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**SYNTHESIS AND CHARACTERIZATION OF
NOVEL
POLY (SULFONE- SULFONATES)**

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 GUIDANCE

OF

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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.: -10-2005
Place: Rajkot.

(Mr. Ragin R. Amrutia)

This is to certify that the present work submitted for the Ph. D. Degree of Saurashtra University by **Ragin R. Amrutia** is his own work and leads to advancement in the knowledge of chemistry. The thesis has been prepared under my supervision.

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CONTENTS

Sr. No.	TITLE	Page No.
1	SYNOPSIS	1
2	CHAPTER-1: LITERATURE SURVEY ON BISPHENOL-C, AROMATIC DISULFONYL CHLORIDES, DIHALO DIPHENYL SULFONE, AROMATIC POLYSULFONES AND POLYSULFONATES	10
3	CHAPTER-2: SYNTHESSES OF MONOMERS, CARDO (ETHER-POLYSULFONE-SULFONATE) COPOLYMERS AND CARDO POLYETHER SULFONE. SECTION-1: SYNTHESIS OF BISPHENOL-C SECTION-2: SYNTHESIS OF 4, 4'-DIPHENYLETHER DISULFO NYLCHLORIDE (DPESC) SECTION-3: SYNTHESIS OF CARDO COPOLY (ETHER-SULFONE-SULFONATES) COPOLYMERS SECTION-4: SYNTHESIS OF CARDO POLY ETHER SULFONE	52 52 53 53 55
4	CHAPTER-3: CHARACTERIZATION OF HOMO AND COPOLYMERS SECTION-1: SOLUBILITY OF POLYMERS SECTION-2: SPECTRAL CHARACTERIZATION OF POLYMERS SECTION-3: PREPARATION OF COPOLYMER FILMS SECTION-4: VISCOSITY MEASUREMENTS SECTION-5: DENSITY MEASUREMENTS SECTION-6: CHEMICAL RESISTANCE SECTION-7: ANTIBACTERIAL AND ANTIFUNGAL ACTIVITY OF POLYMERS SECTION-8: GEL PERMEATION CHROMATOGRAPHY SECTION-9: END GROUP ANALYSIS BY CONDUCTANCE METHOD	58 58 61 71 71 81 87 93 95 99
5	CHAPTER-4: THERMO – MECHANICAL AND ELECTRI --CAL PROPERTIES OF CARDO COPOLY (ETHER-SULFONE-SULFONATES) CO-POLYMERS AND CARDO POLYETHER SULFONES	101

	SECTION-1: THERMAL ANALYSIS OF POLYMERS	102
	SECTION-2: MECHANICAL AND ELECTRICAL PROPERTIES OF POLYMERS	129
6	CHAPTER-5: ACOUSTICAL PROPERTIES OF CARDO POLYETHER SULFONE	140
7	CHAPTER-6: A COMPREHENSIVE SUMMARY OF THE WORK	182

SYNOPSIS

**SYNTHESIS AND CHARACTERIZATION OF
NOVEL POLY (SULFONE-SULFONATES)**

Mr. Ragin R. Amrutia

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

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SUBJECT : CHEMISTRY
TITLE OF THE THESIS : **SYNTHESIS AND CHARACTERIZATION OF NOVEL POLY (SULFONE-SULFONATES)**


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CHAPTER 1
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LITERATURE SURVEY ON BISPHENOL-C
LITERATURE SURVEY ON BISPHENOL-C
AND
AROMATIC CARDO POLYSULFONE- SULFONATES

CHAPTER 1

LITERATURE SURVEY ON BISPHENOL-C AND AROMATIC CARDO POLYSULFONE- SULFONATES

GENERAL INTRODUCTION

Since the formation of the earth over 4 billion years ago in its giant "Laboratory" elements like carbon, hydrogen, oxygen and nitrogen have been combining to form many complex molecules. In that all process the most important is human life.

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 provides 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, disinfections, agriculture 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, oil, fat, soap and carotene; and stabilizer for polyolefin and against UV radiation, and for increasing the flex life of rubbery material. They are also used as fog inhibitors in electro photography, electroplating solvent and as wash fastening agents; they are also useful in manufacturing thermally stable polymers, epoxy resins and polyester resins.

Among the monomers with cardo groups, phenolphthalein is probably alone used 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, fluoro, fluorenone, anthraquinone, phthalic anhydride) and phenols, amines, alkali aromatic compounds, etc. in the presence of Friedal-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

1. Hans-George Elis, "Macromolecules-I", Structure and Properties, 2nd Edn. , Plenum Press New York, 1984

analogous compounds having cardo bisphenols [2] and on the basicity of diamine [3] show that in these properties they do not differ from other bifunctional monomers.

Cardo bisphenols [4-7] 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.

(B) Aromatic cardo polymers

The synthetic polymers such as polyethylene, poly vinyl chloride and polyester are relatively new comers to the face of earth and are important to mankind. Natural polymers have been utilized through many centuries by mankind for different purposes.

Synthetic polymers have a long history before their commercialization began. The polymer industry itself was started in the early 1800's with the use of natural rubber for erasers and rubberized fabrics. Synthetic polymers have not only challenged the conventional materials for their established uses but also have made possible new products, which are constantly replacing older ones. It is difficult to believe modern life without polymers. They are highly useful in the rapidly developing fields, such as space exploration, terrestrial, transportation, modern communications, energy savings, environmental protection, public health, microbiology, medicine, etc Modern technologies (airspace industry, microelectronics, automotive industry) demand easily processable polymeric materials suitable at broad temperature

-
2. V.V.Korshak, A.P.Kreshkov, S.V.Vinogradova, N.S.Aldarova, V.A.Vasnev, E.L.Baranov, M.V.Salvgorodskoya, A.I.Tarasov, and T.I.Mitaishvili, *organic Reactivity*, 7,285,1970; *C.A.***74**, 13539, 1971
 3. B.A.Korolev, Z.V.Geraschenko and Ja. S. Vygodsky, *Ibid*, **8**, 681, 1971
 4. V. V. Korshak, V. A. Sergeev, V. K. Shitikov and A. A. Severov, *Polym. Sci. U.S.S.R.* **9**, 2202, 1967; *Vysokomol Soedin*, **A-9**, 1952, 1967
 5. V.V. Korshak, V.A. Sergeev, V.K. Shitikov, A. A. Severov, I.Kh. Nazmutdinova, S. G. Djeltakova, V. F. Durlutsky, B. A. Kiselev and V.V. Yaremenko, *Polymer Sci. U.S.S.R.*, **10**, 1258, 1968; *Vysokomol Soedin*, **A-10**, 1085, 1968
 6. V.V. Korshak, V. A. Sergeev, V. K. Shitikov, A. A. Severov, V. F. Durlutsky, and S. G. Djeltakova, *Avt. Svudet, U.S.S.R.* 172, 489, 1962; *Bull. Izobr.*, **13**, 70, 1965; *C. A.* **63**, 16, 564, 1965
 7. V.A. Sergeev, V. V. Korshak, and V. K. Shitikov, *Polymer Sci U.S.S.R.*, **10**, 2680 (1968); *Vysokomol Soedin*, **A-10**, 2304, 1968

region involving both cryogenic and temperature as high as aromatic 350-400°C. A great variety of cardo polymers has been developed namely, aromatic polyesters, polyarylates, polyamides, polyethers, polysulfones, polysulfonates and other carbon chain polymers [8].

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 increase 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 hydroquinone instead of catechol, formation of chemical cross links between linear molecules, regular arrangement of units in the chain, preparation of stereo regular polymers and soon.

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 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.

[C] The aim of present investigation

Recently much attention is being paid towards polymers containing cardo (Latin meaning a loop) groups[9], 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 is regarded as loops (cardo groups). The introduction of cardo (Latin meaning a loop) 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 [9].

Literature survey reveals that little work has been done on cardo polyether - sulfones and cardo co poly (ether – sulfone- sulfonates) [10-13], which tempted us to investigate polyether- sulfone and cardo co poly (ether-sulfone –sulfonates) with following objectives:

1. To synthesize bisphenol-C, aromatic disulfonyl chlorides and their cardo polyether-sulfone and cardo co poly (ether sulfone sulfonates).
2. To elucidate the structure of cardo polyether sulfones and cardo co poly (ether- sulfone-sulfonates) by IR and NMR spectroscopy.

-
9. V. V. Korshak, S.V. Vinogradova and Y. S. Vygodskii, J. Macromol. Sci.-Rev., Macromol.Chem. **C11**, 45, 1974
 10. M. Podgorski and W. Podkoscielny, Pol. Pl., **110**, 187, 1981; C.A. **96**, 122, 395, 1982
 11. M. Podgorski, W. Podkoscielny, W. Charnas and H. Maziargyk, Pol. Pl., **134**, 308, 1986; C.A. **112**, 78, 219, 1990
 12. M. Podgorski, W. Podkoscielny, Pol, Pl. 139, 451, 1987; C.A. **113**, 41, 549, 1990
 13. M. Podgorski, W. Podkoscielny, Pol, Pl. 155, 672, 1992; C.A. **119**, 204, 137, 1993

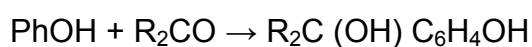
3. To elucidate biological activity of cardo co poly (ether-sulfone - sulfonates) and cardo polyether-sulfones.
4. To characterize polymers by viscosity measurements in different solvents at specific temperature.
5. To determine the density of cardo co poly (ether sulfone sulfonates) and cardo polyether-sulfones.
6. To determine the thermal properties of cardo co poly (ether –sulfone-sulfonates) and cardo polyether-sulfones.
7. To determine the chemical resistance of cardo co poly (ether- sulfone - sulfonates)
8. To determine the mechanical and electrical properties of cardo co poly (ether-sulfone-sulfonates)
9. To understand structure and molecular interactions in solutions by sound velocity measurements in different solvents at different temperatures.

SECTION-1: BISPHENOL-C

Farbenind [14] 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.

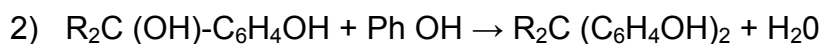
Mc Greal et al [15] have reported the condensation of ketones (0.5moles) and phenols (1.0moles) in acetic acid. The solutions were saturated with dry HCl for 3-4h and kept the reaction mixture for varying periods up to 4 weeks until the mass crystallized. The yield with aliphatic and aromatic ketones were 10-25 % and with cyclic ketones 50-80%. They have also proposed the following mechanism

- 1) The addition of phenol to ketone



14. I.G.Farbenind, Fr. Patent 647, 454, 1928; C.A.23, 2540, 1929

15. M.E.McGreal, V.Niederl and J.B.Niederl, J.Am. Chem. Soc., 61, 345, 1939; C.A.33, 2130, 1939



Johnson and Musell [16,17] have reported synthesis of 1,1'-bis (4-hydroxy phenyl) cyclohexane using 5 moles of phenol, 1 mole of a cyclohexanone, H₂S and BuSH below 40°C with 0.1-0.3 mole dry HCl gave (I) m.p. 186-187°C, 2Me-I 236-240°C; 4Me-I 178°C ; 1,1'-bis (4-hydroxy-3-methyl phenyl) cyclohexane m.p. 187°C and 1,1'-bis (4-hydroxy-3-isopropyl phenyl)cyclohexane, m.p. 109-115°C. Mash containing small quantity of bisphenol (I) protects chickens from coccidiosis better than does a sulfa guanidine. They have also reported that coccidial infection in poultry may be suppressed by feeding a bisphenol (p-OH (C₆H₄)₂-CRR' in which R' is a phenyl or alkyl and R is H or alkyl).

Bender et al [18] 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) cyclohexane (m.p. 187°C); 1, 1'-bis (3-methyl-4-hydroxy phenyl) cyclohexane. (m.p. 186-189°C) and 1, 1'- bis (3-chloro-4-hydroxy phenyl) cyclohexane (m.p. 134-141°C).

Bender et al [19] have reported the preparation of bisphenols by irradiating a mixture of ketone and phenol at 20-100°C with β-rays or ultra violet in the presence of 37% aq. H₂SO₄ as a condensing agent and stirring at 30-37°C. 1, 1'-Bis (4-hydroxy phenyl) cyclohexane (m.p. 186-187° C) was obtained in 93% yield from 1 mole cyclohexanone and 4 moles of phenol.

Farbenfabriken [20] has reported the preparation of 4, 4'-dihydroxydiphenyl cyclohexane (m.p. 186°C) using cyclohexanone (78 Kg) and excess phenol (400 Kg) in the presence of 38% HCl (80 Kg) as a catalyst at room temperature for 6 days.

16. J.E.Johnson and D.R.Musell, U.S.Pat.2, **538**, 725, 1951; C.A. **45**, 4412, 1951

17. J.E.Johnson and D.R.Musell, U.S.Pat.2, **535**, 014, 1950; C.A. **45**, 2635, 1951

18. H.L.Bender, L.B.Conte and F.N.Apel, U.S.Pat.2, **858**, 342, 1958; C.A.**53**, 6165, 1959

19. H.L.Bender, L.B.Conte and F.N.Apel, U.S.Pat.3, 936,272, 1960 C.A.**54**, 19, 604, 1960.

20. Farbenfabriken, Ger. Patent 1,031,788 1958, C.A. **54**,19, 603 ,1960.

Maeda et al [21] have reported that polyurethane can be stabilized thermally and against UV light by adding a mixture of 4, 4'-thio bis (6-tert. butyl-3-methyl phenyl) with 1, 1'- bis (4-hydroxy phenyl) cyclohexane or 1, 1'- bis (3-methyl - 4 - hydroxy phenyl) cyclohexane.

