, primary decomposition of gases will tend to be pumped away from the sample before the molecules collide with the surface and undergo secondary reactions. They may undergo homogeneous reactions or may be reflected back to the sample surface and react there.

2. Container geometry

The container geometry influences the gaseous environment and heat transfer to the samples. Even with a flowing gaseous atmosphere, a deep narrow container will limit the contact between the sample surface and gas, whereas a shallow, broad container will promote the contact.

3. Container material

It is reasonable to expect that in some cases the container material will react with material being tested or some of the products.

4. Sample size

Two major effects are associated with the sample size, namely surface and bulk effects. In carrying out polymer degradation studies, it is customary to reduce film thickness or particle size until the rate of the decomposition becomes independent of size.

5. Rate of heating

In the case where only kinetic considerations are significant, an increase in the rate of temperature will cause the process to be displayed to a higher temperature because the sample will be at the lower temperatures for a shorter length of time. The rate of change of the measured parameters will also be greater for faster heating.

Differential Scanning Calorimetry (DSC)

Physical transformation [9] such as glass transition, cold crystallization and crystallization from melts, crystallization disorientation, and melting can be studied by differential scanning calorimetry (DSC) and differential thermal analysis (DTA).

Glass transition involves the motion of short segments in the amorphous region and is related to the brittleness of the polymer. Crystallization from the melt is of great practical importance. A number of properties of polymers like melting range, heat of fusion and melting point depression, degree of crystallinity, random copolymer structure and stereo regularity and identification of composition of a mixture may be studied through melting.

DSC is a method whereby the energy necessary to establish a zero temperature difference between a substance and a reference material is recorded as a function of temperature or time. When an endothermic transition occurs, the energy input to the sample in order to maintain a zero temperature difference, because this energy input is precisely equivalent in magnitude to the energy absorbed during the transition in direct calorimetric measurement. The combination of programmed and isothermal technique has been used for characterizing unresolved multistep reaction in polymers [10].

DSC provides useful informations about crystallinity, stability of crystallites, glass transition temperature, cross linking, kinetic parameters such as the activation energy, the kinetic order, frequency factor, entropy change and heat of polymerization.

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9. E. Heisenberg; Cellulose Chemie, **12**,159, 1931; C.A. **25**, 59, 823, 1931.
10. A. A. Duswalt; Thermochemica Acta, **8**, 57, 1974.

Thermo gravimetric analysis (TGA)

Different polymers decompose over different ranges of temperature yielding different proportion of volatile and residues. Thermogravimetry is useful analytical technique for recording weight loss of a test sample as a function of temperature, which may be used for understanding the chemical nature of the polymer. Thus, the weight of a substance in an environment heated or cooled at a controlled rate is recorded as a function of time or temperature.

There are three types of thermogravimetry

1. Static or isothermal thermogravimetry
2. Quasistatic thermogravimetry and
3. Dynamic thermogravimetry

Most of the studies of polymers are generally carried out with dynamic thermogravimetry. Normally the sample starts losing weight at a very slow rate up to a particular temperature and there after, the rate of loss becomes large over a narrow range of temperature. After this temperature, the loss in weight levels off. TGA curves are characteristic for a given polymer because of unique sequence of physico-chemical reactions, which occur over definite temperature ranges and at rates that are function of the polymer structure. The change in weight is a result of the rupture and/or formation of various physical and chemical bonds at elevated temperatures that lead to evaluation of volatile products in the formation of heavier reaction products.

Pyrolysis of many polymers yields sigmoidal TG curves. The weight of the sample decreases slowly as reaction begins and then decreases rapidly over a comparatively narrow range of temperature and finally levels off as the reaction is completed. The shape of the curve depends on the kinetic parameters: reaction order n, frequency factor A and activation energy E_a. The values of these parameters have been shown to be of major importance to elucidate the mechanism in polymer degradation [11, 12]. Reich and Levi [13] have described several temperature characteristics for qualitative assessment of relative thermal stability of polymers:

1. Initial decomposition temperature (T_0),
2. Temperature of 10% weight loss (T_{10}),
3. Temperature of maximum rate of decomposition (T_{max}),
4. Half volatilization temperature (T_s),
5. Differential decomposition temperature and
6. Integral procedural decomposition temperature (IPDT).

With dynamic heating T_0 and T_{10} are some of the main criteria of the thermal stability of a given polymer at a given temperature.

For the estimation of kinetic parameters from TG traces, several so called exact methods have been proposed. All these methods involve two important assumptions that thermal and diffusion barriers are negligible and that Arrhenius equation is valid. Since small quantities of materials are employed in TG studies, thermal and diffusion barriers would be negligible.

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11. D. W. Levi, L. Reich and H. T. Lee; Polymer Eng. Sci., **5**, 135, 1965.
12. H. L. Friedman, U. S. Dept. Com., Office. Tech., 24 PP ,1959; C. A. **55**, 26, 511, 1961.
13. L. Reich and D. W. Levi, Macromol. Rev. Eds. Peterlin Goodman Wiley Interscience, New York, 173, 1968

Since the shape of any TG curve is dependent on the nature of apparatus and the way in which it is used. Most kinetic treatments are based on relationship of the type:

$$\frac{dC}{dt} = kf(C) \qquad \ldots 4.1$$

where C = Degree of conversion, t = time, k = rate constant, f(C) = a temperature independent function of C.

The constant k is generally assumed to have the Arrhenius form

$$k = Ae^{-E_a/RT} \qquad \ldots 4.2$$

C is defined as the conversion with respect to initial material

$$C = 1 - \frac{W}{W_0} \qquad \ldots 4.3$$

Where W_0 = Initial weight of the material and W = weight of the material at any time. The residual weight fraction is given by

$$\frac{W}{W_o} = (1 - C)$$

and the rate of conversion is given by

$$\frac{dC}{dt} = -\left(1/W_o\right)\frac{dW}{dt} \qquad \ldots 4.4$$

For homogeneous kinetics, the conversion would be assumed to have the form

$$f(C) = (1 - C)^n \qquad \ldots 4.5$$

where, n = order of the reaction.

Upon substituting Eqns. 4.2 and 4.5 into Eqn. 4.1

$$\frac{dC}{dt} = Ae^{-E_a/RT}(1 - C)^n \quad \text{or} \quad \frac{dC}{dT} = \left(\frac{A}{ß}\right)\left(e^{-E_a/RT}\right)(1 - C)^n \qquad \ldots .4.6$$

where β = Rate of heating.

Methods of single heating rate

1. Freeman – Carroll [14] and Anderson-Freeman [15] method

Freeman-Carroll developed the following relation to analyze TGA data at a single heating rate:

$$\frac{?\ln(dC/dt)}{?\ln(1-C)} = n - \frac{E_a}{R}\left[\frac{?\,(1/T)}{?\ln(1-C)}\right] \qquad \ldots 4.7$$

A Plot of L.H.S. against $\frac{\Delta(1/T)}{\Delta\ln(1-C)}$ for equal interval of $\Delta(1/T)$ would yield a straight line with slope equal to $-E_a/R$ and the intercept equal to n. Using Eqn. 4.7, Anderson-Freeman derived Eqn. 4.8:

$$\mathrm{D}\,\boldsymbol{ln}\left(\frac{dC}{dt}\right) = \boldsymbol{n}?\ln(1-C) - \frac{E_a}{R}?\left(\frac{1}{T}\right) \qquad \ldots 4.8$$

According to Eqn. 4.8, the plot of $\Delta ln(dC/dt)$ against $\Delta 1n(1-C)$ for equal interval of $?\,(1/T)$ would be a straight line with slope equal to n and the intercept equal to $-(E_a/R)?\,(1/T)$

2. Sharp-Wentworth method [16]

For a first order process (n=1), Sharp-Wentworth derived following relation to analyze TGA data:

$$\log\left[\frac{dC/dt}{1-C}\right] = \log(A/\text{ß}) - \frac{E_a}{2.303R}\cdot\frac{1}{T} \qquad \ldots 4.9$$

The plot of log $\left(\frac{dC/dt}{1-C}\right)$ against 1/T would be a straight line, with slope equal to $-(E_a/2.303\,R)$ and intercept equal to $\log(A/b)$.

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14. E. S. Freeman and B. Carroll, J. Phys. Chem., **62**, 394, 1958.
15. D. A. Anderson and E. S. Freeman, J. Polym. Sci., **54**, 253, 1961.
16. J. H. Sharp and S. A. Wentworth, Anal. Chem., **41**, 2060, 1969.

3. Chatterjee method [17]

Chatterjee developed following relation for the determination of n from TG curves based on weight units.

$$n = \frac{\log\left(-\frac{dW}{dt}\right)_1 - \log\left(-\frac{dW}{dt}\right)_2}{\log W_1 - \log W_2} \qquad \text{…4.10}$$

Where, W_1 and W_2 are the sample weight.

4. Horowitz and Metzger method [18]

The value of E_a can be determined from a single TG curve according to Horowitz and Metzger:

$$\ln\left[\ln\left(1 - C\right)^{-1}\right] = \frac{E_a}{RTs^2}? \qquad \text{…4.11}$$

where Ts = Temperature at which the rate of decomposition is maximum and $q = T - Ts$.

The frequency factor A and entropy change ?S can be determined respectively according to Eqns. 4.12 and 4.13.

$$\ln E_a - \ln\left(RTs^2\right) = \ln A - \ln ß - \frac{E}{RTs} \qquad \text{…4.12}$$

$$A = \frac{k_b T}{h} e^{?S/R} \qquad \text{…4.13}$$

where k_b is Boltzmann constant

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17. P. K. Chatterjee, J. Polym. Sci., A-**3**, 4253, 1965.

18. H. H. Horowitz and G. Metzger, Ana. Chem., **35**, 1464, 1963.

Use of multiple heating rates

(1) Anderson [19] method

Anderson [19] and Friedman [20] have developed the methods based on multiple heating rates. These methods are based on the fact that as the heating rates are increased, TG curves tend to shift to higher temperature, since at lower temperature decomposition occurs for shorter times.

The relation is $$\ln R_t = \ln A + n \ln\left(1 - C\right) - \frac{E_a}{RT} \qquad \text{…4.14}$$

where $R_t = ß\, dC/dT$

The plot of $\ln R_t$ against 1/T at various fixed degree of conversion would be a straight line with slope equal to $-E_a/R$ at a fixed degree of conversion.
In order to evaluate the values of n and A, Eqn. 4.15 can be employed by considering 1/T = 1/To when $\ln R_t = 0$

$$\frac{Ea}{RTo} = \ln A + n\ln(1-C) \qquad \text{…4.15}$$

According to Eqn. 4.15, the plot of E/RT_0 against ln (1-C) would be a straight line with slope equal to n and intercept equal to ln A.

(2) Friedman method [20]

Friedman [20] has developed following Eqn. 4.16:

$$\ln\left(\frac{dC}{dt}\right) = \ln A + n\ln(1 - C) - \frac{E_a}{RT} \qquad \text{… 4.16}$$

According to Eqn. (2.16), the plot of ln dC/dt against 1/T at various values of fixed degree of conversion would be a straight line with slope equal to $-E_a/R$ and

$$\text{Intercept} = \ln A + n\ln(1-C) \qquad \text{…4.17}$$

The intercept obtained from the first graph can be plotted against ln(1-C), the slope and the intercept of which yield the values of n and A, respectively,

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19. H. C. Anderson, J. Polym. Sci., **C6,** 175, 1964.
20. H. L. Friedman, J. Polym. Sci., **C6**, 183, 1964.

(3) Ozawa method [21]

Ozawa has developed the following Eqn. 4.18:

$$\log \int_0^C \frac{dC}{(1-C)^n} \approx \log \frac{AE_a}{RT} - \log b - 2.315 - 0.4567 \left(\frac{E_a}{RT} \right) \qquad \ldots 4.18$$

The plot of log b against 1/T would be a straight line for the fixed values of conversion; the slope is equal to –0.4567(E_a/R).

EXPERIMENTAL

The DSC-TGA thermograms of copolyesters were scanned on a Universal V3 .0G TA Instruments at the heating rate of 20°C/min in an N_2 atmosphere without thermal treatment prior to their thermal analysis.

RESULTS AND DISCUSSION

Thermal analysis of polymers is of prime importance from both scientific as well as practical point of view. It is also very useful in predicting the behavior of polymers under various environmental conditions, in understanding molecular architecture and decomposition mechanism and also for their specific high temperature applications [22]. Differential thermal methods find wide spread use in determining the compound of naturally occurring and manufactured products [23-25].

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21. T. Ozawa, Bull. Chem. Soc. Jap., **38**, 1881, 1965.
22. C. D. Doyle, WADD Tech. Rept., **1**, 60, 1960.
23. W. W. Wendlandt, "Thermal Methods of Analysis", 2^{nd} Ed. Willey, New York, 1974.
24. T. Meisel and K. Seytold, Crit. Rev. Anal. Chem., **12**, 267, 1981.
25. R. C. Mackenzie, Ed., "Differential Thermal Analysis", Vols. 1& 2, Academic Press, N. Y. 1970.

DSC and TGA thermograms of copolyesters at the heating rate of 20^oC/ min in an N_2 are shown in Figs. 4.1 to 4.12. Initial decomposition temperature (T_0), temperature of 10 % weight loss (T_{10}), temperature of maximum weight loss (T_{max}) and temperature of final decomposition (T_f), decomposition range, % weight loss involved and % residual weight at the end of the reaction for copolyesters are reported in Table 4.1 from which it is evident that T_g has increased with increase in alkyl chain length of diols but little effect on T_{max} is observed. In case of MHT, T_g is determined from the slope change of the base line. The transition between 275-300^{o}C is probably due to some physical change and it is further supported by no weight change in TG thermogram over the said temperature range. Other transitions below 100^{o}C may be due to traces of moisture along with residual solvent. Because of limitation of higher temperature range in DSC and TGA were not scanned up to about 900^{o}C and therefore it is hard to judge the presence of crystallinity or complete amorphous nature of the samples. The copolyesters are thermally stable up to about 408-787ºC and followed single step degradation involving 35-75 % weight loss with 20-59 % residue.

The kinetic parameters such as order of degradation (n), energy of activation (Ea), frequency factor (A) and the entropy change (ΔS^*) are determined according to Freeman-Anderson method. [14]

The plots of ?Indw/dt against ?lnW for copolyester are shown in Figs. 4.13 to 4.18. The detail calculation schemes are reported in Tables 4.2.

The least square values of n, E_a and A are reported in Table 4.3. along with correlation coefficient (γ). The entropy change (ΔS^*) is determined at corresponding T_{max} and is also reported in Table 4.3 from which, it is clear that copolyesters followed 1.2-3.8 order degradation kinetics. Both Ea and A are affected to some extent by the structure and alkyl chain length of diol. The value of ΔS^* is increased with alkyl chain length up to four carbons and beyond that it has decreased due to conformational changes.