Freudewald et al [22] 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 [23] have reported the synthesis of monomers by condensing PhOH and o-cresol with cyclohexanone to give 1, 1'-bis (4-hydroxy phenyl) cyclohexane and 1, 1'-bis (3-methyl-4-hydroxy phenyl)cyclohexane, respectively. These bisphenols are treated with HNO₃ 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 SnCl₂ 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.

Alexandru [24] has reported the preparation of bisphenols by reaction of a ketone with phenol, BuSH, ClCH₂CH₂Cl and Me₃SiCl. The mixture stirred and heated to 50-55°C and finally at 65°C to give bisphenol-Z.

Subramaniam et al[25] 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

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21. S. Maeda, J. Yurimoto, S. Samukawa, and Y. Kojima, Japan 14, 752 (66) 1963; C.A. **66**, 86, 263, 1967
 22. Freudewald, E.Joachim, Konrad and M.Fredeic, Fr. Patent 1,537,574 1968; C.A. **71**, 21, 868, 1969
 23. T.K.Popova and G.P.Nedonoskova, Zh. Khim, 5Zh338 (1970); C.A. **75**, 6, 391, 1971
 24. B.S.Alexandru, U.S.Pat. 4, 766, 255 1988; C.A. **110**, 38, 737, 1989
 25. G.Subramaniam,R.Savithri and S.Thambipillai, J. Indian Chem. Soc., **66**, 797, 1989.

concentration level used, whereas both the esters are active even at the minimum concentration level used.

Rao et al [26] have reported a convenient method for the preparation of bisphenols. Cyclohexanone was treated with PhOH at 55^o-60^oC 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 [27,28] have studied optimization reaction conditions for the synthesis of 1,1'-bis(R,R'-4-hydroxy phenyl) cyclohexane by condensing 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^oC . They have reported optimum concentration (10-15ml), time (30-90min) and temperature (55-70^oC) 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 [29] 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.

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26. M.V.Rao, A.J. Rojivadiya, P.H.Parsania and H.H.Parekh, J. Ind. Chem. Soc., **64**, 758, 1987
- 27 H.H. Garchar and P.H.Parsania, Asian J. Chem., **6**, 135, 1994
- 28 H.H.Garchar, S.H.Kalola and P.H.Parsania, Asian J. Chem., **5(2)**, 340, 1993
- 29 O.V.Smirnova and E.Ya. Robas Zh.Prikl Khim, 48(3), 578, 1975; C.A.**82**,139, 009, 1975

SECTION-2: AROMATIC POLYETHER- SULFONE

E.I. Dupont de Nemours & Co. [30] has reported synthesis of poly (aromatic ketones) and poly (aromatic sulfones) by condensing the corresponding aromatic carboxylic or sulfonic acid compound using a mixture of $\text{BF}_3\text{-HF}$ as a catalyst. Thus, 14.15 g p- phenoxy benzoic acid was mixed with 13.2 g HF and 26.6 g BF_3 at 80°C and mixture was held 2 h at 20°C for 4h at room temperature. The product was mixed with methanol, extracted with boiling methanol and dried in vacuo giving a quantitative yield of polyketone. A mixture of Ph_2O and isophthalic acid or terephthalic acid was also polymerized. These polymers can be used as surface coating, filling and filaments. The polymers have low melt viscosity and other good properties, which vary from polymer to polymer such as thermal stability, high flux life, oxidation resistance, heat stability and tensile strength.

Rose [31] (ICI Ltd.) has prepared the polymers by nucleophilic substitution (polysulfonation). The possible variations in structure and the acid resistance, alkali resistance and thermal stability of the polymers are reviewed with 25 references.

Vogel [32] has synthesized poly (aryl sulfones) $[-\text{ArSO}_2-]_n - [-\text{ArSO}_2-]_m$ with dyes incorporated in to the polymer chains, which gave colored films and improved resistance to UV degradation. The polymers were prepared by melt or by solution polycondensation at $100^0\text{-}250^\circ\text{C}$. Lewis acids were used as catalysts. Thus, 75.67 g phenyl ether, m'- bis (sulfonyl chloride), 34.04 g Ph_2O 0.85g 1,8- bis thio phenyl anthraquinone and 92.2 g PhNO_2 (I) were heated at 90°C under N_2 . The polymerization was started by adding 1.5 ml of 10% of FeCl_3 in I and heating the mixture to 120°C for 23h. The product was distilled with 300 ml HCONMe_2 precipitated with methanol and extracted twice with 1:1 methanol- acetone. Other monomers used were 4-biphenyl sulfonyl chloride, triphendioxazine sulfonyl chloride, 4, 4'-biphenyl bis (sulfonyl chloride), thioindigo scarlet R, copper phthalo cyanamine, 2, 7- naphthalene bis(sulfonyl chloride) and indanthrene Violet RT.

30. E.I. Dupont de Nemours & Co. Brit. 1,102,679(1965) C.A., **68**: 87751 (1966)

31. J.B.Rose (ICI Ltd. Plastic Div. Welwyn garden city, England) C.A. **68**: 119345(1968)

32. H.A. Vogel (Minnesota Mining and Mfg. Co. U.S. 3,406,149 (1964) C.A. **70**: 20515, 1968

George [33] has synthesized thermoplastic thio phenol polymers useful for moldings and films were prepared by polymerization of the K salts of I(X=CO or SO₂). Thus, I(X=CO) aqueous thiolane, 1,1- dioxide and Ph₂SO₂ were heated within 3h to 260⁰C at 15mm Hg pressure and heated 3h at 350⁰C under N₂ to give poly(4-chloro benzyl) thiophenol(II) of reduced viscosity 0.73 (1 g II/ 100ml conc H₂SO₄ at 25⁰C). Refluxing II with 50%aqueous H₂O₂ 2 h in gave crystallize poly (p-phenylene sulfone) (p-phenylene carbonyl) of reduced viscosity0.61 (1 g polymer/ 100 ml H₂SO₄ at 25⁰C), which on pressing at 390⁰C; gave an amorphous film.

George and Rose [34] have synthesize 4-[(4-chloro phenyl sulfonyl)]-4'-mercapto biphenyl polymer [p- C₆H₄SO₂.C₆H₄. C₆H₄-S-p]_n specially useful for the manufacturing of transparent films was prepared by poly condensation of the monomer in organic solvents. Thus, refluxing ClSO₃H and p-ClC₆H₄SO₂.C₆H₄Ph-p 3h in CHCl₃ gave 55% 4-[4-chlorophenyl sulfonyl] 4'-(chloro sulfonyl) biphenyl, which was reduced with Sn + HCl to give 58% of 4-[(4-chloro phenyl) sulfonyl] -4'- mercapto biphenyl II. Heating of 10.82g of II, 3.66g KF and 12ml sulfolane for 80 min. at 200⁰C and added 10 ml sulfolane. The reaction mass was cooled to 150⁰C and 50ml DMF was added and heated further 5h at 200⁰C to give I, which is press moldable at 340⁰C to form transparent film.

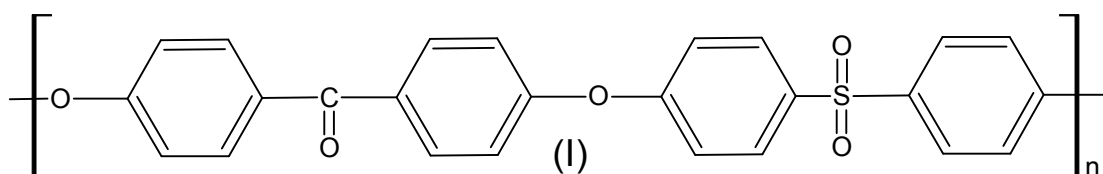
Studinka and Rudolf [35] have synthesized thermoplastic, flame resistant, easily moldable, film forming poly(thio) ethers from condensation of aromatic dithiols, diols or hydroxy thiols with aromatic halides in N-alkylcaprolactum containing acid-binding base or salts. Thus, 4, 4'-bis (4-hydroxy phenyl) propane 11.415 g, 4, 4'-bis (4-chlorophenyl sulfonyl) biphenyl 25.172g, and Na₂CO₃ 6.995g in 50ml N-methyl caprolactum under N were heated 5h at 210⁰C to give copolymer of reduced specific viscosity of 0.63 (0.2g/100mlCHCl₃ at 0⁰C)

33. R. G. Feasey (ICI Ltd.) Ger Offen. 2,164,291 (1970) C.A. **71**: 140,740, 1972

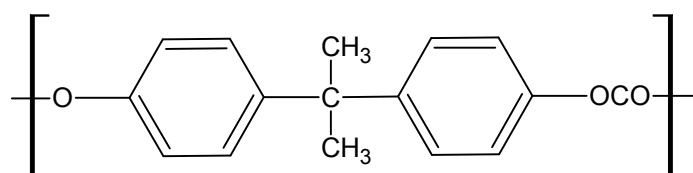
34. R.G. Feasey, and J.B.Rose (ICI Ltd.) Ger. Offen. 2, 156 343, 1970 C.A. **74**: 75774, 1972

35. J.Studinka, G.Rudolf (Inverta A. G. Fnerfors Chung and patentverwetung) Ger. Ofen. 2,220,079, 1971 C.A. **76**: 44219, 1973

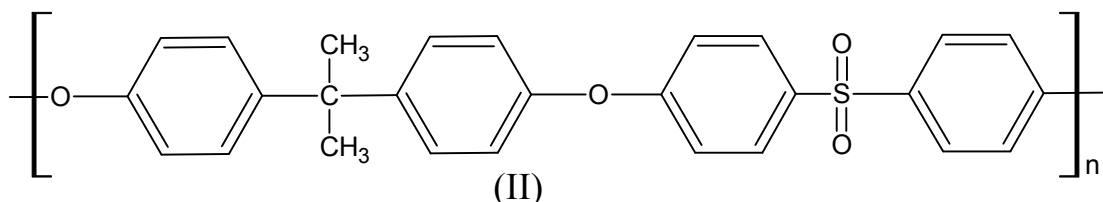
Norio et al. [36] have developed aromatic polymers with improved whiteness (II) by treating di hydroxy aryl ketone alkali metal salt with a dichloro aryl sulfone and poly condensing the prepolymer. Thus, 14.52g 4,4'-di hydroxy benzophenone K salt and 14.36g DCDPS were dissolved in 200ml DMSO to give 76.3% prepolymer(20g), which was further heated 2h at 185⁰C-290⁰C and 2h at 290⁰C to give polyether (I) having intrinsic viscosity 0.5 in tetrachloro ethane at 30⁰C, tensile strength 100kg/cm² and elongation at break 40-50% to 180⁰C.



Owada et al. [37] have prepared thin polymeric film with good blocking resistance. Thus, a 12% poly(bisphenol-A-carbonate) (I) solution in CH₂Cl₂ and 12%poly[bisphenol A bis (4- chlorophenyl) sulfone] ether (II) solution in CH₂Cl₂ were mixed at a proportion 50:50, stirred at room temperature for 10 min, filtered, cast on a polyester film, dried for 10 sec at 150⁰C and 40 sec at 110⁰C and peeled off from the polyester film to give 3mm thick film (almost transparent) with static fraction coefficient 0.466 compared with ≥ 2.14 for I or II alone.]



(I)



36. Yogi, Norio, Okai Hiroshi; Fukuda Makoto; Kishi Ikuji; (Denki. Kagaku Kogyo KK) Japan Kokai **75**, 36, 598, 1973; C.A. **84**: 98396, 1975

37. Y.Owada, T.Itsuki, K.Yosikiyo(Kangufuchi Chemical Industry Co. Ltd.) Japan Kokai75, 59472, 1973; C.A. **83**:132687, 1975

Kellman and Marvel [38] have synthesized oligomeric polyaromatic ether- ketone-sulfones with acetylenic end groups. 1, 3-Bis (phenoxy benzene sulfonyl) benzene was acetylated with 4-acetyl benzoyl chloride and optionally isophthaloyl chloride in the presence of AlCl_3 in CH_2Cl_2 to give the oligomers I (R= AC, n=0) and I (R=AC; n=1). Treatment with the wilsmeier reagent gave I(R=CCl:CHCHO;n=0) and I (R=CCl:CHCHO;n=1), which were converted by dehydrohalogenation-decarboxylation in EtOH-DMF to I (R=C:CH; n=0) and I (R=C:CH; n=1) , respectively. The acetylene terminated compounds were heated under N to effect polycyclotrimerization and provides cross linked polymers with softening point $>200^\circ\text{C}$.

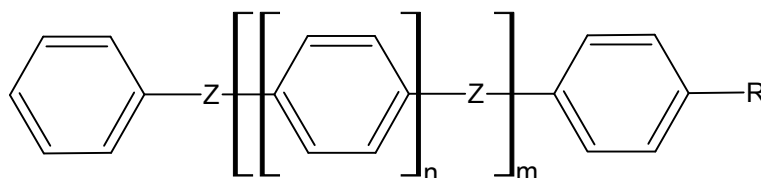
Michael Edward [39] has synthesized aromatic polysulfones and their copolymers by condensing an aromatic sulfonyl halide with a compound containing at least two aromatically bonded hydrogen atoms in the presence of Fe salts or SbCl_5 to give thermoplastics, which are chemically and thermally stable and have good adhesion to glass and metals. Thus, diphenyl ether 4, 4'-disulfonyl chloride 7734.84g, biphenyl 308.52g and FeCl_3 4 parts were fused together at 90°C heated 40mm at $180^\circ\text{-}280^\circ\text{C}$ to give a copolymer having reduced viscosity 0.15. The copolymer was amorphous and transparent film could be cast from DMF solution.

Freeman and Rose [40] have reported aromatic polyethers useful as heat resistant electric cable insulation were manufactured by condensation polymerization at $250\text{-}400^\circ\text{C}$ of equimolar amounts of I (R=halogen; Z=CO or SO_2 , n=1-3, m=0-3) with I (R= OM; M=alkali metal). Thus, 19.4556g hydrated p-[(KOC₆H₄CO)₂C₆H₄]-p was dehydrated and polymerized under N with 15.9768g (p-ClC₆H₄CO)₂C₆H₄-p in 43g of Ph_2SO_2 for 22h at 230°C and 2h at $320\text{-}60^\circ\text{C}$ to give a polymer containing repeat units with the structure [(p-C₆H₄CO)₂ p-C₆H₄O] and having crystallized m.p. was 384°C .

38. K. Raymond and C.S. Marvel J. Polym. Sci. Polym. Chem Ed. **14** (8), 1976

39. Michael Edward B. (ICI Ltd.)U. S. 3,983,300(1976); C.A. **86**: 17566, 1976

40 J. L. Freeman and J. B. Rose (ICI Ltd.)Brit. 1, 563, 224, 1976



The polymer formed brittle opaque film.

Staniland [41] has synthesized polyether sulfone with high viscosity. Bis(4-chlorophenyl)sulfone (I) and 4,4'-dichlorobenzophenone (II) and 4,4'-dihydroxy benzophenone di-K- salt(III) were copolymerized as a mixture containing a slight molar excess of I and II during initial polymerization and a small amount of III was added during the final stage of polymerization to increase the viscosity. 23.70 moles hydrated (III) and 14.3 kg Ph₂SO₂ were added to 0.223 mole I, heated at 230°C in vacuo at 1 atm mixed with 19.10 moles II and 4.18 moles I, heated 4.2 and 4.5 h at 230°, 235°, 320°C and treated with 500 g I to prepare a copolymer with reduced viscosity 0.99, compared with 0.82 before addition of (III).

Taylor [42] has synthesized aromatic polyether-sulfone with high molecular weight in relatively short time by heating hydric phenols with aromatic dihalides or halo phenols containing ketone or sulfone groups in the presence of ≥ 1 equivalent alkali metal carbonate/ OH group with non azeotropic distillation of H₂O. Thus, stirring 22.83g bisphenol A, 28.71g bis (p-chlorophenyl) sulfone and 27.90g K₂CO₃ under reduced pressure to cause refluxing and distillation of 10 ml distillate/h for 3, 4, 5 and 6h to give polyether-sulfone.

ICI Ltd. Japan [43] has prepared poly (ether-sulfone) and poly (ether-ketone-sulfone) by reaction of the alkali metal salt of bisphenol with an equimolar amount of an aromatic dihalide containing CO and SO₂ groups. Thus, mixture of 24.9804g 4,4'- dihydroxy benzophenone di K salt , 16.3382g 4,4'-dichlorobenzophenone , 4.67g bis (4-chloro phenyl) sulfone (I) and 41g Ph₂SO₂ was heated with stirring at 230°C for 5 min, at 270°C for 3h and at

41 P. A. Staniland (ICI Ltd.) Ger. Offen. 2, 612, 755, 1975; C. A. **86**: 90837, 1977.

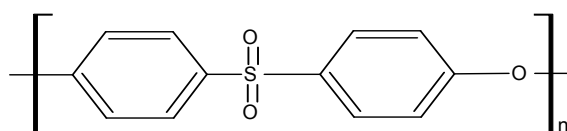
42. I. C. Taylor (ICI Ltd.) Ger. Offen. 2,733,905 (1976) C.A. **88**: 137,183, 1978.

43. ICI Ltd. Japan Kokai Brit. 18, 34, 900, 1976 C.A. **89**: 75841, 1978.

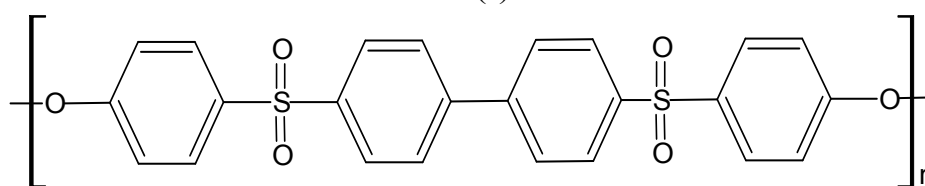
320°C for 3h and mixed with 1 g (I), cooled, washed with MeOH –Me₂CO mixture to give a poly (ether-ketone sulfone) (II) . It was compression molded 5 min at 410°C and cooled to 200°C to give an opaque tough film.

Attwood et al. [44] have reported the synthesis of poly sulfones (I) and (II) by melt and solution poly condensation of I or II of 11 alkali metal halophenylsulfonylphenoxide and 4 copolymers were prepared by polycondensation of 4-halophenyl sulfonyl compounds with dihydric phenols in the presence of KF. The ease of formation of high molecular weight polymers depends on functional group reactivities. Branched polysulfones samples were prepared by polycondensation of K 4-methoxy phenyl sulfonyl 4'-phenoxide and K 4-fluoro phenyl sulfonyl-4'-phenoxide with 2, 4, 4'-trifluoro diphenyl sulfone prepared by AlCl₃ catalyzed reaction of 4-fluoro benzene sulfonyl chloride and m-di fluoro benzene.

Branched polysulfones samples were prepared by polycondensation of K 4-methoxy phenyl sulfonyl 4'-phenoxide and K 4-fluoro phenyl sulfonyl-4'-phenoxide with 2, 4, 4'-trifluoro diphenyl sulfone prepared by AlCl₃ catalyzed reaction of 4-fluoro benzene sulfonyl chloride and m-difluoro benzene.



(I)



(II)

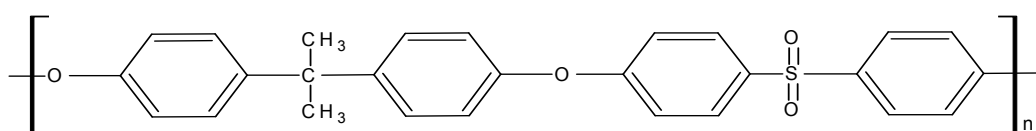
ICI Ltd. Japan [45] has synthesized aromatic polymers. RC₆H₄ZZ¹OH (I) [R= halogen ortho or para to Z; Z= CO, SO₂; Z¹=divalent aromatic residue] was bulk or solution polymerized at 200-400°C in the presence of 0.5 mol (based on 1 mol I) alkali metal carbonate or bicarbonate. For example, 19.40g 4-FC₆H₄COC₆H₄OH-4, 2.52g 4-FC₆H₄SO₂C₆H₄OH-4, 0.144g 4-

44. T. E. Attwood, D.A. Barr, T. King, A.B. Newton, J. B. Rose (Plast. Div. ICI Ltd., Welwyn Garden City Engl.) Polymer, 18 (4), 1977 C.A. **88**: 170547, 1978.

45 ICI Ltd. Japan Kokai Brit. 7,810,696, 1976; C.A. **89**: 110791, 1978.

$\text{ClC}_6\text{H}_4\text{SO}_2\text{C}_6\text{H}_4\text{Cl}$ -4, 6.97g K_2CO_3 and 30g Ph_2SO_2 g were heated at 230°C for 1h, 280°C for 1h and 320°C for 1h to give a polymer, which was compression molded at 400°C to a white film.

Farnham [46] has reported moldable compounds having good toughness, thermal resistance and dimensional stability at elevated temperature. They were prepared by polymerization of an aromatic diol with dihalo substituted aromatic sulfone. Thus, bisphenol-A in DMSO-benzene containing KOH was converted to the K salt and treated with an equimolar amount of $(p\text{-ClC}_6\text{H}_4)_2\text{SO}_2$ to give a quantitative yield of I having reduced viscosity 0.59. Films were prepared by compression molding at 270°C .



(I)

Freeman (ICI Ltd) [47] has reported a Fluorine containing monomer such as 4-(4-fluoro benzoyl phenol) (I) or 1, 4-bis (4-fluoro benzoyl) benzene is solution copolymerized with bis (4-hydroxy phenyl) sulfone (II), bis (4-chloro phenyl) sulfone (III), or similar monomer in the presence of $\text{K}_2\text{CO}_3 < 1 \text{ mol/mol OH}$ of the monomers to prepare high molecular weight polyethers. Thus, a mixture of 0.095 mol I, 0.0025 mol II and 0.003 mol III in 42 g Ph_2SO_2 containing 0.0495 mol K_2CO_3 was polymerized at 330°C for 50 min to prepare a copolymer.

Blinne and Clans [48] have reported synthesis of polyether sulfones at reduced reaction temperature giving products with good color and molecular weight by stepwise treatment of equivalent amounts of bisphenols with dichlorobenzene compound in a polar aprotic solvent and azeotropic solvent in the presence of anhydrous alkali carbonate. Thus, 150.2 parts bis (4-hydroxy phenyl) sulfone and 172.3 parts bis (4-chloro phenyl)sulfone were dissolved in 900 parts N-methyl pyrrolidone and 300 parts PhCl containing

46. A. G. Farnham (Union Carbide Corp.) U.S. 4, 108, 837, 1978; C.A. **90**:88260, 1979.

47. J. L. Freeman (ICI Ltd.) Ger. Off. 2,810, 794, 1977; C. A.: **90**; 6891, 1979.

48. B. Gerd and C. Clans, (BASF A. G.) Ger. Off. 2,731, 816, 1977; C.A. **90**: 138421, 1979

87.2 parts anhydrous K_2CO_3 and a H_2O -PhCl azeotrope was distilled at $150^\circ C$ for 2h. hydroxy phenyl) sulfone and 172.3 parts bis (4-chloro phenyl)sulfone were dissolved in 900 parts N-methyl pyrrolidone and 300 parts PhCl containing 87.2 parts anhydrous K_2CO_3 and a H_2O -PhCl azeotrope was distilled at $150^\circ C$ for 2h. 300 parts PhCl was added further and heated at $180^\circ C$ and distilled on additional 2h. The reaction mixture was then heated 6h at $180^\circ C$ and treated with MeCl to terminate poly condensation over 30 min. The reaction mixture was diluted with PhCl and filtered to remove salt. Polyether-sulfone was isolated and dried.

Hartmann [49] has reported synthesis of polyether sulfone with molecular weight 20,000-1,25,000 and density < 1.20 g/cc. Polyether-sulfone were prepared by reaction of 1 mol of a 3,3',5,5'-tetraalkyl-4,4'-dihydroxy biphenyl with 1 mol of a dihalo diphenyl sulfone in the presence of a dipolar aprotic solvent and 1-1.33 mol alkali metal carbonate and bicarbonate. Thus, a mixture of tetramethyl biphenol, 100 ml N,N'-dimethyl acetamide, 0.025 mol $(4-ClC_6H_4)_2 SO_2$, 0.02625 mol K_2CO_3 , and 30 ml PhMe was heated at reflux temperature for 64h. Water-PhMe azeotrope was distilled off at 150^0 - $165^\circ C$ in 3.5 h and the product was filtered, washed well and dried. The yield of copolymer was 97%. Copolymer has molecular weight 46,000 and Tg $270^\circ C$. A 3 inch thick compression molded poly sulfone disk had density 1.19 g/cc, tensile strength 12000 psi, flexural strength 17,500 psi and Barcol hardness 15-20. A 1.5 mm thick clear film was cast from pyridine solution. The film had tensile strength 8900 psi, modulus 3.3×10^5 psi and elongation 4.5%.

Blinne and Clans [50] have reported the synthesis of polyether containing sulfone groups were prepared without isolation of intermediates by poly condensing bisphenols with dihalobenzene or by poly condensing halophenols in the absence of solvents or diluents eliminating the need for the separation and regeneration of the reaction medium. Thus, a mixture of 250.3 parts bis(4-hydroxy phenyl) sulfone and 276.4 parts K_2CO_3 was heated at $300^\circ C$ under reduced pressure for 3h, mixed with 287.2 parts bis (4-chlorophenyl)sulfone (I) and heated 30 min at $300^\circ C$ and the product mixed

49. L. A. Hartmann, (ICI USA Inc.) U.S. 4,156,068 (1975); C.A. **91**:75088, 1979.

50 B. Gerd and C. Clans (BASF A. G.) Ger. Offen. 2, 749, 645, 1977; C. A. **91**: 40110, 1979.

with an additional 10 parts I and poly condensed for an additional 30 min. The polymer was extracted with water to remove organic salt giving a polyether-sulfone.

Blinne and Clans [51] have prepared polyether-sulfones at reduced reaction temperatures, giving products with good color and high molecular weight, by stepwise treatment of equivalent amounts of bisphenols with a dichlorobenzene in a polar aprotic solvent and azeotropic solvent in the presence of an anhydrous alkali carbonate. Thus, 150.2 parts bis(4-hydroxyphenyl)sulfone and 172.3 parts bis(4-chlorophenyl)sulfone were dissolved in 900 parts N-methyl pyrrolidone and 300 parts PhCl, mixed with 87.2 parts . Water-PhCl azeotrope was distilled at 150°C for 2h. 300 parts PhCl was added and heated to 180°, and distilled an additional 2 h. The reaction mixture was further heated 6 h at 180° and treated with MeCl to terminate polycondensation over 30 min. The reaction mixture was diluted with PhCl, filtered to remove salt, precipitated, filtered, washed well and dried. Polyether-sulfone has reduced viscosity 0.60 and 1% H₂SO₄ solution has 3.4% absorption of light in the wavelength range 400-800nm. The same reaction in the absence of the PhCl azeotropic solvent gave a polymer with reduced viscosity 0.25 and 6.1% absorption of light.