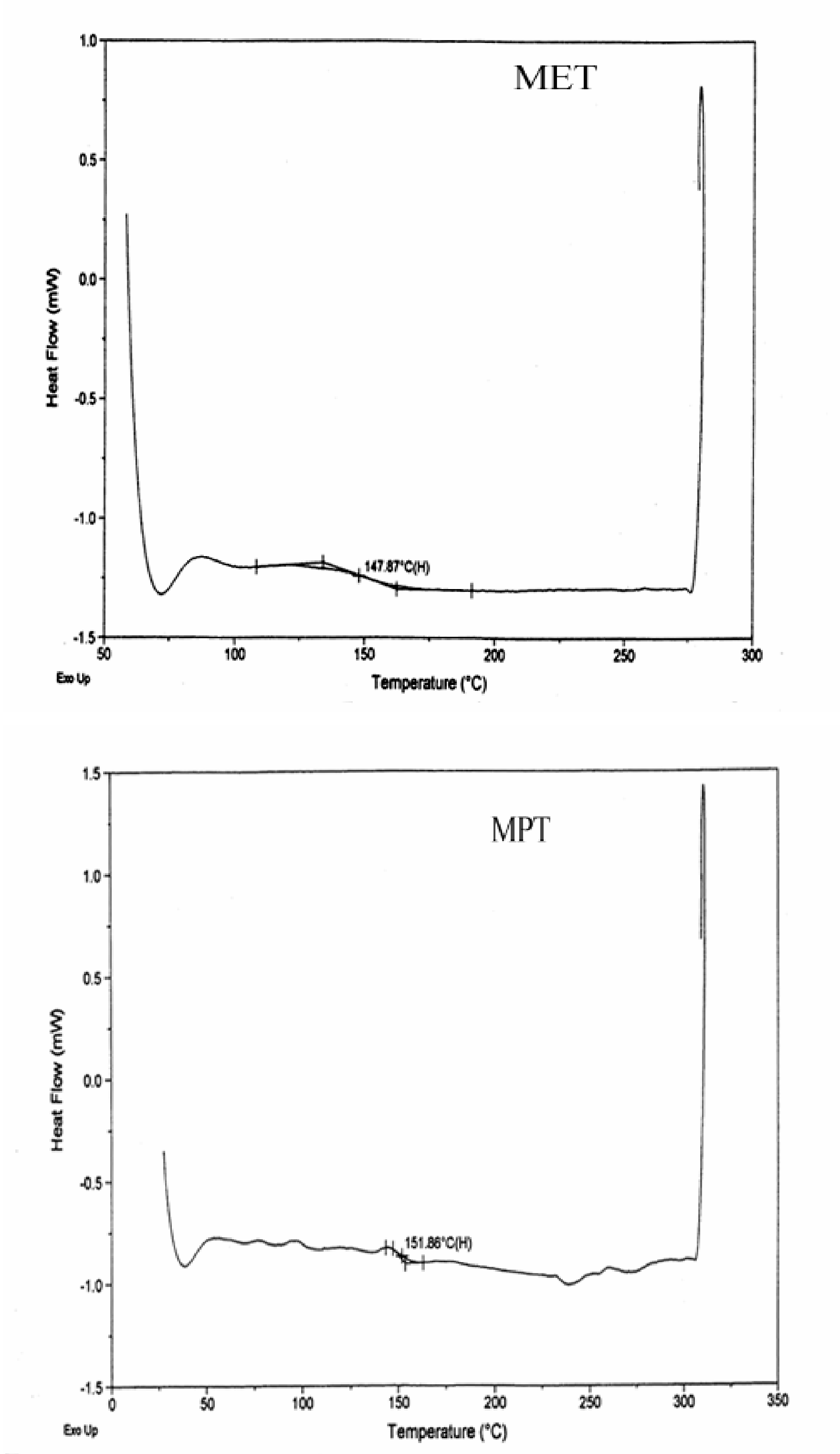


Fig.- 4.1: DSC thermograms of MET and MPT

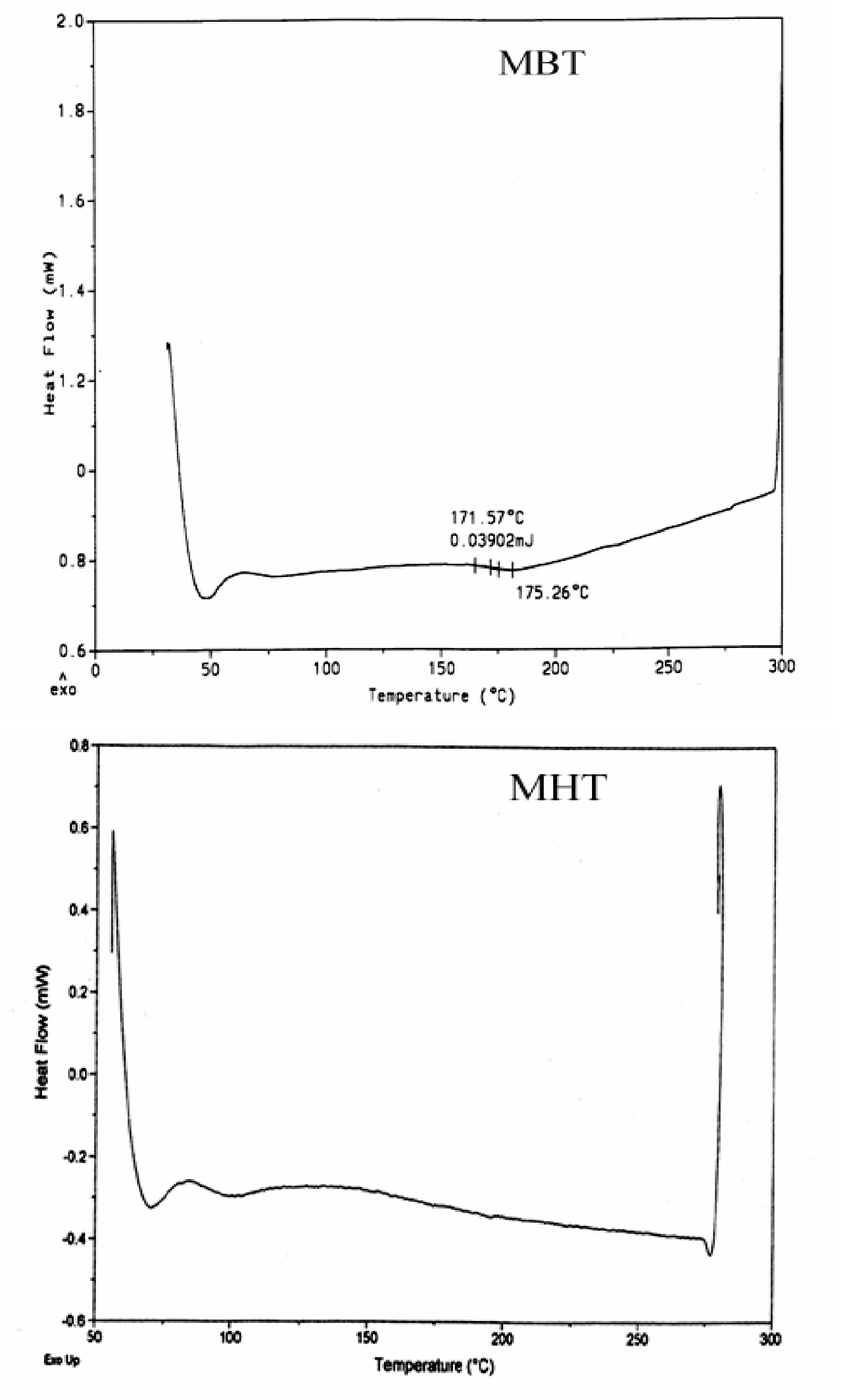
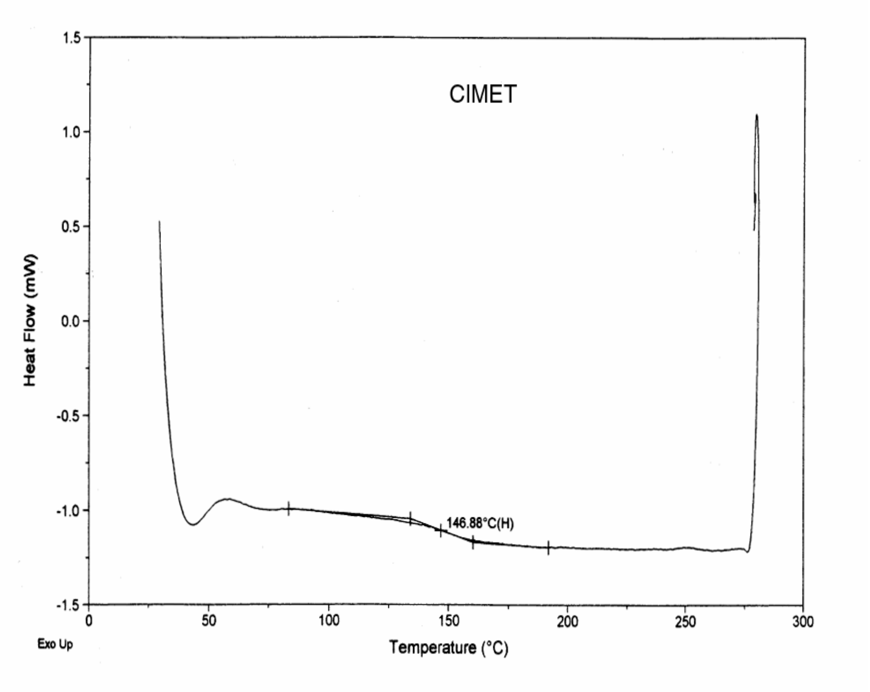


Fig.- 4.2: DSC thermograms of MBT and MHT



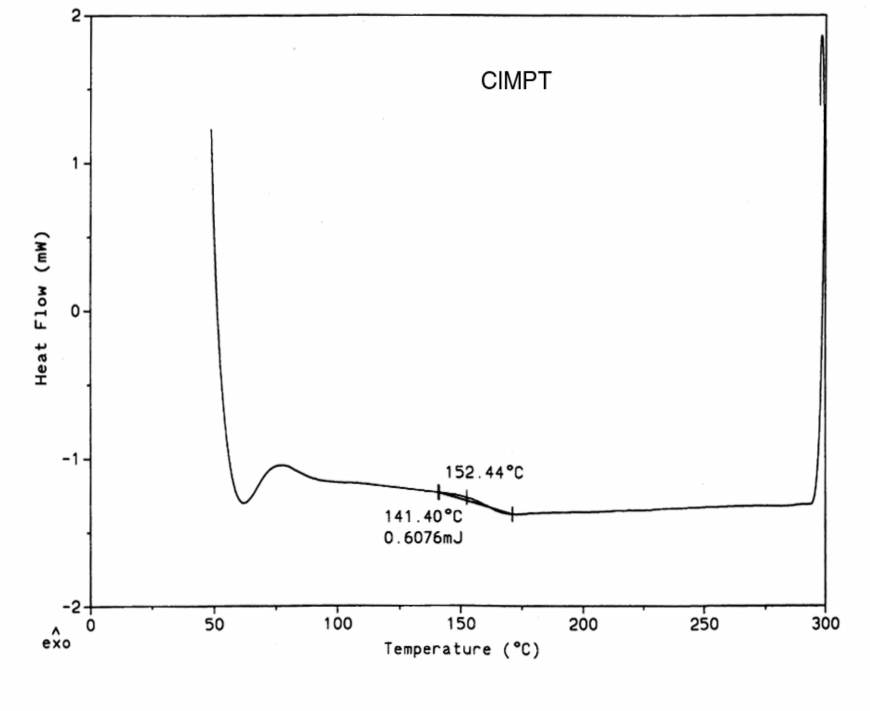


Fig.- 4.3: DSC thermograms of ClMET and ClMPT

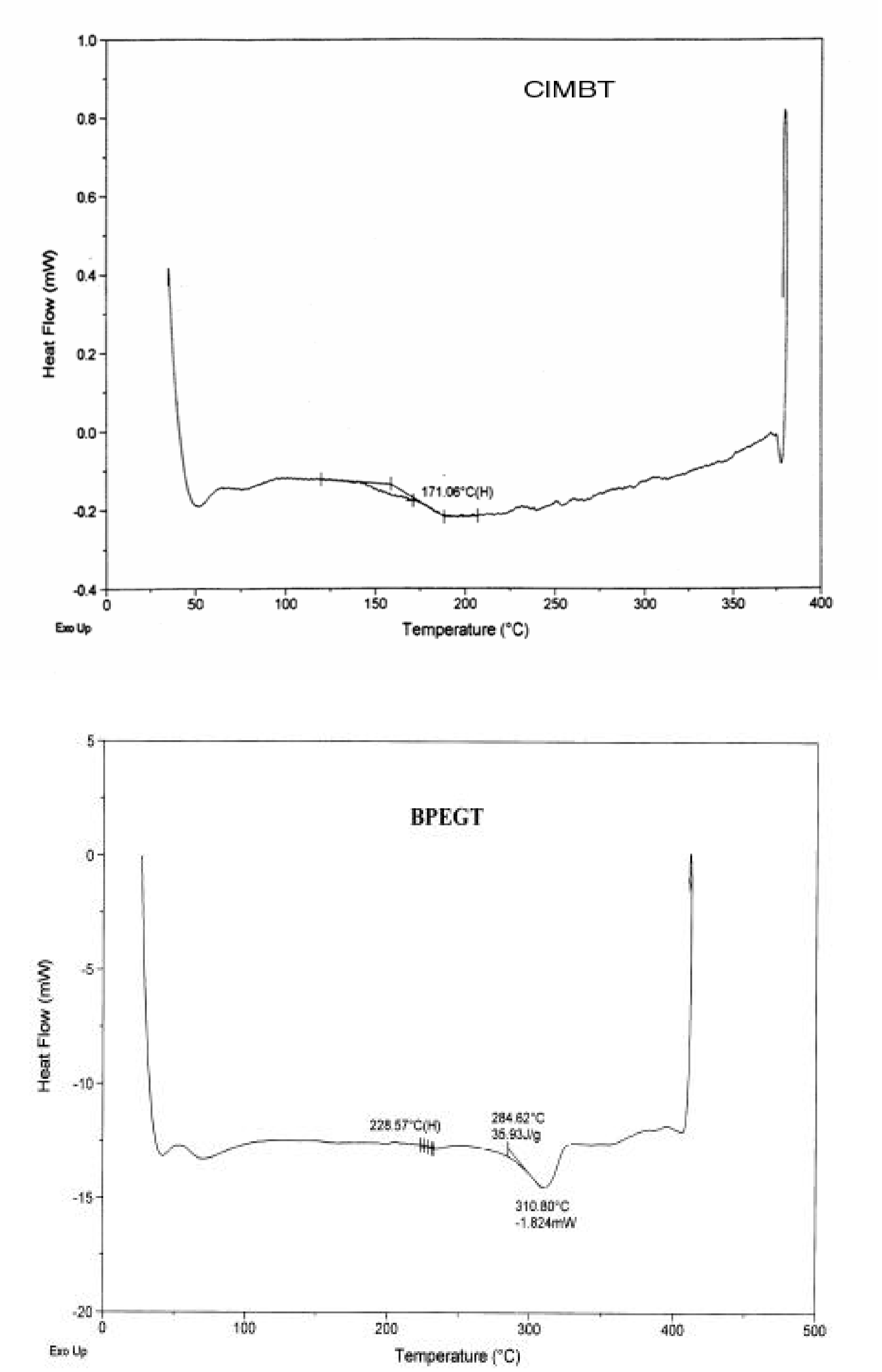
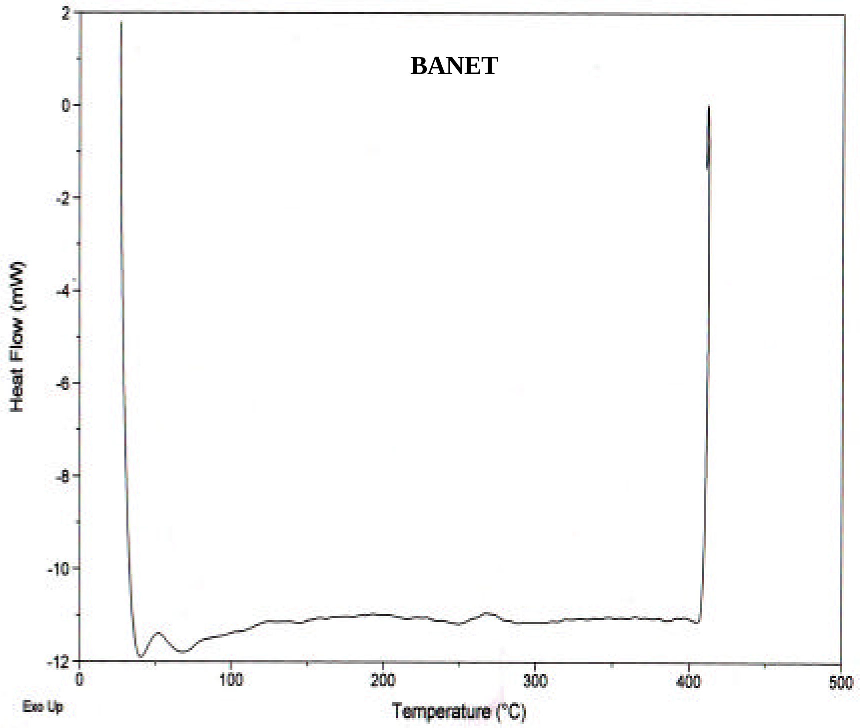