Mohanty et al. [52] have synthesized amine terminated polyether sulfone by reaction of bisphenol A with 4, 4'-dichloro diphenyl sulfone (DCDPS) and p-amino phenol in N-methyl-2- pyrrolidone (NMP) using K₂CO₃ as a base.

Idemitsu Kosan Co. [53] has prepared polymers with good heat resistance and moldability and compounding-dependent glass-transition temperatures were prepared from dihydric phenol alkali metal salts, 4, 4'-dihalodiphenyl sulfones, and methylene halides. Thus, hydroquinone 11.01g, K₂CO₃ 17.97g, and 4,4'-dichlorodiphenyl sulfone 27.28 g in 200 ml N-methyl-2-pyrrolidone and 80 ml toluene were heated 3 h at 140-150°C with removal

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51. Blinne Gerd and Cordes Clans BASF A-G, Ger. Offen, US Patent 4200728.
 52. P.K. Mohanty, J.L. Hedrick, K. Bobetz, B.C. Johnson, I. Yilgor, R. Yang and J. E. McGrath Polym. Prep. **23**, 284, 1982.
 53. Idemitsu Kosan Co. Ltd. Japan, Jap. Patent 60092326, 1983; C.A. **103**: 161016.

of the water-toluene azeotrope and treated with 0.46 g/min CH_2Cl_2 gas at 150° for 3 h to prepare polymer having glass-transition temperature 202°C and initial thermal decomposition temperature 480°C in air.

Percec and Auman [54] have prepared oligomers by the reaction of excess bisphenol-A K salt with $(4\text{-ClC}_6\text{H}_4)_2\text{SO}_2$ were treated with chloromethyl styrene to prepare polyether-polysulfones containing terminal styrene groups.

Polyether-polysulfones containing pendant styrene groups were prepared by chloromethylation of benzyl group-terminated polyether-polysulfones followed by the conversion of ClCH_2 groups to triphenylphosphonium salts and then to vinyl groups by the Wittig method with aq. HCHO in the presence of aq. NaOH and Triton B (phase-transfer catalyst). The thermal curing behavior of the styrene group-containing polymers was examined.

Feiring et al. [56] have synthesized fluorinated poly (ether sulfones) from bisphenols and α, ω bis (4-fluoro phenyl sulfonyl) per- fluoro alkanes. The fluorinated sulfone monomers were synthesized by reaction of 4-fluoro benzene thio salts with perfluoroalkylene diiodides followed by oxidation. Sodium carbonate mediate polymerization gave high molecular weight polymer in excellent yields. The polymers are generally soluble in chlorinated hydrocarbons and having T_g in the range of $120^0\text{-}160^\circ\text{C}$ and are stable to 400°C . They form clear colorless films.

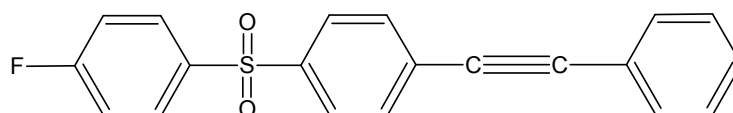
Virgil Percec et.al [57] have synthesized 4,4'-bis(phenoxy)diphenyl sulfone (I), 4,4'-bis(phenylthio)diphenyl sulfone (II), and I and II substituted with various electron-donating groups on the phenoxy units are synthesized and polymerized under oxidative reaction conditions. The presence of Me, tert-Bu, and methoxy groups as substituents on the phenoxy groups of I increased both the yield and the solubility of the resulting polymers. The structure-reactivity relationships of the monomers and of the growing species

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54. Virgil Percec, Brian C.Auman Dept. Macromol. Sci. Case West Reserve Univ. ClevelandOH, USA C.A. **100**: 192473, 1984
 55. Kiyoshi Ishii, Makoto Tamada Daicel Chemical Ind. Ltd. Japan, JP 63258930, 1987
 56. A.E.Feiring, R.W.Edward, S.D.Arthur J.Polym. Sci.Part A: Polym Chem. **28**, 10, 1990.
 57. Virgil Percec, J.H.Wang, Yoshi Oshi; J.Polym. Sci. Part A: Polym. Chem. **29(7)**, C.A. **115**: 9512, 1991.

are discussed based on a radical-cation mechanism of polymerization. Monomers of high nucleophilicity and resonance-stabilized radical-cation growing species are crucial to achieve polymers of high molecular weight. The structure of the polymers and in several cases of their chain ends are determined by $^1\text{H-NMR}$ spectroscopy. The mechanisms of termination and the side reactions occurring during this polymerization process are discussed based on the structures of the resulting polymers.

Virgil Percec and Wang [58] have reported the polymerizability of 4,4'-di(1-naphthoxy)diphenyl sulfone (I) and 1,5-di(1-naphthoxy)pentane (II) was investigated under oxidative polymerization (Scholl reaction) conditions. The polymerization of I consistently gave polymers of higher overall yields and number average molecular weights than polymerization of II. The higher polymerizability of I was discussed based on a radical-cation polymerization mechanism. I is less reactive than II, while the radical-cation growing species derived from I is more reactive than that derived from II. In these polymerizations, the overall polymerizability is determined by the difference in the reactivity of monomers and of their corresponding radical-cation growing species. A discussion on the selectivity as indicated by the polymer gel content also provides additional evidence for the difference in the reactivities between the growing species.

Mecham [59] has reported the synthesis of 4-fluoro-4'-phenyl ethynyl diphenyl sulfone (PEFDPS) was carried out in single step by palladium catalyzed oxidative addition of 4-bromo-4'-fluoro diphenyl sulfone to phenyl acetate tri ethyl amine at 120°C for 6-12h by using 0.01 parts $\text{P}(\text{Ph})_3$, 0.002 parts $\text{Pd}(\text{P}(\text{Ph})_3)_2\text{Cl}_2$ and 0.002 parts CuI .

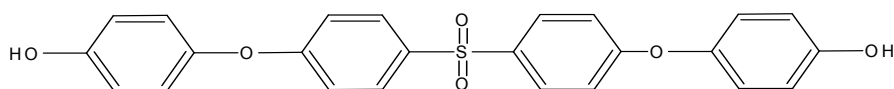


58 Virgil Percec, J.H.Wang *Polymer Bulletin* (Berlin, Germany),25(1); C.A.114:207906,1991.

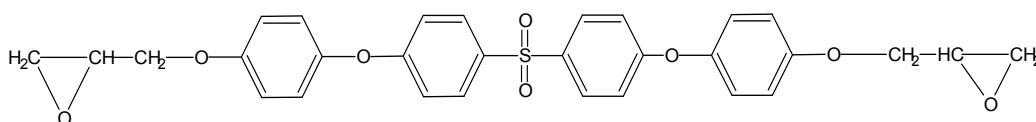
59 Sue Mecham, Ph. D Thesis *Synthesis and characterization of phenyl ethynyl terminated poly arylene ether sulfones as thermosetting structural adhesive and composite material* April 21, 1997

Gong et al. [60] had prepared an epoxy resin containing ether-ether-sulfone (II) units by reaction of 4-(p-hydroxy phenoxy) phenyl sulfone (I) with epichlorohydrin in basic media (I) was prepared from the aromatic nucleophilic substitution from 4-methoxy phenol and 4,4'-fluoro phenyl sulfone followed by deportation reaction of 4-(p-methoxy phenoxy) phenyl sulfone with hydrobromic acid.

Kricheldorf et. al. [61] have synthesized polyether-sulfone from 1,1',1''-tris(4-hydroxy phenyl)ethane with difluoro diphenyl sulfone by using 100 ml DMSO and 25 ml toluene at 140⁰-145⁰C (or 170⁰C). The toluene-water azeotrope was slowly distilled off and simultaneously toluene was replaced from the dropping funnel. After 6h the toluene was completely removed in vacuo and remaining DMSO solution was poured in to water to precipitate polymer, filtered washed and dried.

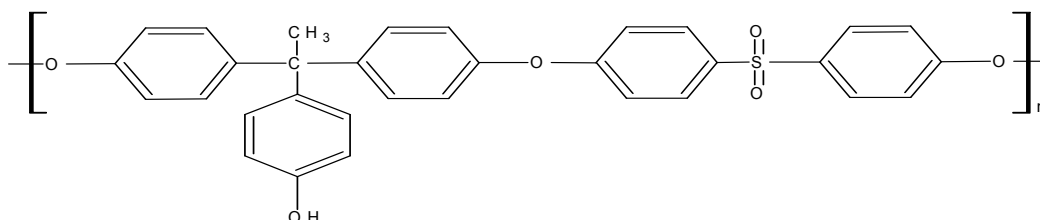


(I)



(II)

Simultaneously toluene was replaced from the dropping funnel. After 6h the toluene was completely removed in vacuo and remaining DMSO solution was poured in to water to precipitate polymer, filtered washed and dried.

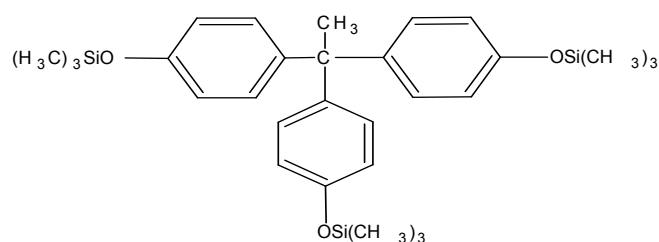


(I)

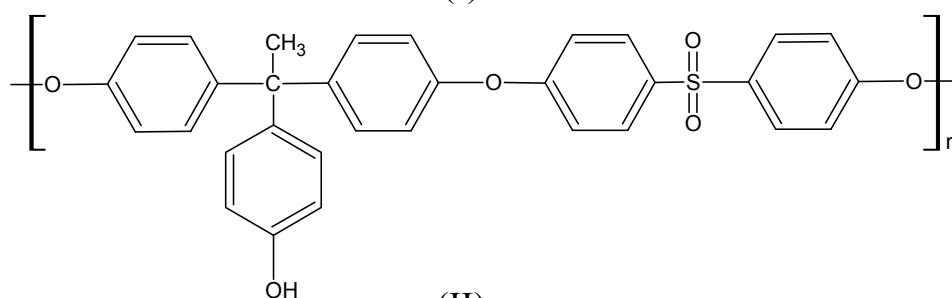
60 M. S. Gong, Y.C. Lee and G. S. Lee, Bull Korean Chem. Soc.,**22**, 12, 2001.

61 H.R.Kricheldorf,L.Vakhtangishvili, D.Fritsch; J.Polym.Sci.:Part A:Polym. Chem. **40**, 12, 2002.

Kricheldorf et. al.[62] have synthesized poly ether -sulfone from silylated 1,1',1''-tris (4-hydroxy phenyl)ethane(I), which was prepared by reaction of 0.4mol 1,1',1''-tris (4-hydroxy phenyl)ethane and 0.7mol hexamethyl disilazane at reflux temperature for 7h in 600ml dry toluene, the toluene was then removed with a rotary evaporator and product was crystallized. The yield was 96%. Silylated THPE was polymerized with 8.8mmol DFDPS in 8.8mmol dry K_2CO_3 in 60ml dry NMP at $180^\circ C$. After 24h, reaction mixture was diluted with NMP and poured in to water to precipitate (II).



(I)



(II)

Cuxian Chen et al [63] have prepared ultrafilter film from phthalazinyl polyether-sulfone-ketone and the second polymer such as polysulfone, polyether- sulfone, sulfonated polyether- sulfone, or polyvinylidene difluoride using solvents like NMP, DMA and/or DMF and additives such as polyethylene glycol, Tween-60, acetone, glycerol, and/or LiCl by mixing the raw materials in solvent at $70-90^\circ C$ for 10-24 h, vacuum deaerating at $25-30^\circ C$ to obtain film coating solution; and knife coating or spinning.

Okamoto and Sato et al [64] have manufactured aromatic polyether by condensation reaction of bisphenols $HOC_6H_4YC_6H_4OH$ (where $Y = SO_2,$

62 H.R.Kricheldorf, L. Vakhtangishvili, D. Fritsch; J. Polym. Sci.:Part A : Polym. Chem. **40**, 12, 2002

63. Cuxian Chen, Guoling Shi, J. Li, Zhen Chen, Takuji Shintani, Masaaki Ando Faming Zhuanil Shenqing Gongkai Shuomingshu, 10pp, C.A. 352986, 2003.

64. Kaunari Okamoto, Kunihisa Sato, Jpn. Kokai, Tokkyo Koho 11pp, C.A. **142**: 356045.

SO_2ArSO_2 , Ar=C₆₋₂₄ bivalent aromatic group; the benzene ring may be substituting by C₁₋₄ alkyl or alkoxy) and biphenyl compound. Dihalides $\text{XC}_6\text{H}_4\text{ZC}_6\text{H}_4\text{X}'$ (Z=SO₂, CO, SO, SO₂ArSO₂, COArCO; Ar = C₆₋₂₄ bivalent aromatic group; X, X'=halo; the benzene ring may be substituted by C₁₋₄ alkyl or alkoxy) in the presence of alkali metal carbonates or bicarbonates and aprotic polar solvents. Reactivity of Y reaches to 99.95 % when a system consisting of the alkali metal carbonates or bicarbonates and whole monomer dissolved in aprotic polar solvent is heated to reach the polymerization temperature. Thus, 100.11 parts 4, 4'-dihydroxydiphenyl sulfone (II) and 111.92 parts dichlorodiphenyl sulfone were dissolved in di-Ph sulfone at 170°C, mixed with 57.5 parts K₂CO₃, heated to 250°C, kept at that temperature for 4h. When reactivity of (II) reached 99.8%, further heated to 280°C (polymerization temperature). When the reactivity reached 99.98% and further polymerized at 280-283°C for 4.5h to give an aromatic polyether showing 400-nm light transmittance 52%.