Fig.- 4.4: DSC thermograms of ClMBT and BPEGT



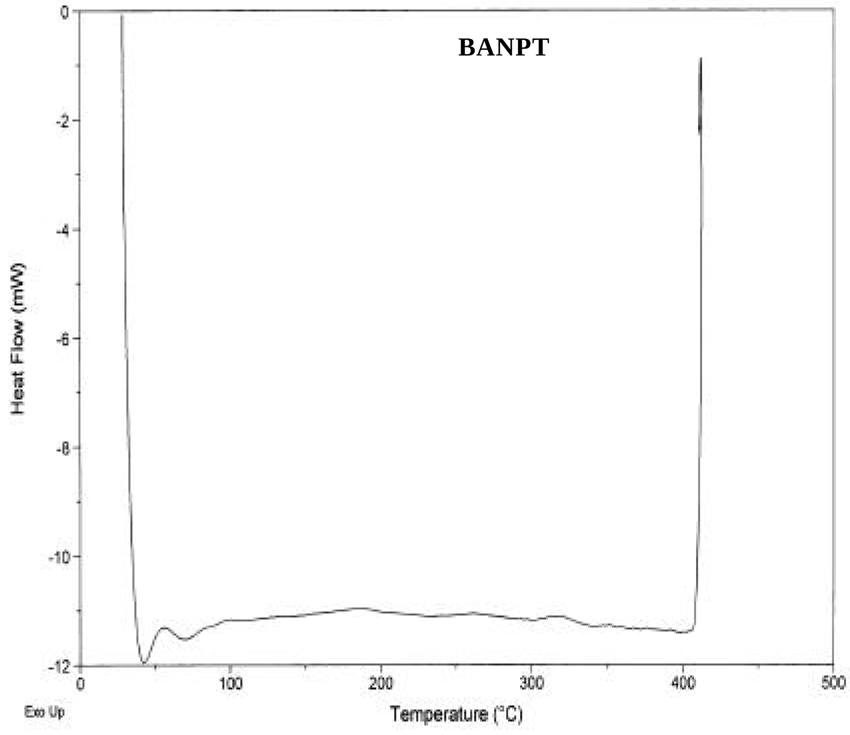


Fig.- 4.5: DSC thermograms of BANET and BANPT

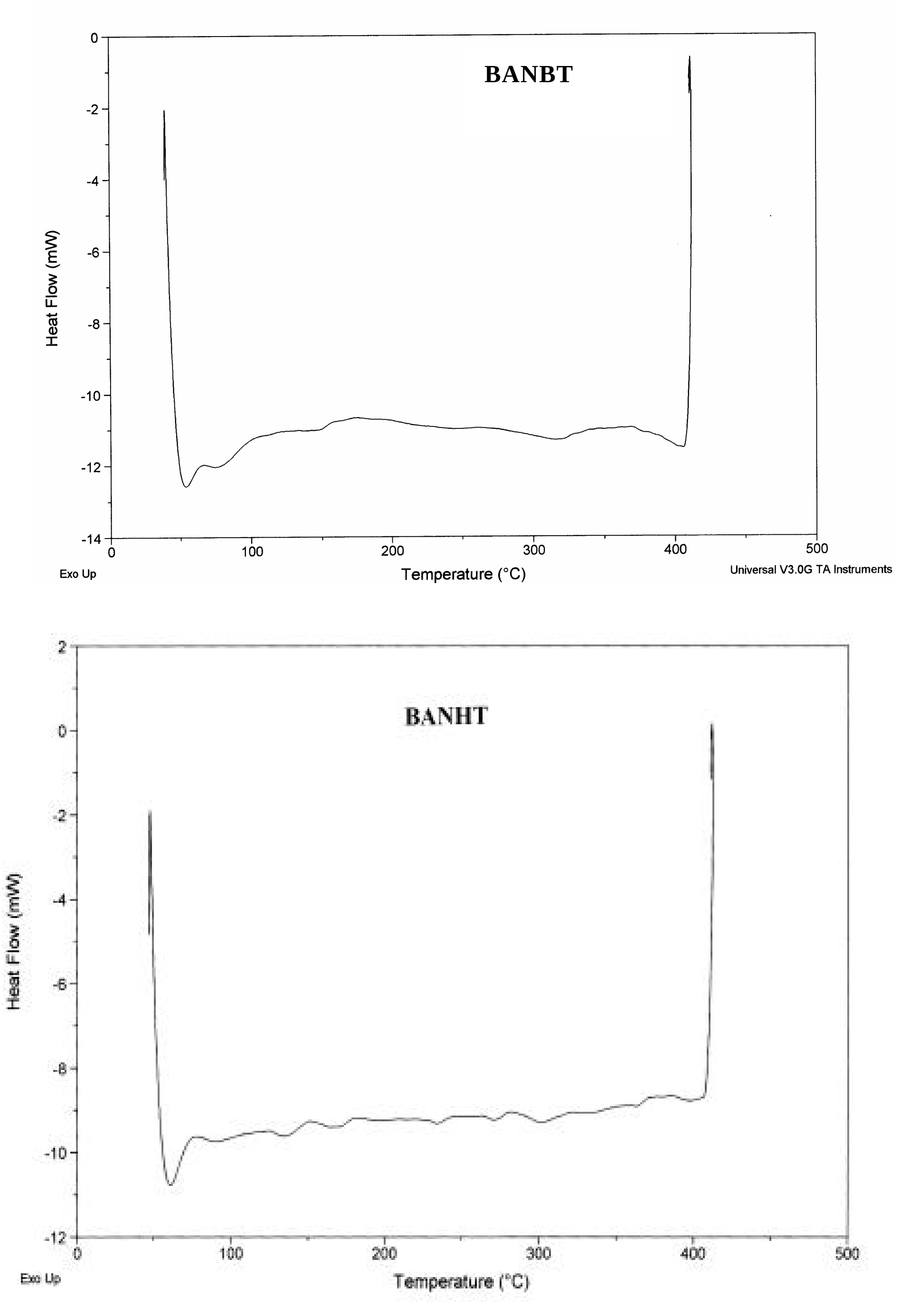


Fig.- 4.6: DSC thermograms of BANBT and BANHT

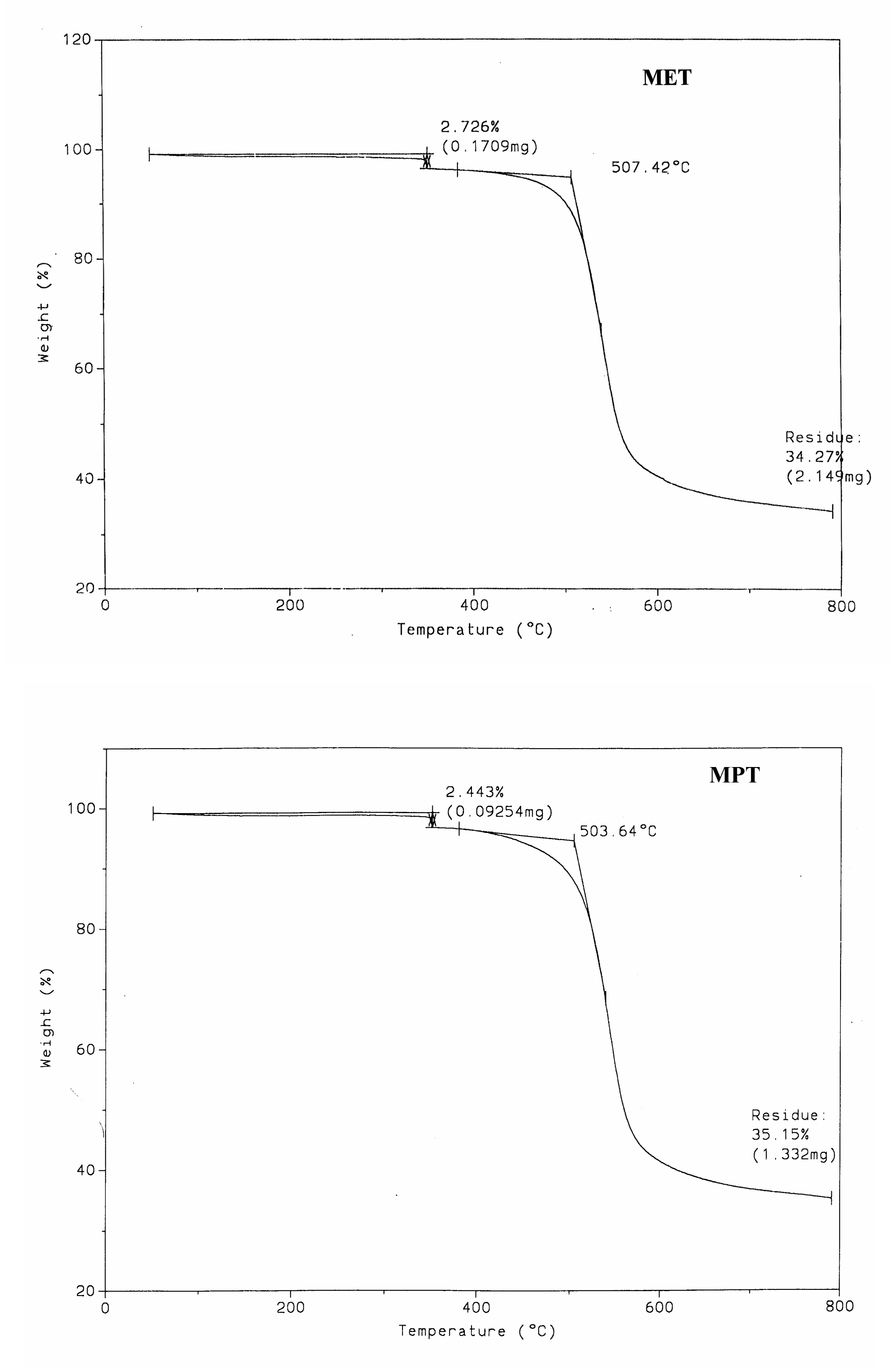


Fig.- 4.7: TGA thermograms of MET and MPT

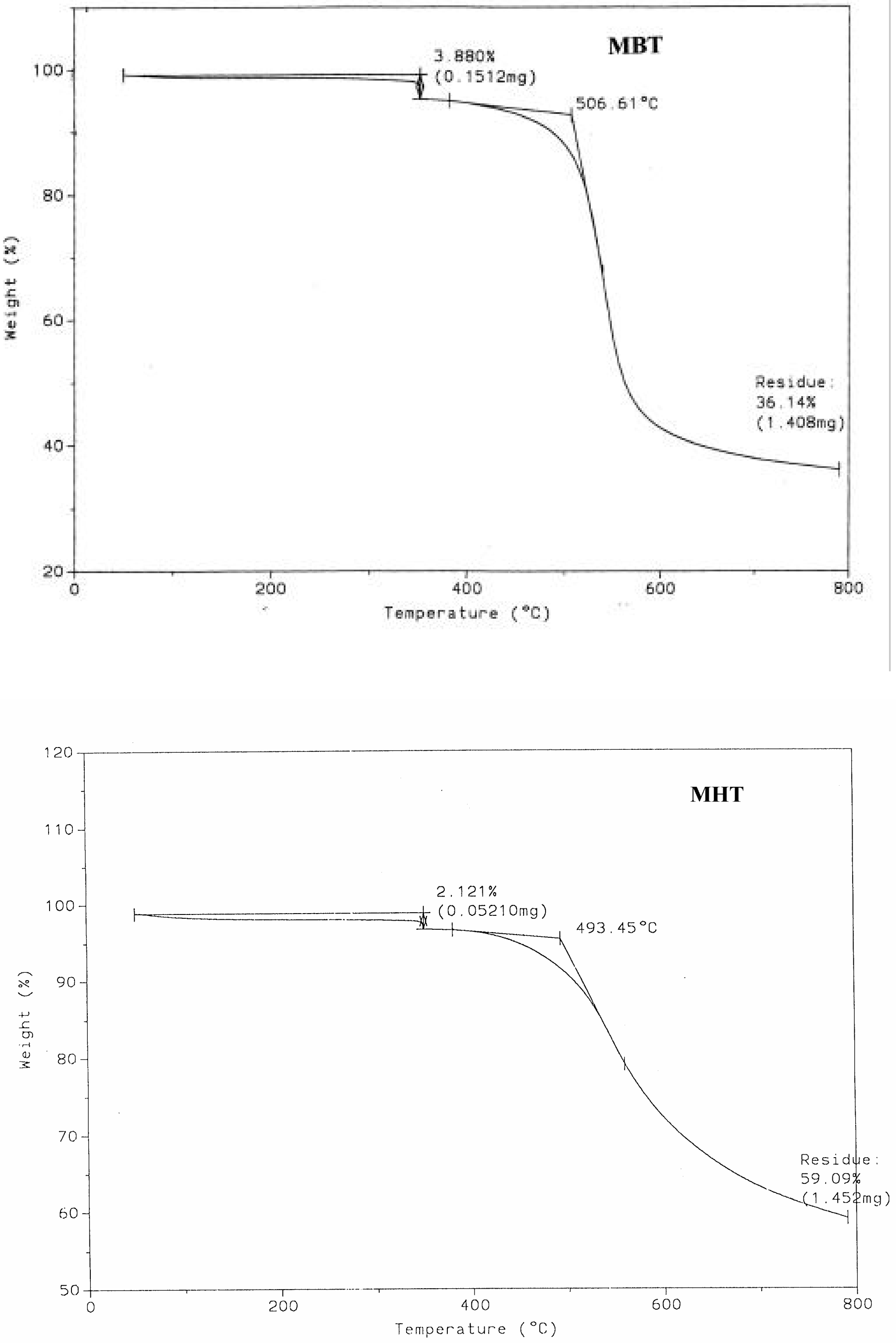
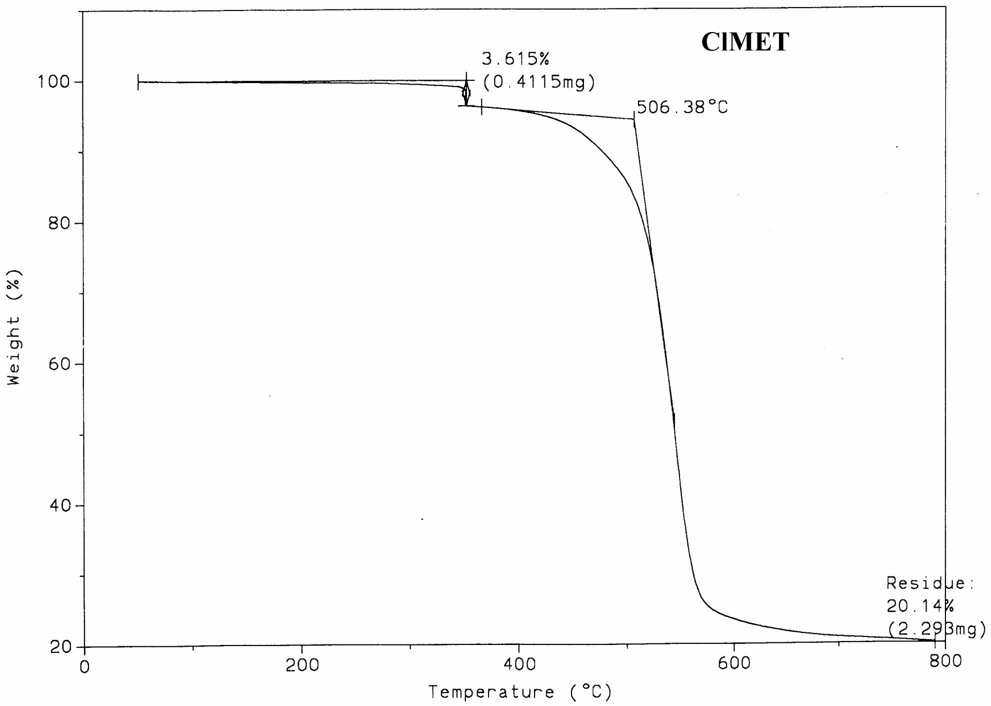