Matthias Schmidt et al [65] have prepared the poly ether- sulfone (I) [R = 5-membered hetero ring containing 1 N atom. When the number of N atom is 1 then the atom attached to the benzene ring is C; n=10-150] is manufactured by halogenation of the parent poly (arylether-sulfone) (I; R₁=nil) (II), metalation of halogenated intermediate and conversion of metalated polymer with electrophilic 5-member heterocyclic compound containing 1N atom. The process is based on a Grignard reaction and is suitable for the large-scale manufactured of I that are useful in polymer electrolyte membrane fuel cells. For example, bromination of II with Br in the presence of Fe powder followed by forming Grignard compound of brominated II with Mg in THF and reacting the Grignard compound with 2-chlorobenzimidazole in THF at reflux gave a title polymer.

Chen et al.[66] have synthesized a novel series of random copolymers composed of poly (aryl-ether-sulfone-ether-ketone- ketone) by low temperature solution polymerization of 2,2',6,6'-tetramethyl-4,4'-

65 Matthias Schimidt, Ingo Schoenfelder, Thomas Soczka-Guth, Ger. Off. 13pp, C.A. 141: 395998, 2003.

66 Song Lie Chen, Wen Cai-Sheng, Tong Hong li, Liu Yong-Fen, Xiao-Ling Guocheng Gongcheng Xuebao, 4(5), C.A. 142 : 336967, 2004.

diphenoxydiphenylsulfone (o-M₂DPODPS), diphenyl ether (DPE) and terephthaloyl chloride (TPC) in 1,2-dichloroethane in the presence of AlCl₃ and DMF. The copolymers were characterized by ¹H-NMR, FT-IR, XRD, DSC, TGA, etc. The results showed that T_g increased with the increasing ratio of o-M₂DPODPS/DPE, the inherent viscosity, melting temperature and crystallinity of copolymers decreased with the increase of the ratio of o-M₂DPODPS/DPE. The solubility of the copolymer is improved greatly. The copolymers possess excellent thermal stabilities and solvent resistance. As a latent functional group, the bis (o-methyl) pendent can be converted to bromomethyl, aldehyde or carboxylic acid groups. The high-performance polymers with functional groups on the polymer mainchain for specialty application such as membrane materials can be prepared by functionalization reaction.

Hoffmann [67] has invented polymers from X-p-phenyl-SO₂NMSO₂R_fSO₂NMSO₂-p-phenyl-X', which are useful for fuel cells, where R_f = C₁-20 (1 etheric oxygen-substituted) linear or branched cyclic poly or per halogenated alkylene; M = monovalent cation; and X, X' = nucleophilic group selected from OH and SH or leaving group selected from F, Cl and NO₂. Thus, 100 g 1,4-diiodoperfluorobutane and 100 g Na₂SO₄ were reacted, treated with chlorine and reacted with potassium bromide to give perfluorobutane-1, 4- bisulfonyl fluoride, 15.0 g of which was reacted with 17.3 g 4-fluorobenzenesulfonamide and treated with KOH to give perfluorobutane-1,4-bis-4-fluorophenylsulfoneimide bipotassium salt, 2.258 g of which was polymerized with 2.010 g 4,4'-dichlorodiphenyl sulfone and 1.862 g 4,4'-bisphenol to give a copolymer with intrinsic viscosity 1.509 dl/g and conductivity 100mS/cm at 80°C and 95% RH.

Roy et al [68] have reported the synthesis of sulfonated poly (arylene-ether-sulfones) based on bisphenol and hydroquinone and related systems by exchange capacity, intrinsic viscosity, water sorption capacity, and proton conductivity increased with the degree of sulfonation. The salt form of the

67. M. A. Hoffmann, E. I. Dupont, De Nemours and Company, Jpn. Kokai. Tokyo, Koho, 19pp. CA:142 ;7200, 2004.

68. A. Roy, B. R. Einsla, W. L. Harrison and J. E. Mcgrath, preprints of symposia- American Chemical Society, division of fuel chemistry, 49(2), 2004; CA:142 ; 41311, 2004.

co polymers has increased thermo-oxidative stability relative to the acid form, and this stability decreases with sulfonation level.

Okamoto and Sato [69] have reported aromatic polyether -sulfone containing repeating units represented by the general formula $\text{OC}_6\text{H}_2\text{R}_1\text{R}_2\text{C}(\text{O})\text{C}_6\text{H}_2\text{R}_3\text{R}_4\text{OC}_6\text{H}_2\text{R}_5\text{R}_6\text{SO}_2\text{C}_6\text{H}_2\text{R}_7\text{R}_8$ ($\text{R}_1\text{-R}_8 = \text{H}, \text{C1-4 alkyl}, \text{C1-4 alkoxy}$) are prepared by reacting dihydroxybenzophenone $\text{HOC}_6\text{H}_2\text{R}_1\text{R}_2\text{C}(\text{O})\text{C}_6\text{H}_2\text{R}_3\text{R}_4\text{OH}$ with difluorodiphenylsulfones $\text{FC}_6\text{H}_2\text{R}_5\text{R}_6\text{SO}_2\text{C}_6\text{H}_2\text{R}_7\text{R}_8\text{F}$ ($\text{R}_1\text{-R}_8 = \text{same as above}$) in the presence of bases. Thus, 214.22 parts 4, 4'-dihydroxybenzophenone (I) was treated in an aqueous KOH to give dipotassium salt of (I), 61.3 parts of which was copolymerized with 51.1 parts 4, 4'-difluorodiphenyl sulfone in 41.9 parts di-Ph sulfone at 250°C to give an aromatic polyether sulfone with weight average molecular weight 124,000, polydispersity 2.8 and impact resistance 68 J/m (1.3 mm thick notched press-molded test piece, ASTM D 256).

Andrew et. al. [70] have reported sulfonated poly(arylene ether-sulfone) copolymers from 4,4'-biphenol and stoichiometric mixture of 3,3'-disulfonated and non-sulfonated 4,4'-di-chlorophenyl sulfone; the degree of disulfonation varied from 10-60%. The copolymers were characterized by intrinsic viscosity, DSC, TGA and molecular weight. The films were cast from 10% solution of DMAc. They were converted to acid and salt form for their biocompatibility.

Shohram and Laila [71] have synthesized poly (sulfone-ether- ester-amides) by the reaction of sulfone ether- ester- amine with diacid chloride in equimolar ratio with improved solubility. 2mmol of diamine was dissolved in 15ml dry NMP and the mixture was stirred at 0°C for 0.5 h and then about 1ml of propylene oxide was added. After a few minutes, 2 mmol of diacid chloride was added and the mixture was stirred at 0°C for 0.5 h. The temperature was raised to room temperature and the solution was stirred for 6h. Polyamide was isolated from water filtered, washed with hot water and

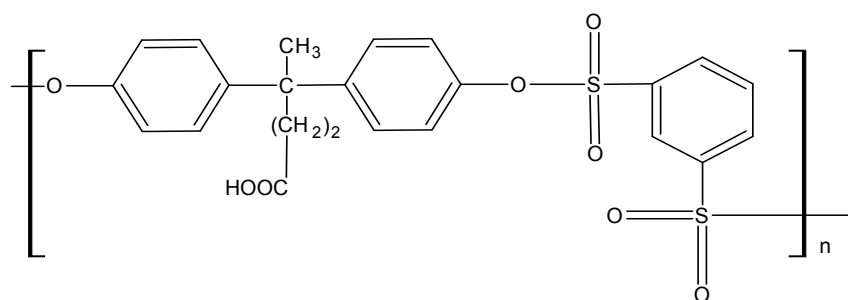
69. Kazunari Okamoto, Kunisha Sato Jpn. Kokai Tokkyo Koho, 9pp , C.A.**142**: 23969, 2004.

70. M. Andrew, T. Mukundam, J.E. McGrath J. Bioactive and Compatible Polymers **194**, 375, 2004.

71. Shohram Mehdipour-Ateai, Laila Akbarian Feizi; Polym. Bull. 0097 2004.

SECTION-3: AROMATIC CARDO POLY (ETHER-SULFONE-SULFONATES) COPOLYMERS.

Gevaert Photo Production [72] has reported the synthesis of linear polysulfonate from metal salt of 4, 4'-bis (4-hydroxy phenyl) valeric acid and 1, 3-benzenedisulfonyl chloride, which is insoluble in acid media but soluble in weak alkaline media. The disulfonyl chloride is dissolved or suspended in an inert organic liquid and the metal salts of bisphenol in a liquid immiscible with this organic liquid. Water-dichloromethane, sodium carbonate and benzyltriethyl ammonium chloride were used, respectively as an interphase system, an acid acceptor and a catalyst to prepare polysulfonate from 4,4'-bis(4-hydroxy phenyl) valeric acid and 1,3-benzenedisulfonyl chloride. The polymer was found soluble in dioxane, DMF, THF, and in a mixture of dioxane and ethylacetoacetate and has intrinsic viscosity of 0.83dl/g in dioxane at 25°C. The polymer is useful as a binder for photographic antihalation, antistress, antistatic or filter layers.



Thomson and Ehlers [73] have reported preparation and properties of aromatic polysulfonates. They have synthesized very pure high molecular weight polymers by interfacial polycondensation of diphenols with aromatic disulfonyl chlorides according to general scheme:

$$\text{OH-Ar-OH} + \text{ClO}_2\text{ArSO}_2\text{Cl} \rightarrow \text{-(O}_2\text{-S-Ar-SO}_2\text{-O-Ar-O-)-}$$

Where Ar may be m-C₆H₄, (p-C₆H₄), (p-C₆H₄)₂O, (p-C₆H₄)₂CH₂, (p-C₆H₄)₂SO₂. They have also prepared a polymer from 1,3,5-benzene trisulfonyl chloride and 4,4'-biphenol by interfacial polycondensation. The polymers were characterized by IR, light scattering, x-ray diffraction and thermal analysis. The IR spectra of

72. Gevaert Photo Production N.V., Belg. Pat. 600,053 (1961); C.A. **58**, 11,491, 1963

73. D.W. Thomson and G.F.L. Ehlers, J. Polym. Sci. Pt. A-2 (3), 1,051, 1964; C.A. **60**, 13, 332, 1964

polysulfonates showed characteristic stretching vibration of sulfonate linkage at $1200\text{-}1145\text{ cm}^{-1}$ and $1420\text{-}1330\text{ cm}^{-1}$. The polymers have average molecular weight of about 50,000 (LS), low degree of crystallinity (XRD) and limiting solubility in common organic solvents. Thermal study showed that the polymers were thermally stable above 200°C in an N_2 atmosphere and softening temperature range from $200\text{-}250^{\circ}\text{C}$ and decomposed readily with the evolution of SO_2 . They have reported the hydrolytic stability of polymers towards both acids and bases at room temperature.

They have concluded that the polymers with high molecular weight and thermal stability were obtained from more rigid structure such as biphenyl and biphenyl sulfone.

Conix and Dohmen [74] have reported thermoplastic and noncombustible polymers from bisphenols with aromatic disulfonyl chloride and bisphenols with aromatic disulfonyl chloride and bisphenols with dihalide of dicarboxylic acids using 0.01-5% catalyst based on the weight of bisphenol (quaternary ammonium or phosphonium or arsonium compounds, tertiary sulfonium compounds consisting of PhPOCl_2), at a temperature between $0\text{-}10^{\circ}\text{C}$ and the b.p. of the solvent used (preferable $<0^{\circ}\text{C}$).

General Electric Co. [75] has reported the two phase synthesis of aromatic polysulfonates of low molecular weight. The polymer was prepared by dissolving the anhydrous monomer in an organic solvent in the presence of HCl acceptor. High molecular weight linear polymer is acid and base resistant and can be used for the preparation of films, molding fibers, etc. Polysulfonate film molded at 260°C has excellent acid and base resistance. X-ray analysis showed that polymer has amorphous structure.

Fontan et al. [76] have reported interfacial synthesis and properties of polysulfonates of 1,3-benzene disulfonyl chloride with bisphenol-A (I), bisphenol-B (II), hydroquinone (III) and bromohydroquinone (IV). Thus, 0.05 mole II in 250 ml dichloromethane was treated with 0.05 mole benzene 1,3-

75. General Electric Company, Neth. Appl. Pat. 6, 600, 874, 1966; C.A. **66**, 19, 035, 1967

76. Y.J.Fontan, O.Laguna and J.Shih, J. An.Quim. 64(4),389 (1968); C.A. **69**, 19,647 1968.

bis(sulfonyl chloride) in the presence of 0.5 ml benzyltrimethyl ammonium chloride, 0.05 g sodium lauryl sulfate and 0.05 g Na₂CO₃ at room temperature for 30 minutes to give polysulfonate in 70% yield.