Fig.- 4.8: TGA thermograms of MBT and MHT



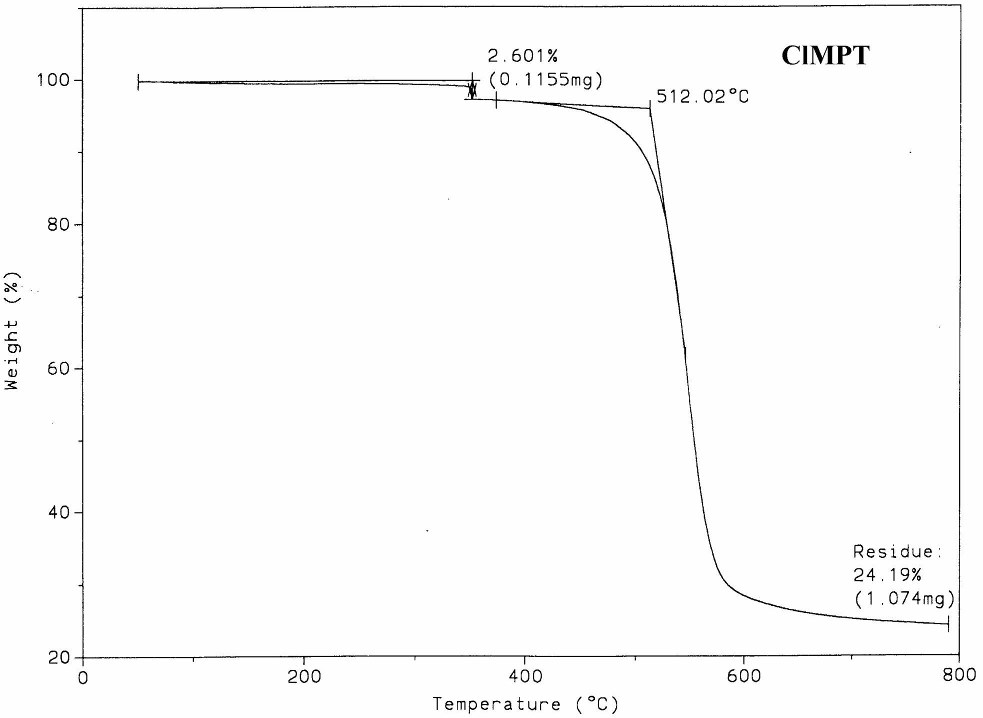


Fig.- 4.9: TGA thermograms of ClMET and ClMPT

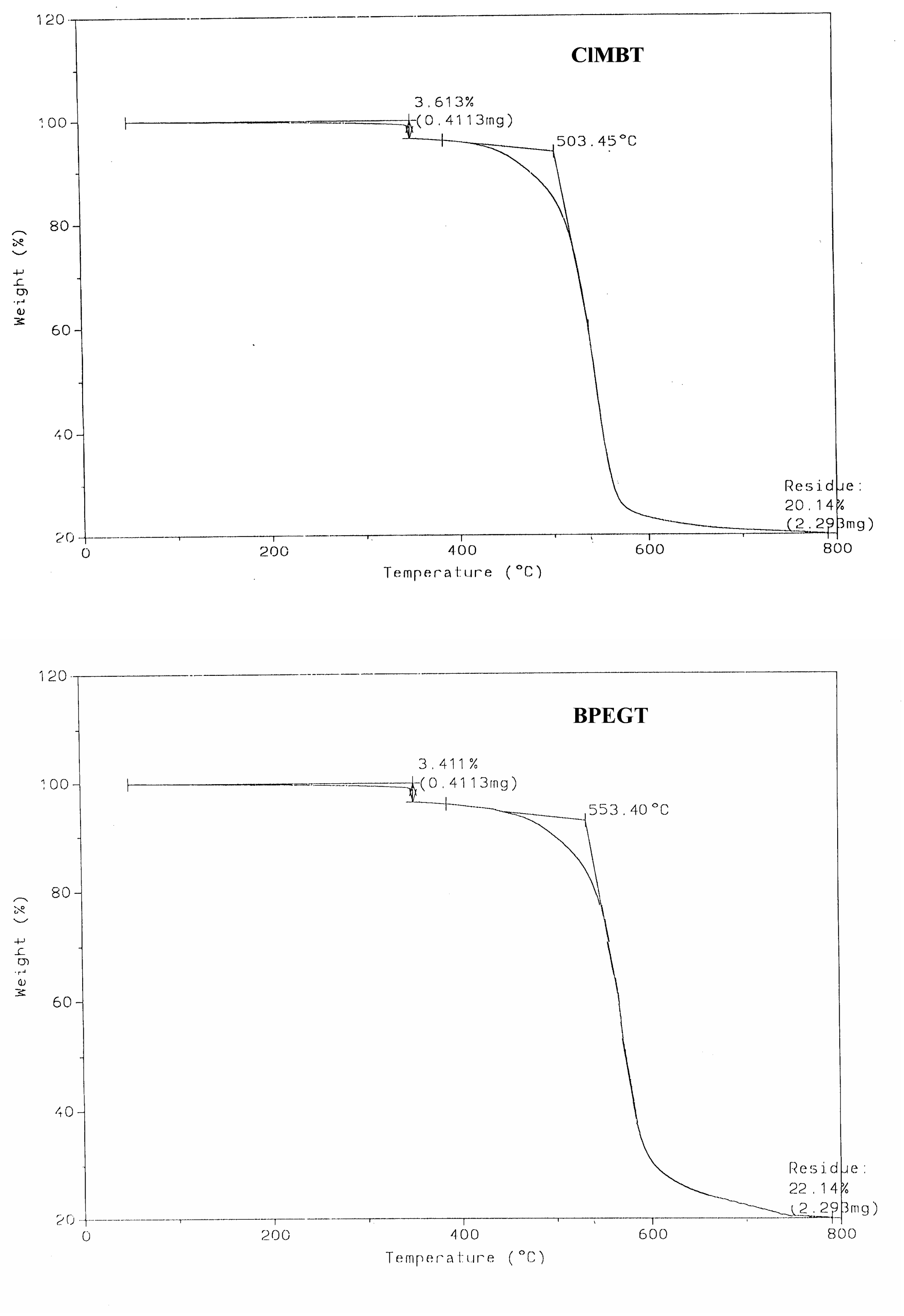
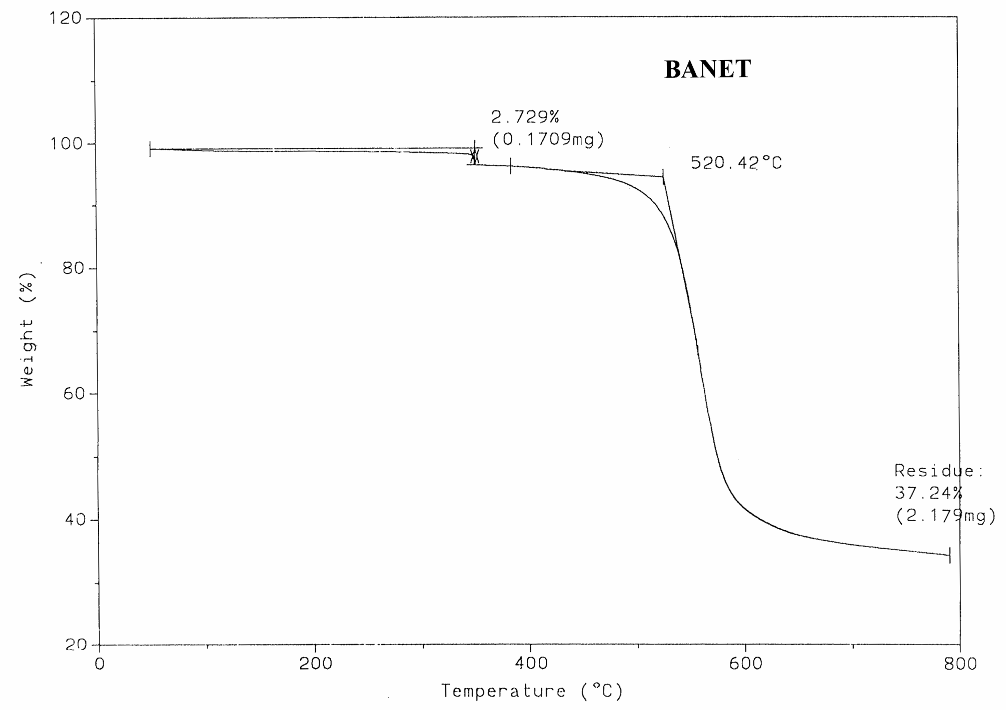


Fig.- 4.10: TGA thermograms of ClMBT and BPEGT



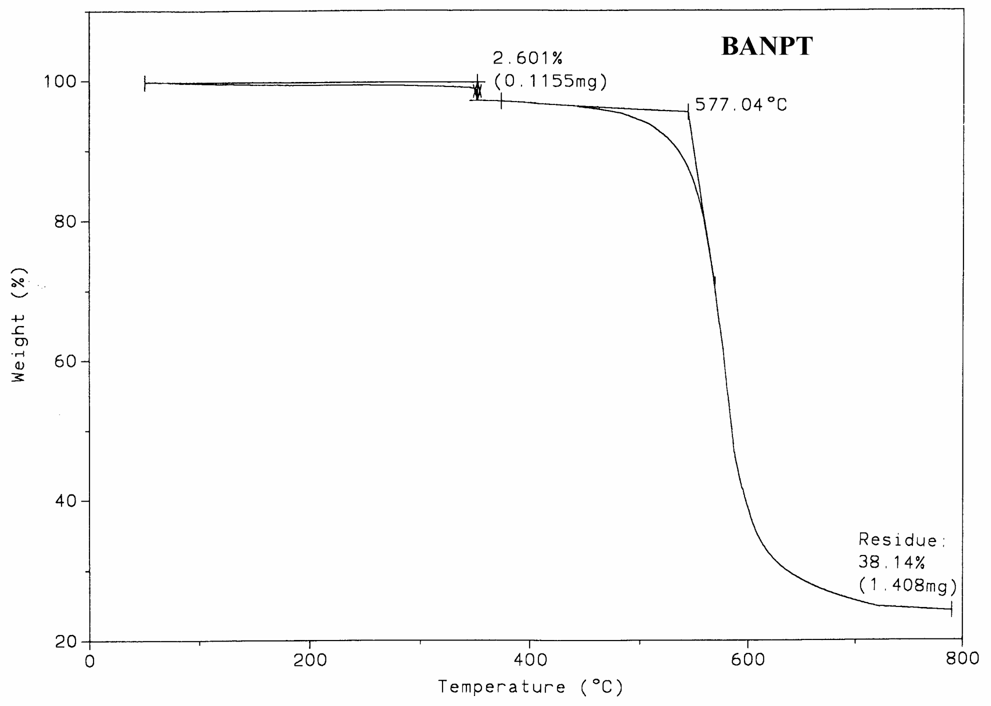
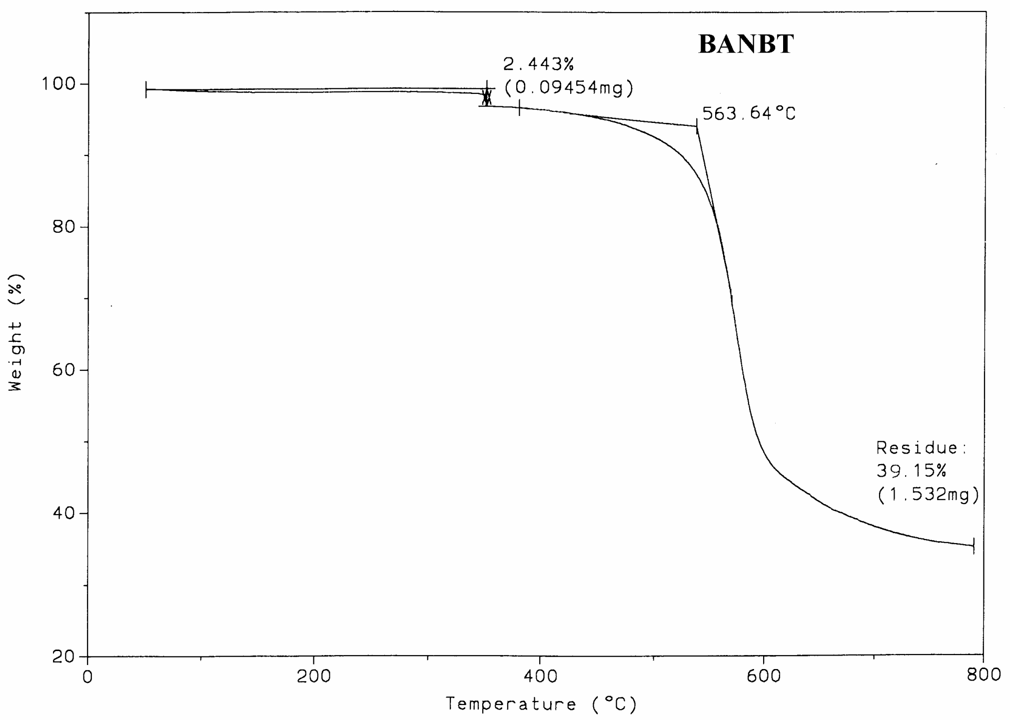


Fig.- 4.11: TGA thermograms of BANET and BANPT



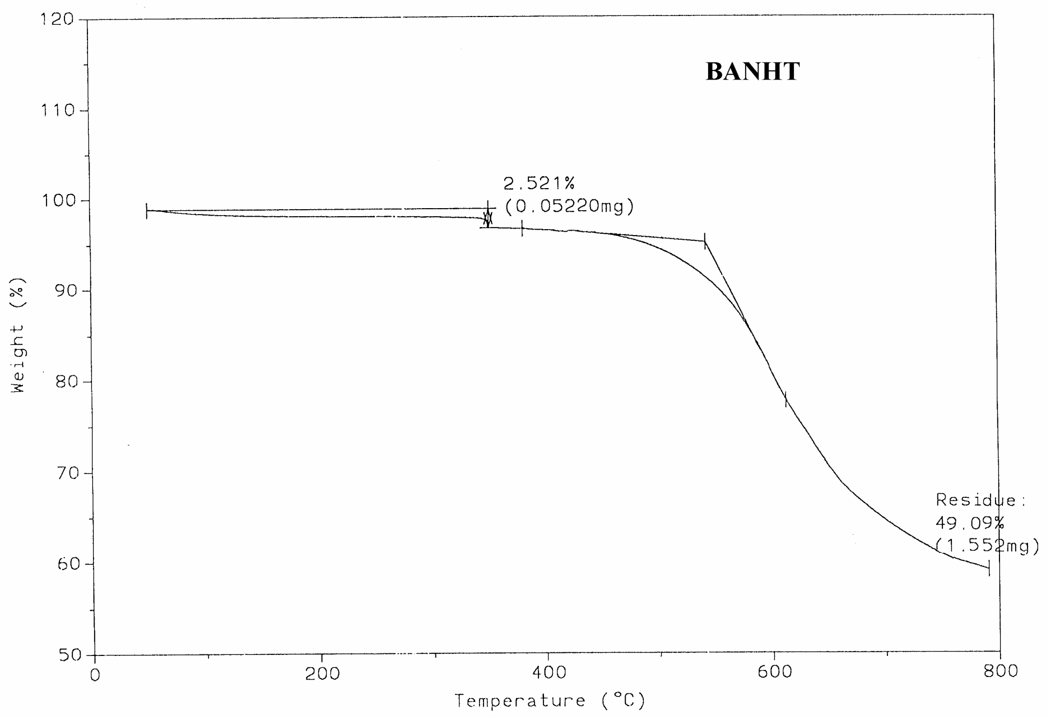


Fig.- 4.12: TGA thermograms of BANBT and BANHT

Table-4.1: DSC and TG data of cardo copolyesters

Co-polyester	$T_{g,}$ ^{o}C	T_0 ^{o}C	T_{10} ^{o}C	T_f ^{o}C	T_{max}, ^{o}C	Decompn range ^{o}C	% Wt. loss	% Residue
MET	147.9	441.5	503.2	656.6	543.8	442-657	57.5	34.3
MPT	151.9	407.9	492.1	669.2	542.5	408-669	58.4	35.2
MBT	171.6	426.9	426.9	653.8	536.3	427-654	54.2	36.1
MHT	194.7	407.5	407.5	747.2	540.5	408-747	37.7	59.1
ClMET	147.9	410.8	479	652	532.7	411-652	74.7	20.1
ClMPT	157.9	425.7	501	648	535.9	426-648	70.4	24.2
ClMBT	171.6	462.1	463	648	534.0	462-648	73.5	20.1
BANET	-	455.9	592.1	660	539.8	456-660	54.8	37.2
BANPT	-	456.2	540.1	696	577.2	456-696	71.0	38.2
BANBT	-	425.3	536.5	787.2	578.6	425-787	60.0	39.15
BANHT	-	460.7	-	769.2	606.4	461-769	35.5	49.09
BPEGT	-	430.9	492.5	705.6	561.6	431-706	75.2	22.14

Table-4.2: The calculation scheme for cardo copolyesters by Freeman-Anderson method

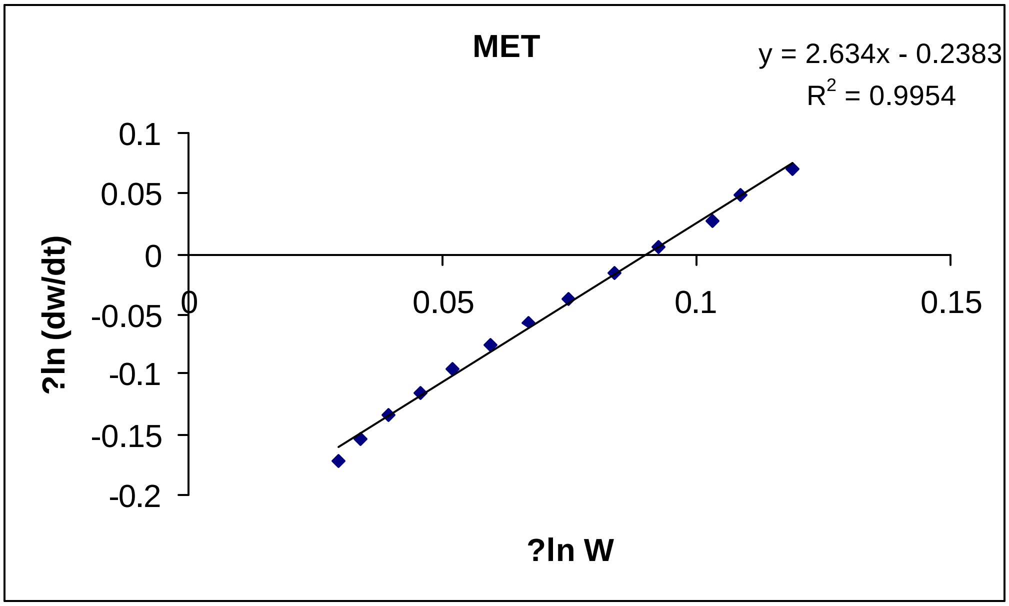
1/T,10^3	% wt. loss	dw/dt	Active Wt.	lnW	ln (dw/dt)	?lnW	?lndw/dt
MET							
1.270	14.18	7.54	48.83	3.888	2.020	0.029	-0.172
1.265	15.59	8.96	47.42	3.850	2.198	0.033	-0.153
1.260	17.17	10.45	45.84	3.825	2.346	0.039	-0.134
1.255	18.93	11.95	44.08	3.786	2.480	0.045	-0.116
1.250	20.89	13.42	42.12	3.740	2.596	0.051	-0.095
1.245	23.02	14.77	39.99	3.688	2.692	0.059	-0.076
1.240	25.32	15.95	37.69	3.629	2.769	0.066	-0.056
1.235	27.76	16.87	35.25	3.562	2.825	0.075	-0.036
1.230	30.31	17.49	32.7	3.487	2.861	0.083	-0.015
1.225	32.94	17.76	30.07	3.403	2.876	0.092	0.005
1.220	35.6	17.66	27.41	3.310	2.871	0.103	0.026
1.215	38.29	17.18	24.72	3.207	2.843	0.108	0.048
1.210	40.84	16.36	22.17	3.098	2.794	0.119	0.070
MPT							
1.245	25.85	14.51	36.61	3.600	2.674	0.063	-0.100
1.240	28.09	16.04	34.37	3.537	2.775	0.071	-0.080
1.235	30.46	17.39	32.00	3.465	2.855	0.083	-0.052
1.230	32.96	18.32	29.50	3.384	2.908	0.093	-0.014
1.225	35.56	18.58	26.90	3.292	2.922	0.104	0.028
1.220	38.23	18.05	24.23	3.187	2.893	0.118	0.074
1.215	40.93	16.76	21.53	3.069	2.819	0.133	0.115
1.210	43.62	14.94	18.84	2.936	2.704	0.149	0.147
1.205	46.23	12.89	16.23	2.786	2.556	0.165	0.170
MBT							
1.275	16.14	7.07	44.20	3.788	1.955	0.028	-0.138
1.270	17.39	8.12	42.95	3.760	2.094	0.032	-0.142
1.265	18.77	9.34	41.57	3.727	2.234	0.037	-0.137
1.260	20.29	10.72	40.05	3.690	2.372	0.042	-0.131
1.255	21.96	12.23	38.38	3.647	2.503	0.048	-0.120
1.250	23.78	13.80	36.56	3.599	2.624	0.055	-0.102
1.245	25.74	15.29	34.60	3.543	2.727	0.062	-0.076
1.240	27.85	16.50	32.49	3.480	2.803	0.072	-0.042
1.235	30.11	17.22	30.23	3.408	2.846	0.081	-0.005
1.230	32.47	17.31	27.87	3.327	2.851	0.093	0.032

$1/T,10^3$	% wt. loss	dw/dt	Active Wt.	lnW	ln (dw/dt)	?lnW	?lndw/dt
MHT							
1.245	15.44	4.11	26.35	3.271	1.413	0.025	-0.007
1.240	16.10	4.14	25.69	3.246	1.420	0.026	-0.004
1.235	16.76	4.16	25.03	3.220	1.425	0.028	-0.002
1.230	17.45	4.17	24.34	3.192	1.427	0.028	0.000
1.225	18.14	4.17	23.65	3.163	1.427	0.030	0.004
1.220	18.84	4.15	22.95	3.133	1.423	0.031	0.007
1.215	19.54	4.12	22.25	3.102	1.415	0.032	0.009
1.210	20.25	4.08	21.54	3.069	1.406	-0.004	0.014
1.205	20.16	4.02	21.63	3.074	1.391	0.072	0.017
1.200	21.67	3.95	20.12	3.001	1.373	0.035	0.020
ClMET							
1.245	35.28	27.18	43.05	3.762	3.302	0.088	-0.024
1.240	38.91	27.86	39.42	3.674	3.327	0.103	0.006
1.235	42.78	27.69	35.55	3.570	3.321	0.121	0.033
1.230	46.83	26.79	31.50	3.450	3.288	0.140	0.058
1.225	50.97	25.28	27.36	3.309	3.230	0.164	0.083
1.220	55.11	23.26	23.22	3.145	3.146	0.189	0.108
1.215	59.12	20.86	19.21	2.955	3.037	0.216	0.137
1.210	62.86	18.19	15.47	2.738	2.900	0.244	0.168
1.205	66.22	15.37	12.11	2.494	2.732	0.269	0.205
ClMPT							
1.260	19.31	18.84	54.81	4.004	2.936	0.040	-0.151
1.255	21.50	21.93	52.62	3.963	3.087	0.047	-0.104
1.250	23.94	24.34	50.18	3.916	3.192	0.055	-0.067
1.245	26.64	26.03	47.48	3.860	3.259	0.064	-0.036
1.240	29.61	26.99	44.51	3.796	3.295	0.075	-0.008
1.235	32.84	27.23	41.28	3.720	3.304	0.088	0.017
1.230	36.32	26.76	37.80	3.632	3.286	0.076	0.043
1.225	39.10	25.62	35.02	3.556	3.243	0.145	0.070
1.220	43.84	23.88	30.28	3.411	3.173	0.138	0.099
1.215	47.76	21.62	26.36	3.272	3.073	0.161	0.131
1.210	51.69	18.95	22.43	3.110	2.941	0.186	0.169
1.205	55.51	15.99	18.61	2.924	2.772	0.215	0.217
1.200	59.11	12.87	15.01	2.709	2.554	0.245	0.276
1.195	62.38	9.76	11.74	2.463	2.278	0.277	0.355

1/T,10^{3}	% wt. loss	dw/dt	Active Wt.	lnW	ln (dw/dt)	?lnW	?lndw/dt
ClMBT							
1.270	27.41	16.19	51.30	3.938	2.784	0.049	-0.120
1.265	29.88	18.25	48.83	3.888	2.904	0.057	-0.098
1.260	32.58	20.12	46.13	3.832	3.002	0.065	-0.076
1.255	35.49	21.71	43.22	3.766	3.078	0.075	-0.055
1.250	38.62	22.94	40.09	3.691	3.133	0.086	-0.035
1.245	41.94	23.75	36.77	3.605	3.168	0.099	-0.013
1.240	45.42	24.07	33.29	3.505	3.181	0.114	0.008
1.235	49.01	23.88	29.70	3.391	3.173	0.131	0.031
1.230	52.66	23.15	26.05	3.260	3.142	0.151	0.056
1.225	56.31	21.90	22.40	3.109	3.087	0.173	0.082
1.220	59.86	20.16	18.85	2.937	3.004	0.196	0.113
1.215	63.22	17.99	15.49	2.740	2.890	0.225	0.149
1.210	66.34	15.50	12.37	2.515	2.741	0.253	0.191
BANET							
1.230	21.39	13.65	37.08	3.613	2.614	0.066	-0.102
1.225	23.74	15.12	34.73	3.548	2.716	0.076	-0.093
1.220	26.28	16.59	32.19	3.472	2.809	0.088	-0.079
1.215	28.98	17.95	29.49	3.384	2.888	0.100	-0.057
1.210	31.80	19.00	26.67	3.284	2.945	0.114	-0.029
1.205	34.69	19.55	23.79	3.169	2.973	0.130	0.006
1.200	37.59	19.43	20.89	3.039	2.967	0.147	0.044
1.195	40.45	18.61	18.02	2.892	2.924	0.167	0.080
1.190	43.23	17.17	15.25	2.725	2.843	0.190	0.113
1.185	45.86	15.33	12.61	2.535	2.730	0.217	0.140
BANPT							
1.205	17.69	9.48	53.31	3.976	2.250	0.042	-0.258
1.200	19.88	12.28	51.12	3.934	2.508	0.050	-0.259
1.195	22.35	15.90	48.65	3.885	2.766	0.059	-0.243
1.190	25.13	20.28	45.87	3.826	3.009	0.070	-0.201
1.185	28.21	24.80	42.79	3.756	3.211	0.083	-0.126
1.180	31.61	28.12	39.39	3.674	3.337	0.098	-0.025
1.175	35.29	28.83	35.71	3.575	3.361	0.117	0.076
1.170	39.22	26.72	31.78	3.459	3.285	0.139	0.151
1.165	43.35	22.99	27.65	3.320	3.135	0.166	0.192
1.160	47.57	18.98	23.43	3.154	2.943	0.198	0.206

1/T,10^3	% wt. loss	dw/dt	Active Wt.	lnW	ln (dw/dt)	?lnW	?lndw/dt
BANBT							
1.190	23.18	13.90	35.77	3.577	2.632	0.056	-0.099
1.180	25.55	16.44	33.40	3.509	2.800	0.075	-0.032
1.175	28.04	16.97	30.91	3.431	2.832	0.084	0.009
1.170	30.61	16.82	28.34	3.344	2.823	0.093	0.049
1.165	33.23	16.02	25.72	3.247	2.774	0.103	0.083
1.160	35.85	14.75	23.10	3.140	2.691	0.112	0.109
BANHT							
1.205	10.18	2.64	25.28	3.230	0.971	0.019	-0.066
1.200	10.66	2.82	24.80	3.211	1.037	0.021	-0.065
1.195	11.17	3.01	24.29	3.190	1.102	0.023	-0.061
1.190	11.72	3.20	23.74	3.167	1.163	0.024	-0.058
1.185	12.29	3.39	23.17	3.143	1.221	0.027	-0.057
1.180	12.90	3.59	22.56	3.116	1.278	0.028	-0.052
1.175	13.53	3.78	21.93	3.088	1.330	0.031	-0.047
1.170	14.19	3.96	21.27	3.057	1.376	0.033	-0.042
1.165	14.89	4.13	20.57	3.024	1.418	0.036	-0.036
1.160	15.61	4.28	19.85	2.988	1.454	0.039	-0.028
1.155	16.36	4.40	19.10	2.950	1.482	0.042	-0.022
1.150	17.14	4.50	18.32	2.908	1.504	0.044	-0.015
1.145	17.93	4.57	17.53	2.864	1.520	0.048	-0.007
1.140	18.75	4.60	16.71	2.816	1.526	0.051	-0.002
1.135	19.58	4.61	15.88	2.765	1.528	0.054	0.009
1.130	20.42	4.57	15.04	2.711	1.520	0.059	0.011
1.125	21.28	4.52	14.18	2.652	1.509	0.062	0.022
1.120	22.13	4.42	13.33	2.590	1.486	0.067	0.025
1.115	23.00	4.31	12.46	2.523	1.461	0.072	0.031
BPEGT							
1.215	33.86	19.12	40.35	3.698	2.951	0.082	-0.116
1.210	37.02	21.47	37.19	3.616	3.067	0.092	-0.087
1.205	40.29	23.42	33.92	3.524	3.154	0.103	-0.046
1.200	43.61	24.52	30.60	3.421	3.199	0.115	0.005
1.195	46.93	24.40	27.28	3.306	3.195	0.127	0.059
1.190	50.18	23.01	24.0	3.179	3.136	0.140	0.108

			3				
1.185	53.31	20.65	20.90	3.040	3.028	0.153	0.147
1.180	56.27	17.83	17.94	2.887	2.881	0.166	0.173