They have also synthesized other polysulfonates using dichloromethane and toluene as solvents. The polysulfonates of bisphenol-A with 1, 3-benzenedisulfonyl chloride was prepared in the absence of catalyst. They have obtained following results:

No	Phenolic monomer	Yield %	Softening Point, °C	No. Ave.mol.wt	[η]	Temp. of Max. degradation °C
I	Bisphenol-A	53-77	110-36	2200-8000	0.04-0.2	340-400
II	Bisphenol-B	50-70	123-47	8000-16000	0.36-0.61	330-55
III	Hydroquinone	60	170-200	3200-110000	0.023-0.06	293-300
IV	Bromohydro quinine	52-60	120-47	—	Insoluble	245-83

Work and Herweh [77] have reported interfacial synthesis and thermo-mechanical properties of polysulfonates of 1, 3-benzene disulfonyl chloride, 3, 3'-bis (chlorosulfonyl) benzophenone and bis(m-chloro sulfonyl) methyl phosphine oxide. They have reported the shear storage modulus, melt temperature, crystallinity, specific viscosity and Tg curves.

Kuznetsov and Faizullina [78] have reported the synthesis of phosphorus containing polysulfonates. The polysulfonates of benzene-1,3- and toluene-2,4-disulfonyl chlorides with propyldimethylol phosphine and dimethylol phosphate were prepared by solution polycondensation in p-xylene at 90-120°C. The activation energy for the reaction of toluene-2, 4-disulfonyl chloride with propyldimethylol phosphine was 11.5±0.8kcal/mole and with dimethylol phosphate 14.1±0.9kcal/mole. The sulfonate of propyldimethylol phosphine showed IR characteristics absorption bands

77 J. L. Work and E. Herweh, J. Polym. Sci. Pt. **A-1**, 6(7), 2022, 1968; C.A. **69**, 28,022, 1968

78 E. V. Kuznetsov and D.A.Faizullina, Tr,Kazan.Khim. Tekhnol. Inst.No.**36**, 415, 1967; C.A. **69**, 107, 143, 1968

at 1149, 1077 and 1226 cm^{-1} due to OSO_2 , S:O and P:O groups. They have also reported properties of polysulfonates prepared:

Disulfonyl chloride	Diol compound	Solubility	$[\eta]$
Benzene-1,3	Propylene Dimethylol phosphine	$\text{HCON}(\text{CH}_3)_2$, $(\text{CH}_3)_2\text{SO}$, CH_3OH	0.18
Toluene- 2,4	Propylene dimethylol phosphine	$\text{HCON}(\text{CH}_3)_2$, $(\text{CH}_3)_2\text{SO}$, CH_3OH	0.13
Benzene-1,3	Dimethylol phosphonate	$\text{HCON}(\text{CH}_3)_2$, $(\text{CH}_3)_2\text{SO}$	0.22
Toluene- 2,4	Dimethylol phosphonate	$\text{HCON}(\text{CH}_3)_2$, $(\text{CH}_3)_2\text{SO}$	0.24

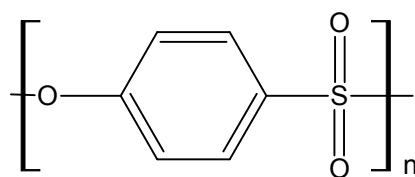
Schlott et al. [79] have reported preparation and properties of aromatic polysulfonates. Aromatic polysulfonates are thermoplastic materials having unique stability towards hydrolytic attack. The incorporation of aromatic sulfonated – ($-\text{Ar}-\text{SO}_2-$) - linkage into copolymer structures provides good chemical stability to the copolymer. Engineering thermoplastics can be developed based upon aromatic sulfonated co polyesters, which possess an outstanding balance of mechanical properties.

Ehlers et al. [80] have reported thermal degradation of poly (p-phenylene sulfide), poly(arylene sulfone) and poly (arylene sulfonate) in vacuum at 225⁰-260°C. The elimination of sulfur dioxide is practically completed at 450°C for the polysulfone and at 350°C for the polysulfonates.

Campbell [81] has reported the synthesis of high molecular weight poly(phenylene sulfonate) (I) having good mechanical properties from hydroxy

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79. R.J.Schlott, E.P.Goldberg, D.F.Scardiglia and D.F.Hoeg, Adv.Chem. Ser. No. 91,703, 1969; C.A. **72**, 21,966, 1970.
80. G.F.L.Ehlers, K.R.Fisch and W.R.Powell, J. Polym. Sci. Part A-1, 7(10), 2931, 1969; C.A. **72**, 3,904, 1970.
81. R.W.Campbell, U.S.Pat. 3,549,595, 1970; C.A. **74**, 54, 403, 1971.

benzenesulfonyl halides, dissolved in cyclic ketone or polar carboxylic acid amide solvent in the presence of a tertiary amine or alkaline earth hydroxide as an acid acceptor. Thus, a mixture of 1.93g 4-hydroxybenzenesulfonyl chloride, 8ml N-methyl-2-pyrrolidone and 6ml dimethylacetamide was treated with triethylamine at 37°C to yield 71% poly(phenylene sulfonate) having intrinsic viscosity of 0.56 dl/g (4% LiCl in N-methyl-2-pyrrolidone at 30°C). The polymer is soluble in hot acetone, cyclohexanone, cyclodecanone but soluble in DMF.



Campbell and Hill [82] have synthesized high molecular weight poly(phenylene sulfone) by the self condensation of hydroxy benzene sulfonyl halides in the presence of tertiary amine or alkali earth metal catalyst using hexahydrocarbyl phosphoramidate as a reaction diluent under nitrogen atmosphere.

The polymer showed inherent viscosity of 0.89dl/g in hexamethylene phosphoramidate at 30°C and may be used for preparing fibers, films and molded articles.

Kuznetsov et al [83] have prepared nitrogen and phosphorous containing polysulfonates in the side chain by the condensation of $(\text{HOCH}_2\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{P}(\text{O})(\text{OR})_2$ type organo phosphorous diols (R= Me, Et, Pr, Bu, or n-C₆H₁₃) with arylene disulfide of $\text{ClSO}_2\text{R}'\text{SO}_2\text{Cl}$ (R'= p-C₆H₄, 2,4-toluene or 1,5-naphthylene) in the melt at 180-210°C. The solid glass like polymers showed the solubility in DMF and Me₂SO, activation energy of 11-18 kcal/mole and second order reaction kinetics. The % amount of phosphorous, sulfur and nitrogen were found to be 5-7%, 10-15% and 2-4%, respectively.

Nishimura et al [84] have reported the synthesis of polyether-

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- 82 R.W.Campbell and H.W.Hill, U.S.Pat. 3, 656, 862, 1971; C.A.**74**, 1, 27, 378, 1971.
 83 E.V.Kuznetsov, D.A.Faizullina, I.N.Faizullina and T.N.Lavrent'eva, Tr.Kazan.Khim.Tekhnol. Inst., 40(2), 351, 1969; C.A.**75**, 77, 311, 1971.
 84 S.Nishimura, S.Amano and H.Kojo, Japanese Pat. 71, 12, 149, 1971; C.A. **75**, 141, 598, 1971.

polysulfonate resin of bisphenol-epichlorohydrin (I) with an aromatic bis (sulfonyl halide) (II) in the presence of excess alkali metal at $<50^{\circ}\text{C}$. (I) and (II) were used in amounts such that the initial ratio of OH to SO_2X group was 1:1. Thus, 4, 4'-diphenyl ether bis (sulfonyl chloride) reacts with bisphenol-A epichlorohydrin polycondensate in a mixture of chloroform and aqueous sodium hydroxide at $24\text{-}27^{\circ}\text{C}$ to give bisphenol-A-epichlorohydrin polycondensate-4, 4'-diphenyl ether bis (sulfonyl chloride) copolymer.

Studinka and Gabler [85] have synthesized thermoplastic film forming and heat resistant polythioethers by condensing aromatic diols, dithiols or hydroxy thiols with aromatic dihalide in N-alkyl caprolactum containing acid binding bases or salts. Thus, the mixture of 11.415 g 2,2'-bis(4-hydroxy phenyl) propane, 25.172 g, 4,4'-bis (4-chloro phenyl sulfonyl) biphenyl and 6.995 g Na_2CO_3 in 50ml N-methyl caprolactum was heated at 210°C for 5h in an N_2 atmosphere gave a copolymer with reduced specific viscosity of 0.63 (0.2 g in 100 ml CHCl_3) at 0°C .

Firth [86] has reported synthesis of high molecular weight film forming polysulfonate from bis(fluorosulfate) of bisphenol-A.(228.3parts) was heated with SO_2F_2 (204 parts) to give a bisphenol-A bis(fluorosulfate) (134 parts) (I).The polysulfate was synthesized by treating (I) with bisphenol-A and NaOH in Me_2SO and heating the mixture 2h at $150\text{-}165^{\circ}\text{C}$.

Campbell and Hill [87] have reported synthesis of high molecular weight polysulfonate by solution polymerization of 4-hydroxybenzenesulfonyl chloride (I) in the presence of tertiary amine as a catalyst in polar amine solvent. The highest molecular weight polymer has obtained at 1.25 equivalent amount of tertiary amine in hexamethyl phosphoramidate at 0°C . The polymer has Tg of 119°C and a crystalline melting temperature of 276°C . They have also synthesized polymer of 3, 5-dimethyl-4-hydroxybenzenesulfonyl chloride (II) as well as copolymer of (I) and (II).

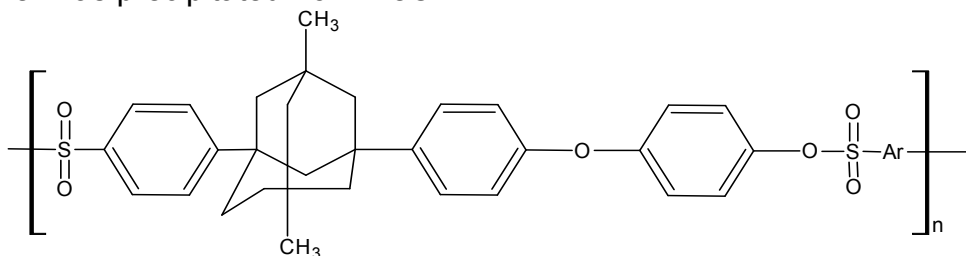
85. J.Studinka and R.Gabler, Ger. Pat. 2,220,079 (1972); C.A. **78**, 44, 219, 1973

86. W.C.Firth, U.S.Pat. 3,733,304 (1973); C.A. **79**, 92, 789, 1973

87. R.W.Campbell and H.W.Hill, Macromolecules, 6(4), 492(1973); C.A. **80**, 15, 237, 1974

Thompson and Duling [88] have reported the moldable thermoplastic polysulfonates (I) from adamantane bisphenols and disulfonyl chlorides of aromatic substituted ether:

They have also reported 5, 7-dimethyl adamantane 1, 3-bisphenol and 4, 4'-disulfonyl chloride of diphenyl ether by refluxing the monomers (0.02:0.02 mole) in the presence of 0.048 mole triethylamine in CH_2Cl_2 and polymer was precipitated from MeOH.



They have also reported 5, 7-dimethyl adamantane 1, 3-bisphenol and 4, 4'-disulfonyl chloride of diphenyl ether by refluxing the monomers (0.02:0.02 mole) in the presence of 0.048 mole triethylamine in CH_2Cl_2 and polymer was precipitated from MeOH. The copolymer showed the inherent viscosity and heat distortion temperature of 1.2 in tetrachloroethylene and of 180°C , respectively.

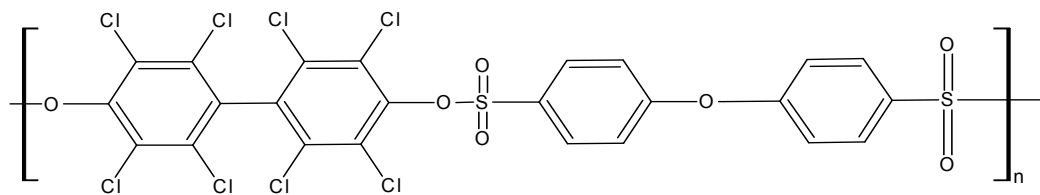
Thomas [89] has reported the synthesis of high performance polysulfonate resin from 4, 4'-[4, 4'-carbonyl bis (4, 1'-phenyleneoxy)] bisbenzenesulfonyl chloride (I) and bisphenol-A. I was prepared by reaction of diphenyl ether with phosgene and chlorosulfonic acid. Thus, a solution of bisphenol-A (4.56g) in 41 ml NaOH (1N) was treated with a mixture containing (I) (11.26g) and benzyltrimethylammonium chloride (0.1g) in 50 ml dichloromethane stirred at room temperature. The polymer was precipitated in methanol to give polymer with intrinsic viscosity of 2.12 in trichloroethylene at 25°C .

Hata and Takase [90] have reported the synthesis of fire-resistant aromatic polysulfonates by interfacial poly condensation of aromatic disulfonylchloride with octahalobisphenol (I).

88. R.M.Thompson and I.N.Duling, U.S.Pat.3, 753, 950, 1973; C.A. **80**, 15,636, 1974

89. R.J.Thomas, U.S.Pat. 3, 845, 015, 1974; C.A. **82**, 112,647, 1975

90. N.Hata and Y.Takase, Japanese Pat. 7, 432, 797, 1974; C.A. **82**, 125, 845, 1975.



Thus, a mixture of 4, 4'-dihydroxy octachlorobiphenyl (115, 541 parts), KOH(28, 054 parts), water (120 parts), benzyltrimethylammonium chloride (0.2 parts) and 15% aq. surfactant (10 parts) was added to a solution of 4, 4'-diphenyl ether disulfonyl chloride (91, 545 parts) in CHCl_3 (74.5 parts) and polymerized for 1h at $20\text{-}5^\circ\text{C}$ and 5h at 60°C . The polymer has T_g 190°C , tensile strength 610 kg/cm^2 , tensile modulus 2.00×10^4 and elongation 7.0%.

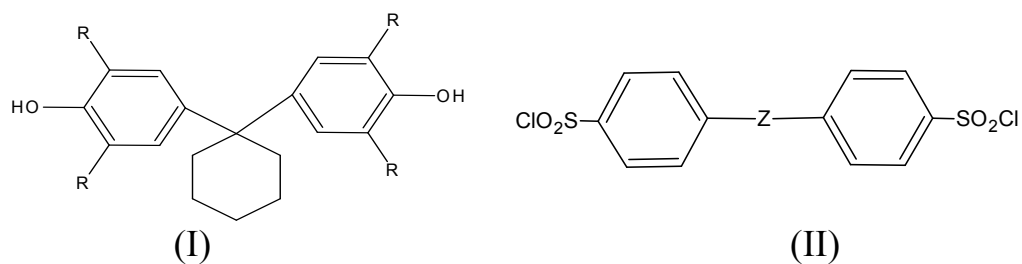
Imai et al [91] have reported the phase transfer catalysed polycondensation of aromatic polysulfonates. They have found that crown ethers: 15-crown-5, 18-crown-6, dibenzo-18-crown-6, dicyclohexyl-18-crown-6 (I), dibenzo-24-crown-8 and dicyclohexyl-24-crown-8 are effective catalyst for the preparation of polysulfonate from 4,4'-oxydiphenylsulfonyl chloride and bisphenol-A in dichloromethane-aqueous alkaline solutions at room temperature. Dicyclohexyl-18-crown-6 is the best catalyst for the quantitative yield of polysulfonate with inherent viscosity < 1.4 .

Imai et al [92] have reported the synthesis of high molecular weight aromatic polysulfonates by interfacial poly condensation of aromatic disulfonyl chloride with sodium salts of bisphenols using quaternary ammonium salts as phase transfer catalyst. The polysulfonates are soluble in dichloromethane and tetrahydrofuran; and have thermal decomposition temperature of 300°C in an air or nitrogen.

Podgorski and Podkoscielny [93] have reported the interfacial polycondensation of cardo bisphenols (I) (where $R = \text{Br}, \text{Cl}$) with disulfonyl chloride (II) (where $Z = \text{direct bond, O, S, CH}_2, \text{CH}_2\text{CH}_2, \text{SO}_2, \text{CO}$) using water-alkyl halide ($\text{CHCl}_3, \text{C}_2\text{H}_2\text{Cl}_2, \text{CCl}_4$, etc) as an interface in the presence or

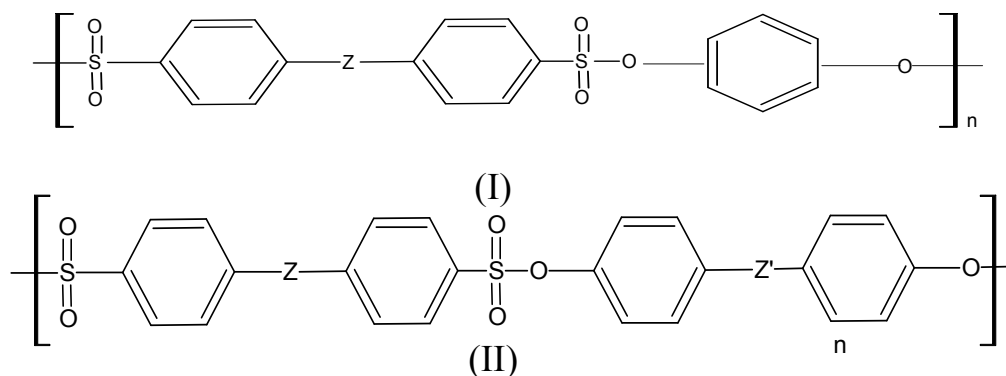
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91. Y. Imai, M. Ueda and M. Ii, Makromole. Chem. 179(8), 2085 (1978); C.A. **89**, 1, 29, 985, 1979
92. Y. Imai, M. Ueda and M. Ii, Kobunshi Ronbunshu, **35(12)**, 807 (1978); C.A. **90**, 87, 899, 1979
93. M. Podgorski and W. Podkoscielny, POL PL. 110, 187 (1981); C.A. **96**, 1, 22, 395 (1982).

absence of an emulsifier benzyltrimethylammonium chloride (III) at 15-30°C.



Thus, to a solution of 0.02 mole (I) (R=Br) in 50 ml water containing 0.04 mole NaOH, 0.1 g benzyltrimethylammonium chloride, a solution of 0.02 mole (II) (Z=O) in 40 ml CH₂Cl₂ was added within 40 min. The mixture was stirred at room temperature for 1h and then poured into 150 ml isopropanol to give 73.7% polymer. The polymer had melting range of 205-220°C, reduced viscosity of 0.1 (0.1% in CH₂Cl₂ at 25°C). Extension of reaction time from 1h to 2.5 h increased the yield of polymer (92.3%) and its melting temperature and reduced viscosity 280-295°C and 0.96, respectively.

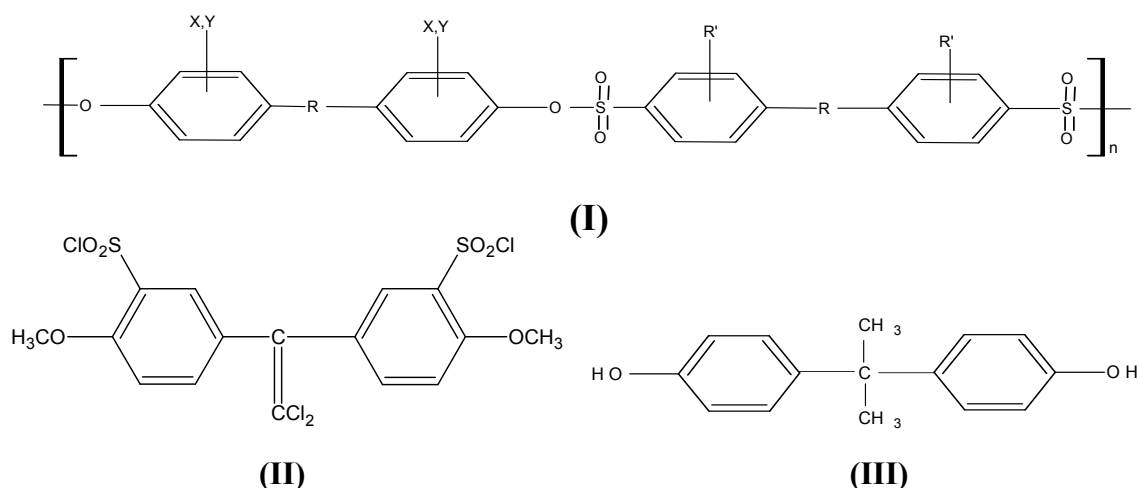
Vizgert et al [94] have synthesized polysulfonates (I) and (II) by the polycondensation of mono or binuclear bisphenols with 4,4'-disulfonyl chlorides of biphenyl, diphenylene oxide, diphenyl sulfide and diphenyl sulfone at low temperature in the presence of triethylamine as a catalyst and hydrogen chloride as an acid acceptor where Z=direct bond, O, SO₂, S and Z'= CMe₂, SO₂. The polysulfonates are heat resistant with high hydrolytic stability and good electrical insulating properties. They have found that polymers changed gradually from solid to a molten state over the temperature range from 340-450°C and polysulfonate containing a sulfone bridge does not melt up to 500°C.

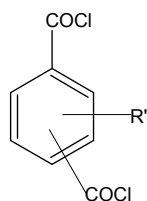


Podgorski and Podkoscielny [95] have reported the interfacial synthesis of thermally and chemically stable aromatic polysulfonates of 4, 4'-norboran-2-ylidene bis (2, 6-dibromo phenol) (II) with aromatic disulfonyl chlorides in the presence of alkali hydroxide or carbonates and optionally with catalyst or emulsifier. Thus, 11.92 g (II) in CH_2Cl_2 was stirred with 7.34 g 4,4'-oxy dibenzene sulfonyl chloride and aqueous hydroxide gave polysulfonates with 89.7% yield. The polymer showed reduced solution viscosity of 0.27 dl/g and melting range of 260-280°C.

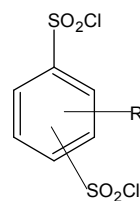
Brzozowski et al. [96] have reported the preparation of polyaryl-sulfonate (I), its modification and significant applications as fire proofing lacquers and paints. The polyaryl-sulfonates (X,Y=H, alkyl, alkoxy, Br, Cl; R, R'=dichloroethylene, 1,2-dichloroethane, isopropylidene, methylene group) were synthesized by the polycondensation of disulfonyl chloride (II) with 2,2'-bis(4-hydroxyphenyl) 1,1'-dichloroethylene (III) or bisphenol-A. Thus, a solution of 4.05 g (II) in methylene chloride was added with vigorous stirring to a mixture containing 2.81 g (III) in aqueous NaOH and aqueous triethyl benzyl ammonium chloride, and then acidified for pH-1.

The polymer has been isolated from cooled MeOH with stirring. The polymer showed solubility in solvent mixture of acetone (40ml), dioxane (12ml) and cyclohexanone (5ml).





(VI)

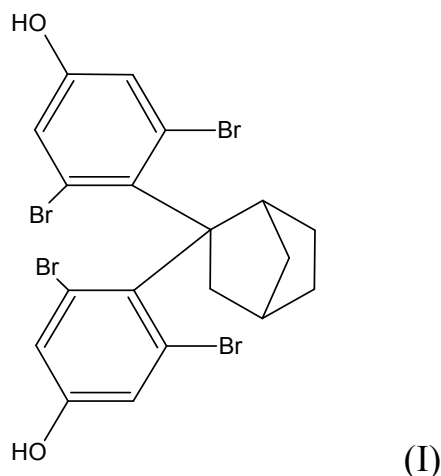


(V)

Polymer (I) has optionally modified with dicarbonyl dichloride (IV) and disulfonyl chlorides (V) They have prepared fireproofing lacquer consisting: polyaryl sulfonates (I) (1-50 parts), solvent such as acetone, methyl ethyl ketone, cyclohexanone and/or dioxane (10-35 parts), synergistic Sb and/or P compounds, dyes, pigments, plasticizers, lubricants, surfactants and antistatic agents (<30 parts), respectively.

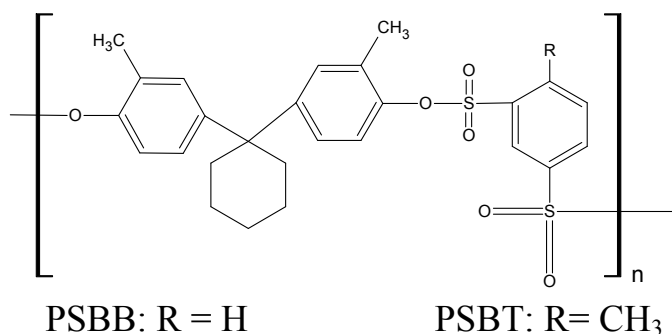
Brzozowski and Warpechowska [97] have reported the condensation of bisphenols with organic diacid chloride and/or organic disulfonyl chloride at an interface of immiscible aqueous and organic phase by using ultrasound at 20-40 kHz for 15-60 min. Thus, the solution of 3.55 g 2, 2'-bis (3-chlorosulfonyl-4-methoxyphenyl) 1,1'-dichloro ethylene and 0.61 g terephthalic acid chloride in CH_2Cl_2 was added to a solution of 2.81 g 2,2'-bis(4-hydroxy phenyl) 1,1'-dichloro methylene, 100 mg NaOH in water and a solution of 0.073 g triethyl benzyl ammonium chloride in water and with stirring mixture was exposed to sound at 30kHz at 20-25°C. Then, the mixture was acidified to $\text{p}^{\text{H}}-1$ by treating with 5% HCl and polymer was isolated from boiling water. They concluded that the ultrasonic treatment increased the phase interface and accelerate the reaction rate.

Podgorski and Podkoscielny [98] have reported the interfacial synthesis of heat resistant norborane group containing polysulfonates from bisphenols (I) and benzenedisulfonyl chloride or its alkyl derivatives in the presence of catalyst, emulsifier and alkali metal hydroxide or carbonates as hydrogen chloride acceptor at 5-50°C.



Thus, 0.02 mole (I) (X=Br) condensed with 0.02 mole m-benzenedisulfonyl chloride using water-CH₂Cl₂ as an interface, 0.04 mole sodium hydroxide as an acid acceptor and 0.1 g benzyl trimethyl ammonium chloride as a catalyst for 1h, 40min at 25-29°C. The copolymer had 0.23 dl/g reduced viscosity in 1, 1'2, 2'-tetrachloroethane and m.p. of 270-300°C.

Desai et al [99,100] have reported the synthesis of cardo polysulfonates of 1,1'-bis(4-hydroxy phenyl) cyclohexane with benzene-1,3 and toluene-2, 4-disulfonyl chlorides by interfacial poly condensation using water-chloroform as an interface, alkali as an acid acceptor and cetyl trimethyl ammonium bromide as an emulsifier at 0°C for 3h. PSBB and PSBT possess excellent solubility in common solvents.