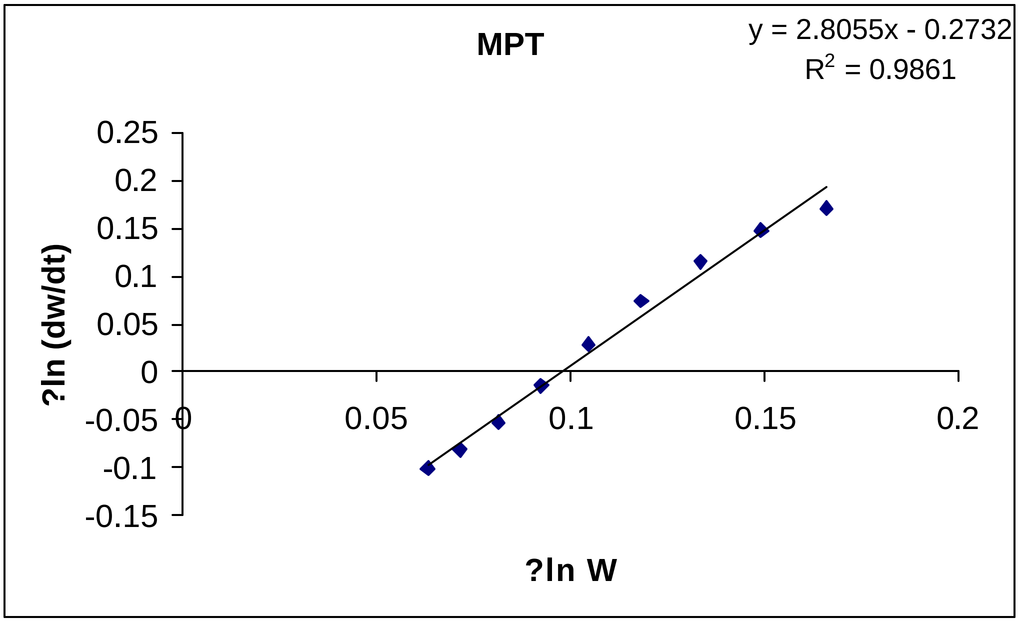
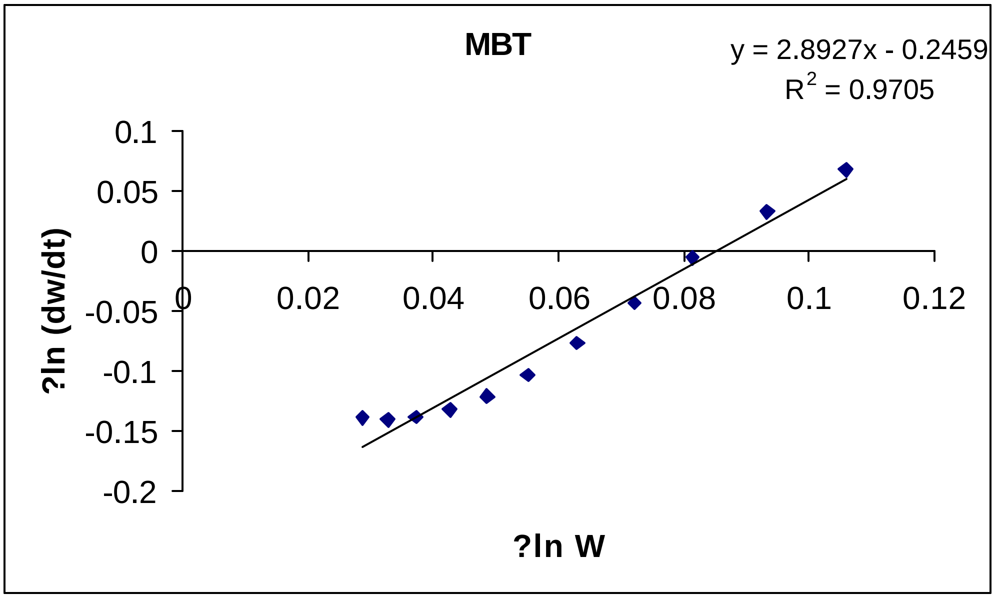


Fig.4.13 The Freeman-Anderson plots of MET and MPT



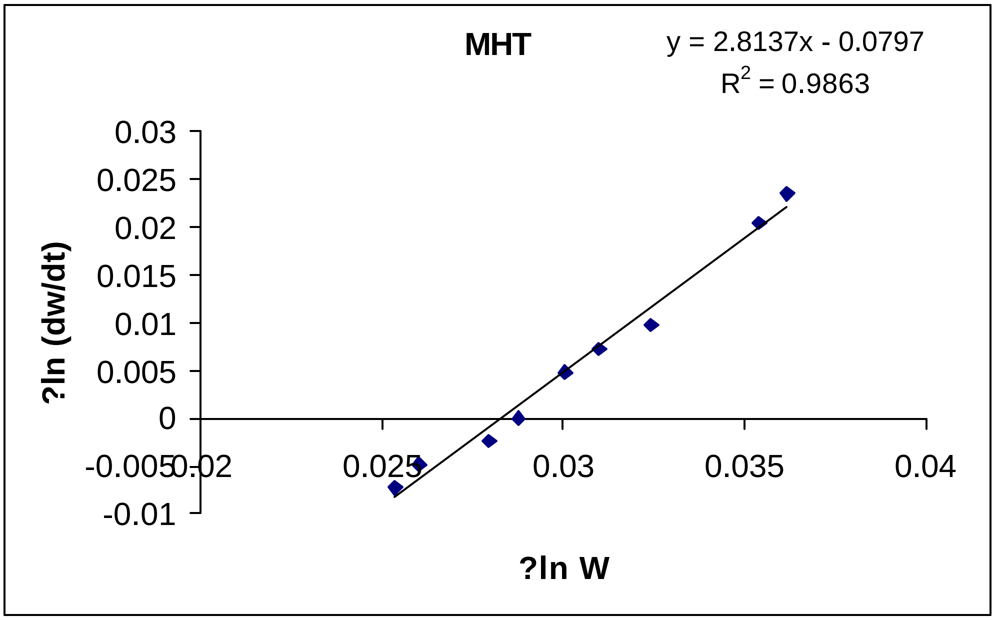
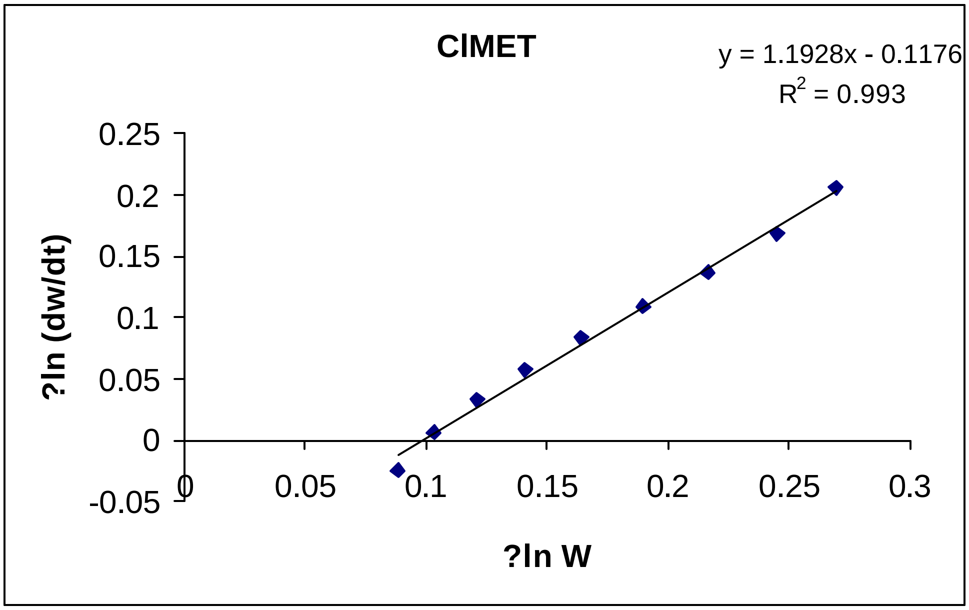


Fig.4.14 The Freeman-Anderson plots of MBT and MHT



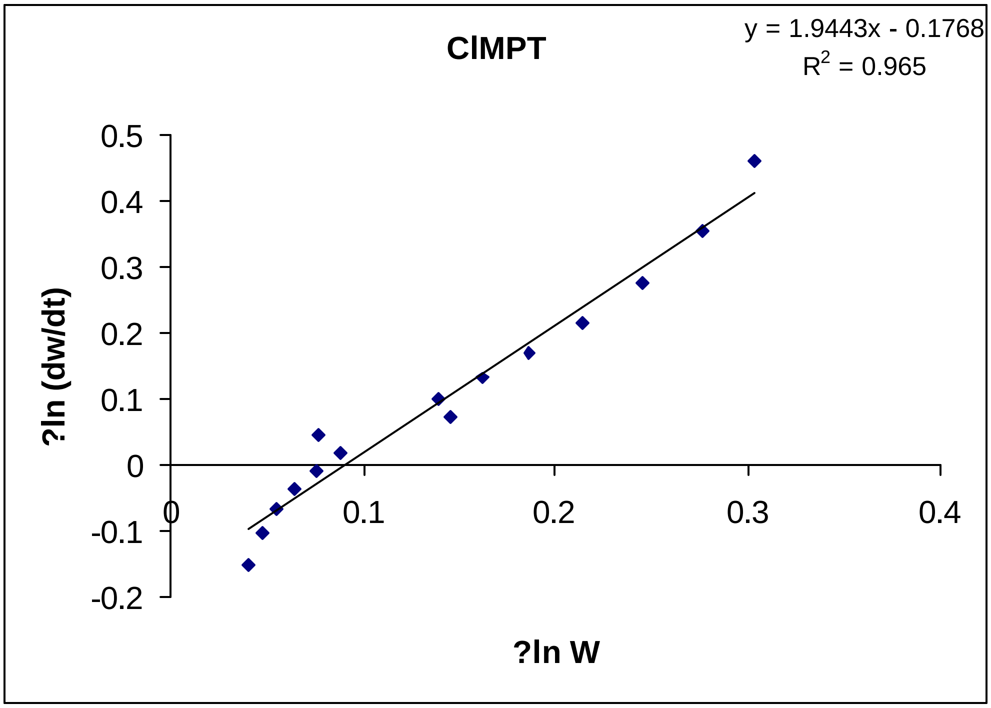
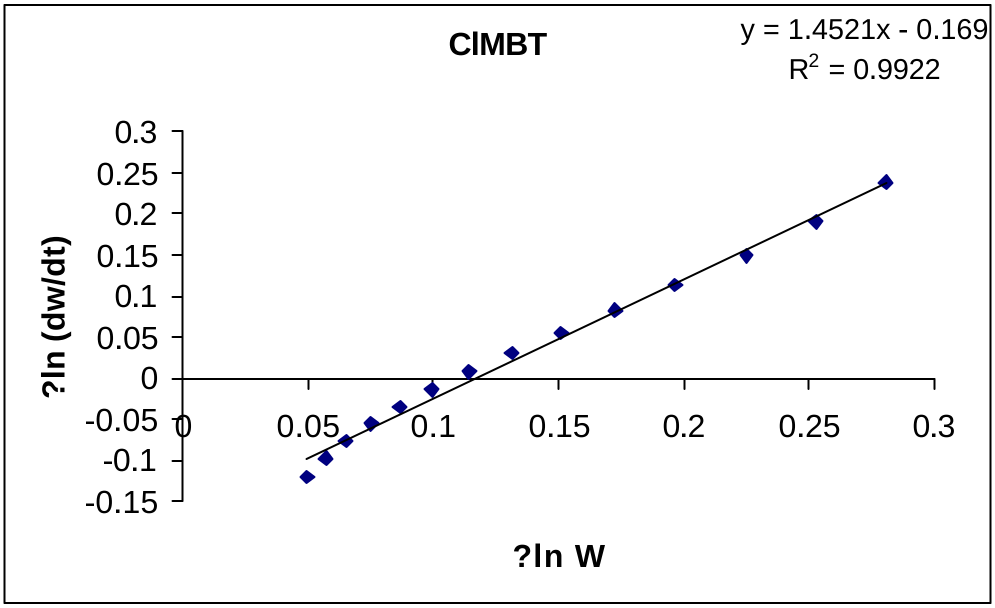


Fig.4.15 The Freeman-Anderson plots of ClMET and ClMPT



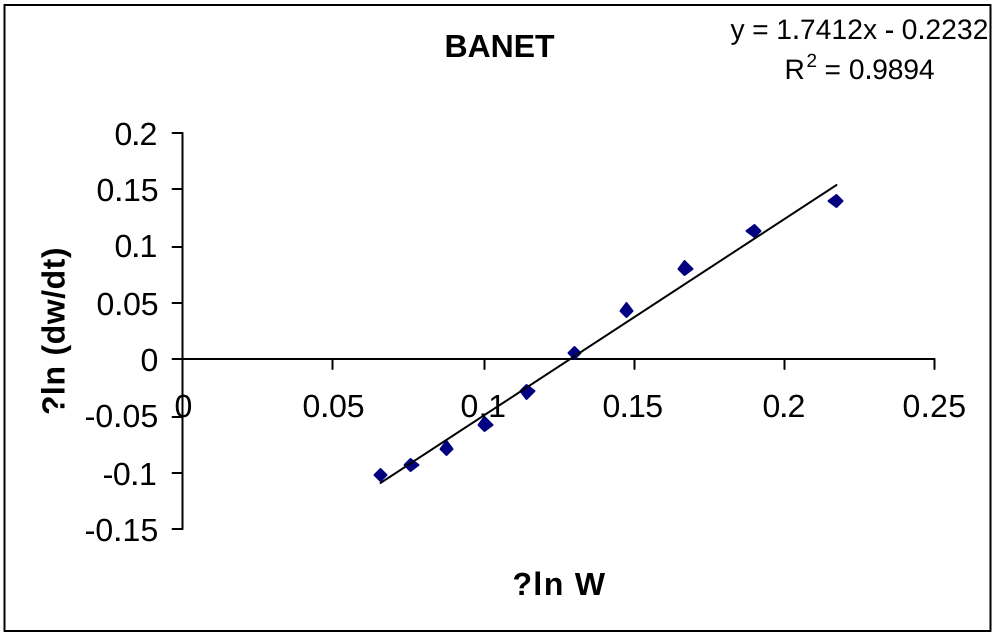
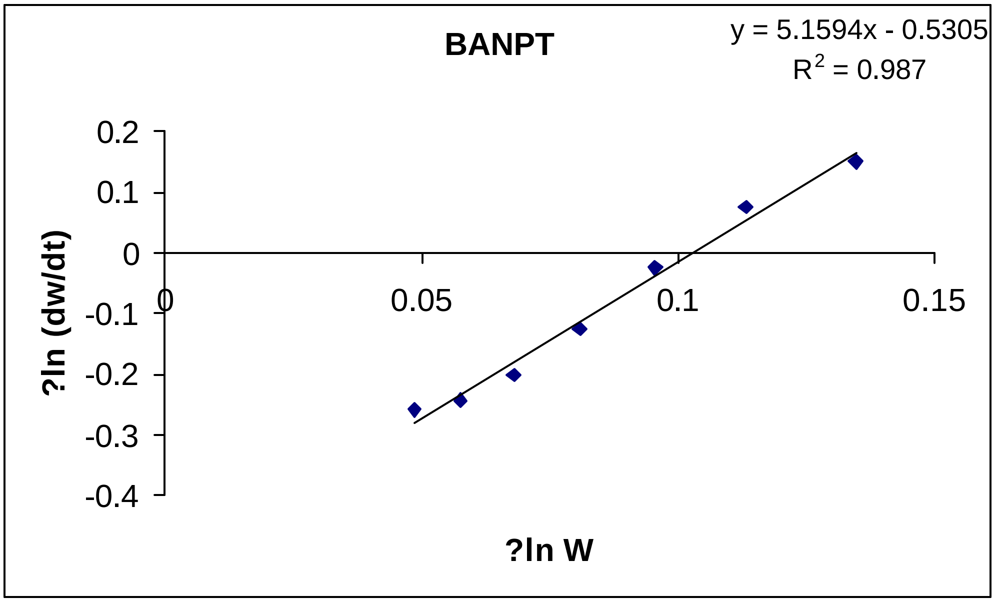


Fig.4.16 The Freeman-Anderson plots of ClMBT and BANET



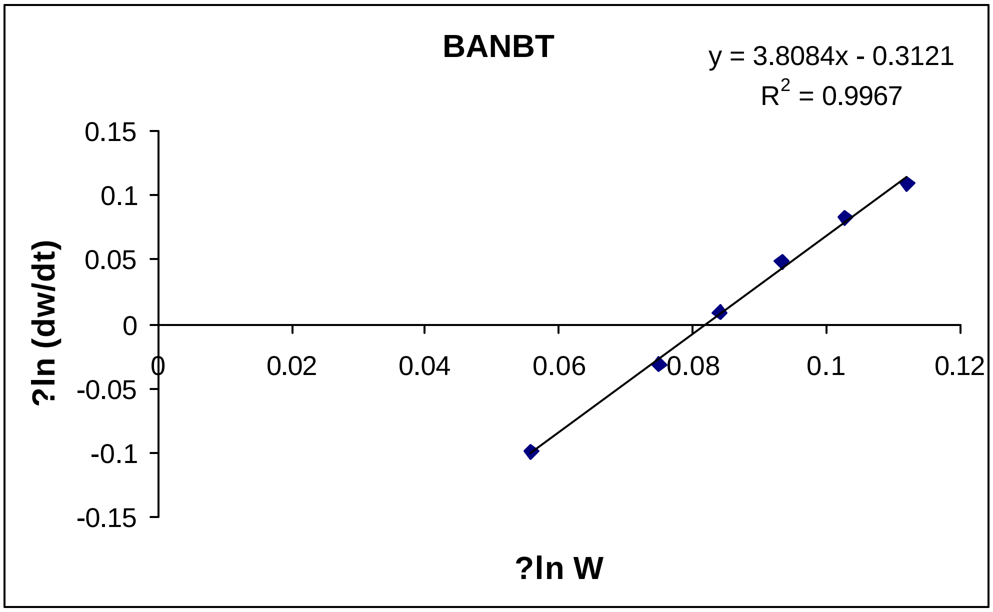
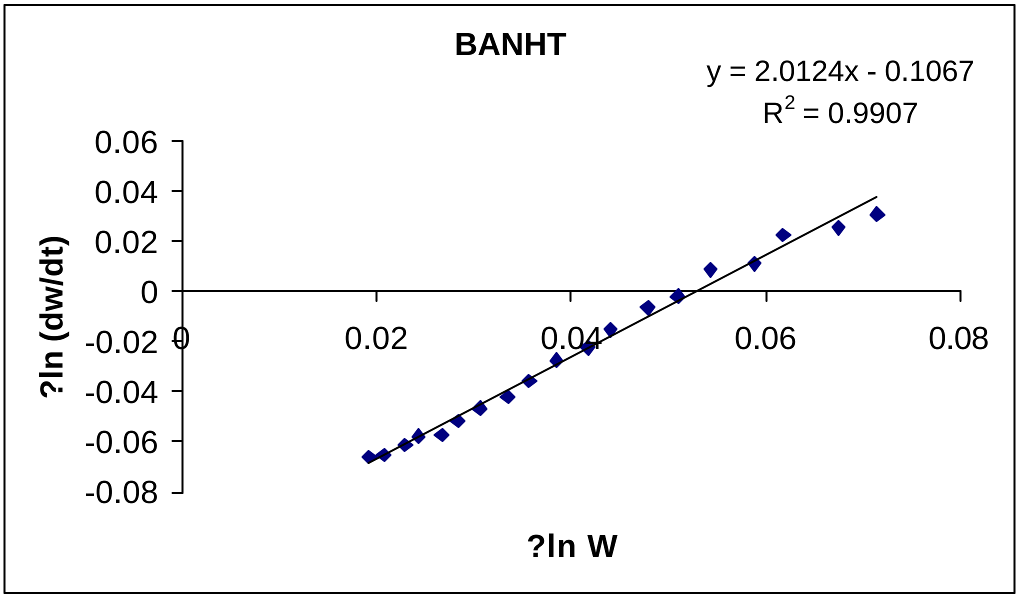


Fig.4.17 The Freeman-Anderson plots of BANPT and BANBT



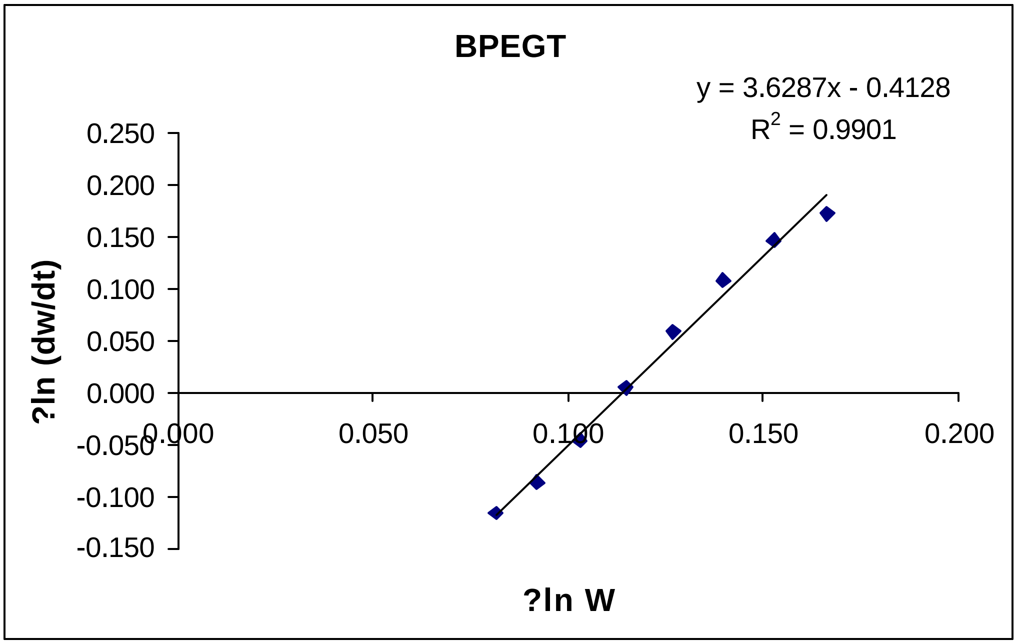


Fig.4.18 The Freeman-Anderson plots of BANHT and BPEGT

Table-4.3: The kinetic parameters of copolyesters derived according to Freeman- Anderson method

Copolyester	n	E_a, kJ	A, S^{-1}	ΔS^*, JK^{-1}	Regression coefficient, γ
MET	2.6	396.3	$5.2X10^{23}$	200.7	0.995
MPT	2.8	454.3	$3.4X10^{27}$	273.8	0.986
MBT	2.9	408.9	$5.1X10^{24}$	219.8	0.971
MHT	2.8	132.5	$2.6X10^{6}$	-130.2	0.986
ClMET	1.2	195.6	$5.7X10^{10}$	-47.2	0.993
ClMPT	2.0	294.0	$1.7X10^{17}$	76.8	0.965
ClMBT	1.5	281.0	$2.7X10^{16}$	61.3	0.992
BANET	1.7	371.2	$1.6X10^{22}$	171.7	0.989
BANPT	5.2	882.2	$7.5X10^{52}$	758.7	0.987
BANBT	3.8	518.9	$1.9X10^{30}$	326.1	0.996
BANHT	2.0	177.4	$3.2X10^{8}$	-91.2	0.991
BPEGT	3.6	686.4	$3.6X10^{41}$	541.9	0.990

A large and positive magnitude of ∆S* indicated less ordered transition state, while negative entropy change supported ordered transition state.

The ester linkages are weak points in the copolyesters and they degrade selectively to form free radicals. These radicals may further undergo recombination or rupture. The degradation is a complex process and involves a variety of reactions namely decomposition, cross-linking, branching, rearrangement, etc. A 20-59 % residual weight above 650ºC indicated formation of cross-linked products. Thermal decomposition of polyesters usually starts with the scission of the polymer chain through a six membered ring transition state. It is believed that this scission is mostly heterolytic and not a free radical process [26]. However this is not yet resolved. Kinetic analysis has shown that the thermal decomposition of polyesters is a complex process with activation energy varying from 100-250 kJ/mole. The observed activation energy (177-882 kJ/mol) for copolyesters containing aliphatic diol up to four carbon chain length is much higher than general range (100-250 kJ/mol) confirming complex degradation process.

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26. S. V. Levchik and E. D. Weil, Polym. Adv. Technol., **15**, 691, 2004.

SECTION-2: MECHANICAL AND ELECTRICAL PROPERTIES OF COPOLYESTERS

INTRODUCTION

For a plastic product designer, the knowledge of thermo-mechanical and electrical properties of polymers is the foremost requirement. In recent years plastics have been increasingly used for mechanical applications principally as gears, bearings, etc. The usage of plastics for mechanical applications offers the advantages such as elimination of parts through design, elimination of finishing operations, simplified assembly, reduced maintenance, obviations of lubrications, weight saving, noise reduction, freedom from corrosion.

Most applications of polymers need load-bearing capacity. The geometrical response to loading lead to a wide range of mechanical properties grouped under stress-strain properties, visco-elasticity and failure properties. These properties are in turn largely determined by the polymer structure (molecular weight, cross-linking, branching, segmental structure and morphology) and the nature and extent of compounding when characterizing the mechanical behavior of a polymeric system, external conditions like temperature, loading rate and environment must be considered [27-30].

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27. A.Krause, A.Lange, M.Ezrin,"Plastics Analysis Guide, Chemical and Instrumental Methods", Harver Pub, New York, 1983
28. T.R.Crompton, "The Analysis of Plastics", Pergamon Press, Oxford, 1984
29. R.P.Brown, "Physical Testing of Rubbers", Applied Science, London, 1979
30. P.Ghosh, "Polymer Science and Technology of Plastics and Rubbers", Tata McGraw Hill Publishing Co. Ltd, New Delhi, 1982.

Mechanical and electrical properties of polymers depend upon temperature, humidity, time, loading conditions, rate of loading, morphology, molecular architecture, molecular weight, fillers, impurities, geometry of electrodes, electrode material, sample thickness, structure and presence of polar groups in the polymer chains, etc [31].

EXPERIMENTAL

Tough and transparent films of copolyesters were cast from concentrated chloroform solutions (~4%) on a leveled glass plate. The rate of evaporation of chloroform was kept slow by covering the glass plate. The films were dried under vacuum at 80^oC until the entrapped solvent molecules have been removed completely as indicated by constant weight. The polymer films were analyzed for their mechanical and electrical properties.

MEASUREMENTS

Tensile strength (IS: 11298-Pt-2-1999), volume resistivity (ASTM-D-257-92) and the electric strength (IEC: 243-Pt.1-1988) measurements were made on a Universal Tensile Testing Machine Model No.1185 at a speed of 50mm/min, a Hewlett Packard high resistance meter at 500V DC after charging for 60 sec in air at 25^0C and a high voltage tester (Automatic Mumbai) in air at 27^o C by using 25/75 mm brass electrodes, respectively.

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31. A. B. Mathur, I. S. Bhardwaj, Testing and Evaluation of Plastics, Allied Publishers Pvt Ltd New Delhi, 2003.

MECHANICAL PROPERTIES

The mechanical behavior of a polymer is divided into three main groups (i) elastic (ii) plastic and (iii) brittle. The same can behave as brittle, tough or rubber-like above or below the glass transition temperature. Slow rates of testing will stimulate stiffer molecules and harder properties. The mechanical tests are classified as impact, tensile, flexural, hardness, etc. on the basis of applied deforming stress.

Among the mechanical properties tensile strength, thermal expansion, thermal conductivity, high temperature resistance and chemical resistance, which determine the suitability of a plastic for a mechanical application. The wear resistance, fatigue resistance and impact resistance are particularly most important in the field of mechanical applications.

The mechanical properties of polymers can be divided into three types:

(1) Reversible mechanical properties
(2) Mechanical failure, and
(3) Complex mechanical properties

Of great importance in mechanical testing is the conditions in which the forces are applied. The loading can be considered basically static as in structure such as a bridge or building or dynamic as in an aeroplane wing or in an oil-well drill rod. The strength of a material subject to dynamic loading is usually much less than its strength under the static loading.

A few mechanical tests have become popular because the results have been correlated well with performance data from a variety of applications. American Society for Testing Material (ASTM) has standardized several testing procedures for more universally accepted mechanical properties.

The tensile behavior of polymer is probably most fundamental mechanical property used in the evaluation of polymers. The tensile strength of a material is the ratio of the stress applied to the material at the rupture to its original cross-sectional area. This property is typically called the ultimate tensile strength i.e. the strength at break.

RESULTS AND DISCUSSION

In the present investigation, the tensile strength of Copolyester films was determined according to Eqn. 4.19:

$$\text{Tensile strength (kg/cm}^2\text{)} = \frac{\text{Load at break (g) x 10}}{\text{Thickness in mm}} \qquad \ldots\mathbf{4.19}$$

Tensile strength data of copolyester films are reported in Table-4.5 along with some useful plastics [30,32]. From Table -4.5 it is clear that copolyesters possess moderate tensile strength indicating moderately molecular weight supported by viscosity data (Table-3.6). Polyethylene terephthalate (PET) is the most useful commercial polyester having 58.6-72.4 MPa tensile strength, 158 kV/mm electric strength and 10^{21} ohm volume resistance. Upon comparing mechanical and electrical properties of copolyesters with PET, it is clear that PET is superior polyester in physical properties than copolyesters under study. From Table -4.5 it is also clear that copolyesters of ethylene glycol (EG) and 1,4-butane diol (BD) have low tensile strength as compared to propylene glycol (PG) mainly due to low molecular weights and different molecular architecture. The comparable tensile strength of copolyesters of ethylene glycol (EG) and 1,4-butane diol (BD) is due to almost same molecular weights as judged on the basis of viscosity data and almost same molecular architecture. Copolyesters posses moderate tensile strength. The tensile strength of BANPT is low compared to MPT due to bulky nature of cardo group.

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32. F.W. Billmeyer, “Text Book of Polymer Science”, 3rd Edn. John Willey and Sons, New York, 1994.

Table-4.4 Tensile strength of copolyester films

Copolyester	**Thickness, mm**	**Tensile strength, N/mm^2**
MET	42.1	12.0
MPT	45.0	37.5
MBT	30.5	11.0
ClMPT	30.0	17.8
BANPT	31.2	25.0
BANBT	33.0	11.0
BPEGT	28.5	26.0

Table-4.5 **:** Tensile strength of copolyesters and some useful plastics [30]

Polymer	**Tensile strength, MPa**	**Polymer**	**Tensile strength, MPa**
Nylon-66	62-82.7	Cellulose acetate	13.1-62
PMMA	48.3-75.8	ABS	0.24-0.43
UF-R	70	MET	12.0
PPO-PS Blend	66.2	MPT	37.5
PC	55.2-65.5	MBT	11.0
PF-R	50	ClMPT	17.8
PS	50	BANPT	25.0
PVC	49	BANBT	11.0
PP	32	BPEGT	26.0
Teflon	13.8-34.5		

ELECTRICAL PROPERTIES

Till about the first few decades of the twentieth century, insulator items consisted primarily of glass, wood, paper, rubber, asphalt, mica, amber and related materials mostly of natural origin. The availability of a large spectrum of synthetic polymers has changed our option in this regard quite remarkably. Matter can be classified according to its specific conductivity into electrical insulators, semiconductors and conductors. Macromolecules with certain constitutional characteristics possess semiconductor properties. The majority of the commercially used polymers however are insulators. For common organic polymers, high resistivity of the order of 10^{12} to 10^{18} Ohm cm is typical and decrease on addition of conducting fillers. The electrical resistivity also depends on the frequency and voltage.

For electrical applications, the selection is required to be made on the basis of evaluation of electrical property parameters. The basic properties of dielectrics are dielectric constant or permittivity, dielectric breakdown voltage, dielectric strength, volume conductivity, volume resistivity, dielectric loss, power factor and surface resistance, etc. The choice of dielectric for each particular purpose is determined by the temperature and electric field frequency dependencies of these quantities.

Volume resistivity

A good insulating material is one that offers a high electrical resistance under a variety of conditions. Volume resistivity of a material is the resistance between opposite faces of unit cube when the current flow is confined to the volume of rest specimen. This quantity is defined [33] as the ratio of the potential gradient that is the electric field strength E, in a specimen to the current density J.

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33. O.M.Kazarnovasky, “Testing of Electrical Insulating Materials”, Mir Pub.Moscow, 1982

The volume resistivity ρ_v is proportional to the volume resistance R_v. the quantity that is reciprocal of ρ_v is known as the volume conductivity:

$$g_v = 1/r_v \qquad \textbf{... 4.20}$$

In measuring R_v of a flat specimen, we determine the volume resistance of the specimen portion confined between the guarded and the unguarded electrode. In this case the calculated (effective) diameter d_m is equal to the arithmetic mean of d_1 and d_2:

$$\mathbf{d_m = (d_1+d_2) / 2}$$

where, d_1 is the diameter of the guarded electrode and d_2 is the inner diameter of the ring shaped guarded electrode. The resistance R_v of the flat specimen is expressed in the form:

$$\mathbf{R_v = r_v. 4t / p (d_m)^2} \qquad \textbf{... 4.21}$$

Where d_m is the diameter of the electrode and t is the thickness of the specimen. If R is measured in Ohm cm and t and d_m in meters the unit of measurement of ρ is the Ohm m. From Eqn. 4.21

$$\mathbf{r_v = 0.785 R_v (d_m)^2 / t} \qquad \textbf{... 4.22}$$

Most high polymeric materials [34] are very good to excellent insulating materials and they are less subject to conduction by imperfection and structural irregularities than other types of insulating materials such as ceramics in view of the polymeric materials being non-porous or of very low porosity in comparison. The ductility of many of polymeric insulators and the great control in keeping them free from ionic and metallic impurities during synthesis and progressing are also added factors in their favor.

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34. H.L.Curtis, "Insulating Properties of Solid Dielectric", Bulletin, National Institute of Standards and Technology, Vol. **11**, 1915.

Humidity affects the volume resistance of different insulators to markedly different extents. Non-polar polymers such as polystyrene and polyethylene are unaffected but the moisture measurably affects polar organic polymers. The extent to which they are affected depends on the degree of their moisture absorption and consequent solvation. Porosity favors moisture absorption and lowers volume resistance. Polar inorganic polymers such as quartz and glass however remain practically unaffected by moisture if they are non-porous because they undergo little solvation. Resistance of polymeric insulators suffers appreciably with increase in temperature. Volume resistivity or conductivity can be used as an aid in designing insulators for a specific application.

The change of resistivity with temperature and humidity may be great [34-36] and must be known when designing for operating conditions. Volume resistivity or conductivity determination are often used in checking the uniformity of insulating materials, either with regard to processing or to detect conductive impurities that affect the quality of the material and may not be readily detectable by other methods.

Dielectric breakdown voltage or dielectric strength

The working voltage applied to an electrical insulating material must be much lower than the voltage, which causes the material rupture. Electrical breakdown results from an electrical discharge through a material at a minimum voltage called breakdown or disruptive voltage V_{br} [34]. In some cases voltages for lower than the breakdown voltage give rise to a surface discharge that does not penetrate deep into the bulk of a material.

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35. R.F.Field, “How Humidity Affects Insulation, Part-I, D.C.Phenomena”, General Radio Experimenter, Vol. **20**, 1945

36. R.F.Field, “The Formation of Ionized Water Films on Dielectrics under Condition of High Humidity”, J. Appl. Phys. Vol.**5**, 1946.

This is a surface or creeping, breakdown occurring at a surface breakdown voltage. Breakdown voltage is dependent on the duration and the rate of voltage application, thickness of the test sample, frequency of the applied voltage, temperature, dimensions and geometry of the electrodes and also the nature of the prevailing environmental conditions [27-30].

The basic characteristic of an electrical insulating material is its breakdown or dielectric strength E_{br} (also called electric strength) which is a minimum strength of the uniform electric field that causes dielectric breakdown. The calculation of breakdown strength requires the measurement of the breakdown voltage of the material under test.

The breakdown voltage (U_{br}) is proportional to the electric field strength (E_{br}) only if the field is uniform. Such a field exists between two electrodes, which have the shape of the bodies of revolution; the surface of these electrodes may be described by Rogovsky equations [34].

It is common practice to use electrodes of a simple shape, in the form of discs with rounded edges or as spheres; the field produced between such electrodes is very nearly uniform under certain conditions in a uniform field,

$$E_{br} = U_{br} / t \qquad \textbf{… 4.23}$$

Where, t is the thickness of the material. Thus, the determination of breakdown voltage allows calculation of dielectric strength with measure of the thickness of the specimen at the point of rupture. The dielectric strength is expressed in volts per mil (0.001 in) or volts per millimeters.

The voltage required to produce breakdown is dependent on many factors. The electric strength is influenced by various factors such as duration and rate of the voltage application, thickness of sample, frequency of the applied voltage, temperature, dimensions and geometry of the electrodes and nature of the prevailing environment [33].

Dielectric strength determinations are used to determine uniformity of the material and the manufacturing process. Although, such determinations are not adequate for design purposes. They do give some relative indication of amount of insulating material that will be required to support a certain voltage level. Flexible plastics are characterized by high dielectric and mechanical strength in thin sections is useful as insulating tapes.

The observed electrical strength and volume resistivity of copolyesters are listed in Table-4.6 along with some useful plastics [30]. From Table-4.6, it is clear that copolymers possess excellent to good electrical properties as compared to some useful plastics. It is interesting to note that electric strength have decreased with increasing alkyl chain length in the copolymer chains. MET and MPT have comparable electric strength but MBT has 2.3 times lesser electric strength than MET and MPT. All the three copolyesters possess excellent volume resistivity. MET has 20.4 times more volume resistivity than MBT and 67.2 times than MPT. The observed change in volume resistivity is due to different molecular architecture of the copolyesters.

Tablel-4.6: Electrical properties of copolyesters and some useful plastics [30]

Polymer	**Electric strength kV/mm**	**Volume resistivity Ohm cm**
Acrylics	17.7 – 21.6	$> 10^{14}$
Cellulose acetate	10.2 -14.4	$10^{12} – 10^{13}$
Cellulose acetate butyrate	9.8 – 15.7	$10^{10} – 10^{13}$
Nylon-6	17.3 – 20.0	10^{12} -10^{13}
PF-R	7.9 – 16.7	10^{9} -10^{12}
PVC	55.1	10^{13}
Polyacetals	18.3	6×10^{14}
Cellulose propionate	11.8 – 17.7	10^{12} -10^{15}
MET	45.7	2.56×10^{17}
MPT	44.4	3.81×10^{15}
MBT	19.4	1.26×10^{16}
ClMPT	50.1	2.2×10^{12}
BANPT	32.5	4.00×10^{13}
BANBT	16.3	5.50×10^{11}
BPEGT	19.3	1.70×10^{14}

CHAPTER – 5

A BRIEF REVIEW
OF THE
WORK DONE

This chapter of the thesis deals with brief summary of the work, which incorporated in the thesis.

CHAPTER-1

This chapter describes the up to date literature survey on the synthesis and physico-chemical properties of monomers and cardo copolyesters.

CHAPTER-2

This chapter deals with the synthesis of 1,1'-bis(4-hydroxy phenyl) cyclohexane , 1, 1'-bis (3-methyl-4-hydroxy phenyl) cyclohexane, 9, 9'-bis (4-hydroxy phenyl) anthrone-10 , terephthaloyl chloride and their copolyesters; and their purification by appropriate methods.

CHAPTER-3

This chapter describes the characterization of copolyesters by solubility, IR, NMR, viscosity, density, chemical resistance and biological activities. Copolyesters of MeBC and ClMeBC are only soluble in chloroform, 1,2-dichloroethane and dichloromethane, while copolyesters of BAN are found soluble in common solvents like chloroform, 1,2-dichloroethane, dichloromethane , DMF, DMSO, THF, etc. Tough and transparent films of copolyesters were prepared from 3% chloroform solutions. The structure of copolyesters is supported by IR and NMR spectral data. The IR spectra of all copolyesters showed strong absorption peaks (cm^{-1}) around 3355-3400 (OH str.), 1792-1788 and 1740-1720 (C=O str.), 1246-1242 cm^{-1} (C-O str.) besides normal modes of alicyclic, aliphatic and aromatic groups. The moderate peak at about 3355 cm^{-1} is due to OH str. indicated more number of unreacted OH and COOH end groups supporting formation of moderately low molecular weight copolyesters as supported by low values of intrinsic viscosities. The quantitative estimation of copolymer compositions are also determined by NMR peak areas. The copolymer compositions are in good agreement with theoretical compositions. Slight disagreement is due to unreliable measured peak areas because of peak broadening.

The densities of copolyester films were determined by a floatation method at room temperature. The density has decreased with increase in the alkyl chain length of diol in the copolymer chains, indicating increase in the chain flexibility, Upon comparing densities of halogenated copolyesters with unhalogenated copolyesters of the same type revealed that halogenated copolyesters possess somewhat high densities confirming compact packing as compared to unhalogenated copolyesters. The compact molecular packing is due to strong molecular interactions in the solid state.

Dilute solution viscosity measurements were carried out at three different temperatures: 30^0, 35^0 and 40^0 C in 1,2–dichloroethane (DCE) and chloroform (CF) by using an Ubbelohde suspended level viscometer. The intrinsic viscosity [η] and Huggin's constant (k') were determined from Huggin's relationship. The intrinsic viscosity [η] has decreased with increasing alkyl chain length in the copolymer chains and hence decrease in reactivity of the diols. Methyl pendant group in aliphatic diol (PG) resulted in improvement in molecular weight to a small extent and [?] is slightly greater in chloroform system and it is decreased with temperature. A little temperature effect on [?] indicated flexible nature of the copolyesters. The increase of k' with increase of temperature indicated increase of molecular interaction in the solutions.

The hydrolytic stability of the copolyesters was carried out at room temperature for varying period in water and 10% each of aqueous HNO_3, H_2SO_4, HCl, KOH, NaOH and NaCl. It is found that copolyesters possess fairly good hydrolytic stability in acids, alkalis and salt solutions. Chemical degradation and cracking or blistering can cause high moisture uptake, while slight change in weight loss or gain due to surface degradation, leaching of small molecules or solvation of ions with polar groups present in the polymer chain.

The antibacterial activity of copolyesters was screened against different microorganisms: Escherichia coli, Bacillus megaterium, Proteus vulgaris, Staphylococcus aureus, Aspergillus niger by cup-plate method. It is found that copolyesters possess mild activities against microorganisms selected.

CHAPTER-4

This chapter of the thesis deals with the thermo-mechanical and electrical properties of copolyesters. The copolyesters possess fairly good mechanical property in comparison with PET. In present case fairly good mechanical and excellent electrical properties are mainly due to moderate molecular weight, composition and polar groups present in the monomers. Excellent electrical properties of the copolyesters signify their usefulness as insulating materials. It is interesting to note that electric strength have decreased with increasing alkyl chain length in the copolymer chains. copolyesters of ethylene glycol (EG) and 1,4-butane diol (BD) have low tensile strength as compared to propylene glycol (PG) mainly due to low molecular weights and different molecular architecture. The comparable tensile strength of copolyesters of ethylene glycol (EG) and 1,4-butane diol (BD) is due to almost same molecular weights as judged on the basis of viscosity data and almost same molecular architecture. Copolyesters posses moderate tensile strength. The tensile strength of BANPT is low compared to MPT due to bulky nature of cardo group.

The TG and DSC thermograms of copolyesters were scanned at the heating rate of 20ºC/min in an N_2 atmosphere by using universal V1.12 E and V3 0.09 G TA instruments, respectively, which it is evident that T_g has increased with increase in alkyl chain length of diols but little effect on T_{max} is observed. In case of MHT, T_g is determined from the slope change of the base line. The transition between 275-300^{o}C is probably due to some physical change and it is further supported by no weight change in TG thermogram over the said temperature range. Other transitions below 100^{o}C may be due to traces of moisture along with residual solvent. Because of limitation of higher temperature range in DSC and TGA, were not scanned up to about 900^{o}C and therefore it is hard to judge the presence of crystallinity or complete amorphous nature of the samples. The copolyesters are thermally stable up to about 408-787ºC and followed single step degradation involving 35-75 % weight loss with 20-59 % residue.

it is clear that copolyesters followed 1.2-3.8 order degradation kinetics. Both Ea and A are affected to some extent by the structure and alkyl chain length of diol. The value of ΔS^* is increased with alkyl chain length up to four carbons and beyond that it has decreased due to conformational changes. A large and positive magnitude of ΔS^* indicated less ordered transition state, while negative entropy change supported ordered transition state.

ACHIEVEMENTS

ACHIEVEMENTS

(A) Paper published

1. "Synthesis and a Comparative Physico-chemical Investigation of Partly Aromatic Cardo Copolyesters" , Miss N. B. Joshi, Atul Raja and P. H. Parsania, J. Appl. Polym. Sci. In Press.

(B) Paper communicated

1. "Synthesis and physico-chemical characterization of halogenated partly aromatic cardo copolyesters", Nimisha B. Joshi and P. H. Parsania, Polymer Plastic Technology and Engineering.
2. "Synthesis and physico-chemical characterization of partly aromatic cardo copolyesters of 9, 9'-bis (4-hydroxy phenyl) anthrone-10", Nimisha B. Joshi and P. H. Parsania.
3. "Study of partly aromatic cardo copolyester of 9, 9'-bis (4-hydroxy phenyl) anthrone-10", Miss N. B. Joshi and P. H. Parsania

(C) Papers presented at National/ International conferences/ symposia/ workshop:

1. "Synthesis and characterization of aromatic cardo copolyesters", Miss N. B. Joshi, P. J. Vasoya and P. H. Parsania, "National Seminar on Polymers, Surfactants and Gels", Maharaja Sayajirao University of Baroda, March 11-13, 2005, (Poster presentation), Baroda.
2. "Synthesis and physico-chemical studies of aromatic cardo copolyesters", Miss N. B. Joshi, P. J. Vasoya and P. H. Parsania, - Ahmedabad Textile Industry's Research Association, Dec. 10-11, 2005, (Oral presentation), Ahmedabad.

3. “Synthesis and physico-chemical characterization of halogenated partly aromatic cardo copolyesters”, Miss N. B. Joshi and P. H. Parsania, 4th All Gujarat Research Scholars Meet, Maharaja Sayajirao University of Baroda , Jan. 22, 2006, (Oral presentation), Baroda.

(D) Conferences attended

1. National Workshop on “Understanding Reaction Mechanism”, Saurashtra University, 28-29 February-2004, Rajkot.
2. National Workshop on “Spectroscopy And Theoretical Chemistry” ,Maharaja Sayajirao University of Baroda, 8-12 February-2005, Baroda.
3. National Workshop on “Nanotechnology: Opportunities & Challenges”, Saurashtra University and GUJCOST, 17th Oct.-2005, Rajkot.
4. National Workshop on “E-Resources in Chemical Synthesis and Natural product” Saurashtra University, 2-3 March-2006, Rajkot.
5. National Seminar on “Recent Advances in Chemical Sciences and An Approach to Green Chemistry”, Saurashtra University and GUJCOST, 11-13 Oct.-2006