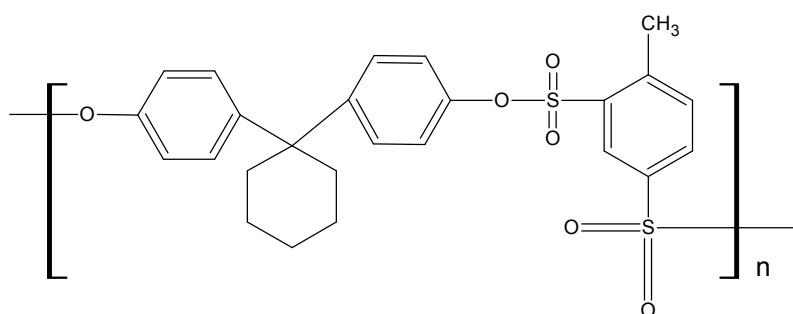


The polysulfonates had 0.3 to 0.6 dl/g reduced viscosity and possess excellent hydrolytic stability towards acids and alkalis. PSBB and PSBT have good biological activities against *E. coli.* and *S. citrus* microbes. A 0.610 mm

99. J.A.Desai, U.Dayal and P.H.Parsania, J. Macromol. Sci.-Pure and Appl. Chem. **A33**, (8), 1113, 1996
100. J.A.Desai,P.A.Krishnamoorthy and P.H.Parsania, J. Macromol. Sci.-Pure and Appl. Chem. **A-34**, 1171, 1997

PSBB and 0.537 mm PSBT thick films have 8.23 ± 0.25 and 9.6 ± 0.45 kV, respectively dielectric breakdown voltage (ac) in an air at room temperature. The same films have 8.8×10^{11} and 7.2×10^{14} ohm cm volume resistivity, respectively. A $40 \mu\text{m}$ PSBB and $50 \mu\text{m}$ PSBT thick films have 1971 and 1677 kg/cm^2 tensile strength and 1.3 and 1.2% elongation, respectively. A 0.178 mm PSBB and 0.190 mm PSBT thick films have 12.8-15.6 and 12.4-16.5 kg/m^2 static hardness, respectively. Both polymers are thermally stable up to about 355°C in an N_2 atmosphere and involve two-step degradation. PSBB and PSBT have $125\text{-}127^\circ\text{C}$ and $138\text{-}142^\circ\text{C}$ Tg.

Kamani and Parsania [101,102] have reported synthesis of cardo polysulfonate (PSMBC) of 1,1'-bis(3-methyl-4-hydroxy phenyl)cyclohexane with toluene-2,4-disulfonyl chloride by interfacial poly condensation using water-chloroform as an interface and alkali as an acid acceptor, cetyl trimethyl ammonium bromide as an emulsifier at 0°C for 3h. PSMBC has moderate antibacterial activity against E. coli and S.citrus and has good hydrolytic stability. A $71 \mu\text{m}$ thick film has 170kg/cm^2 tensile strength, 5.2% elongation and 22 kg/cm toughness. A 0.192 mm thick film has 13 to 16 kg/mm^2 static hardness at different loads (20-60g). PSMBC is stable up to about 340°C in an N_2 atmosphere and involves two step degradation and has 141°C Tg.



Shah et al. [103,104] have reported the synthesis and biological activity and chemical resistance of poly (4, 4'-cyclohexylidene-R, R'-diphenylene-3, 3'-benzophenone sulfonates) (I) by interfacial poly condensation.

101. M.M.Kamani and P.H.Parsania, J.Polym.Mater. **12**, 217, 1995.

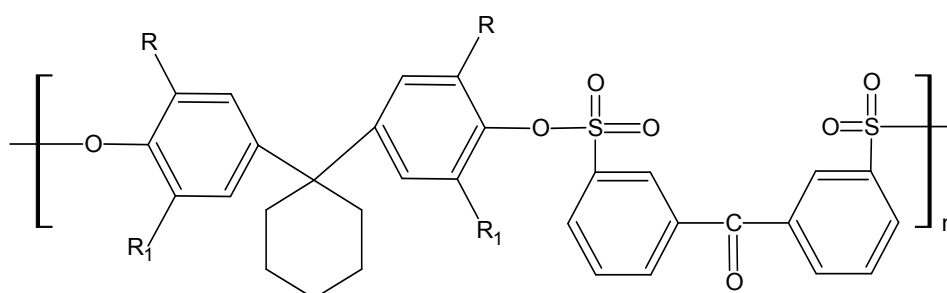
102. M.M.Kamani and P.H.Parsania, J.Polym.Mater. **12**,223, 1995.

103. A.R.Shah, Shashikant Sharma and P.H.Parsania, J.Polym.Mater. **14**, 1997.

104. A.R.Shah and P.H.Parsania, J.Polym.Mater. **14**, 171, 1997.

Polysulfonates have excellent solubility in common organic solvents and have moderate to comparable biological activity against *E. coli*, *A. arogen*, *S. citrus*, *B. mega*, *B. subtilis* and *A. niger*. PS-2 has excellent acid and alkali resistance.

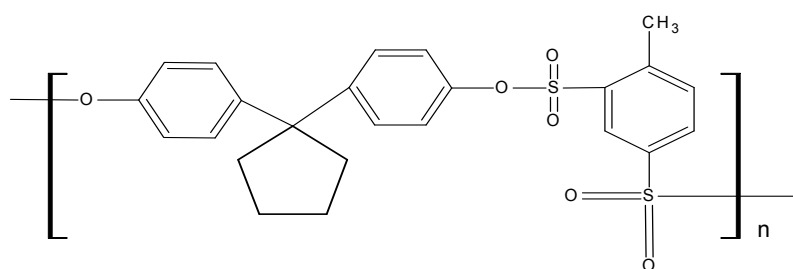
PS-1 to PS-4 have 126°C, 120°C, 121°C and 123°C T_g and are thermally stable up to about 350-365°C. A 77.3 μm thick PS-2 film has 10.4 kV breakdown voltage at room temperature and a 70μm thick film has 26.5kg/cm² tensile strength and about 2% elongation. PS-2 has 15-17 kg/mm² static hardness.



PS-1: R=R₁=H
PS-2: R=R₁=Cl

PS-2: R=CH₃ and R₁=H
PS-4: R=CH₃ and R₁=Cl

Rajkotia et al. [105] have reported the synthesis of poly (4, 4'-cyclopentylidene diphenylene toluene-2,4-disulfonate) (PSBPT) by interfacial polycondensation using water-chloroform as an interface, alkali as an acid acceptor and cetyl trimethyl ammonium bromide as an emulsifier. PSBPT has excellent solubility in common organic solvents and excellent hydrolytic stability towards acids and alkalis. A 40 μm thick film has 200.1 kg/cm² tensile strength and 0.6% elongation at break. A 0.19 mm thick film has 14.5 to 16.5kg/cm² static hardness. PSBPT has 134° C T_g and is thermally stable up to about 355°C in an N₂ atmosphere and involves two-step degradation.



Karia and Parsania [106,107] have reported the cardo polysulfonates of diphenyl methane-4,4'-disulfonyl chloride and 1,1'-bis (4-hydroxy phenyl) cyclohexane/1,1'-bis(3-methyl-4-hydroxy phenyl) cyclohexane by interfacial poly condensation using water-chloroform as an interface, alkali as an acid acceptor and cetyl trimethyl ammonium bromide as an emulsifier at 0°C for 3h. PSBD and PSMD possess good acid and alkali resistance and moderate biological activities against *E. coli* and *Aspergillus awamori* microorganisms. A 90 μm thick PSBD film and 60 μm thick PSMD have 7.7 and 10.1 N/mm^2 tensile strength and ~2 and ~1% elongation at break, respectively. The same films exhibited electrical strength and volume resistivity of the order of 27.1-27.5 kV/mm and $5.5\text{-}5.8 \times 10^{15}$ ohm cm, respectively. PSBD and PSMD are thermally stable up to about 325°C in an N_2 atmosphere and has 130°C and 125°C T_g , respectively.

Godhani et al.[108] have reported synthesis of cardo polysulfonates of phenolphthalein (0.01mol)with 4,4'-diphenyl disulfonyl chloride/4,4'-diphenylether disulfonyl chloride/4,4'-diphenyl methane disulfonyl chloride/3,3'-benzophenone disulfonyl chloride (0.01mol) by using water-1, 2-dichloroethane (2:1 v/v) as an interphase, alkali as an acid acceptor and cetyl trimethyl ammonium bromide as an emulsifier. The reaction time and temperature were 3h and 0°C, respectively. IR and NMR spectral data support the structures. Polysulfonates possess excellent solubility in common solvents except PHDPM, moderate to comparable antimicrobial activity against *E. coli* and *S. aureus*, good hydrolytic stability towards acids, alkalis and salt, moderate tensile strength (24-50 N/mm^2), high T_g (212-228°C), excellent thermal stability (316-388°C), excellent volume resistivity ($3\text{-}13 \times 10^{15}$ ohm cm), good to excellent electrical strength (12-41 kV/mm) and good dielectric constant (1.4-1.8).

Patel and Parsania [109-111] have reported the synthesis of cardo

106. F.D.Karia and P.H.Parsania, *Eur. Polym. J.*, **35**, 121, 1999.

107. F.D.Karia and P.H.Parsania, *J. Polym. Mater.*, **16**, 161, 1999.

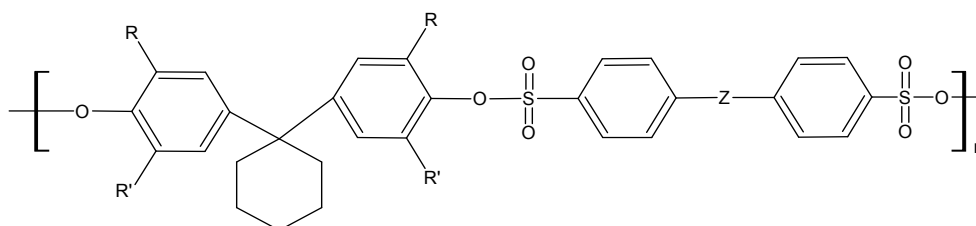
108. D.R.Godhani, M.R.Sanaria, Y.V.Patel and P.H.Parsania, *Eur. Polym. J.*, **38**, 2171, 2002.

109. Y.V.Patel and P.H.Parsania, *Eur. Polym. J.*, **21**, 711, 2002

110. Y.V.Patel and P.H.Parsania, *Eur. Polym. J.*, **38**, 1827, 2002

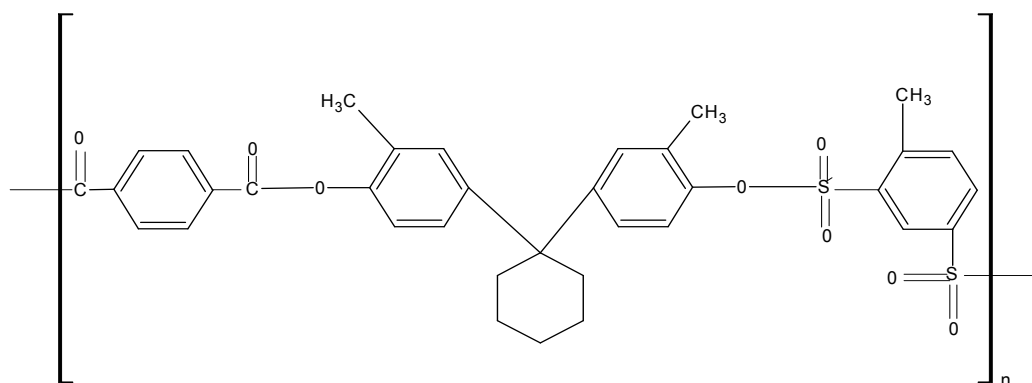
111. Y.V.Patel and P.H.Parsania, *J. Macromol. Sci.-Pure and Appl. Chem.* **A-39**, 145, 2002.

polysulfonates (PS-1, PS-2, PS-4, PS-7 and PS-9) of 1,1'-bis(R,R'-4-hydroxy phenyl) cyclohexane (R=H, Cl and Br) with 4,4'-diphenylether sulfonyl chloride by interfacial poly condensation of corresponding bisphenol (0.005mol) and DPESC/DPSC (0.005 mol) by using water-1,2-dichloroethane /chloroform /dichloromethane (4:1 v/v) as an interphase, alkali as an acid acceptor and cetyl trimethyl ammonium bromide (50mg) as an emulsifier at 0°C for 3h.



All the polysulfonates possess good antibacterial activity against *E. coli* and *S. aureus* microbes and excellent resistant to hydrolytic attack against acids, alkalis and salts. PS-1, PS-2 and PS-4 possess low tensile strength (6.2-21.1 N/mm²) and good to superior volume resistivity (1.1×10^{14} - 4.8×10^{16} ohm cm) in comparison with some other useful plastics. The methyl and chlorine substituents enhanced electric strength (7.4-16.2 kV/mm). PS-7 and PS-9 possess respectively tensile strength of 38.4 and 1.1 N/mm²; electric strength of 16.2 and 25.0 kV/mm and volume resistivity of 5.7×10^{16} and 1.0×10^{17} ohm cm. The low tensile strength of PS-9 is due to low molecular weight, rigid and brittle nature of the polymer chain.

Manwar et al. [112] have reported synthesis and physico-chemical properties of copoly (ester-sulfonates) of 1, 1'- bis (3-methyl-4-hydroxy phenyl) cyclohexane with 2, 4-toluene disulfonyl and terephthaloyl chlorides. They have synthesized copoly (ester-sulfonates) of varying compositions (90:10 to 10:90 %) by interfacial polycondensation using H₂O-CHCl₃ as an interphase, alkali as an acid acceptor and sodium lauryl sulfate – cetyl trimethyl ammonium bromide as mixed emulsifiers at 0°C for 4.5h. Copolymers were characterized by IR and NMR spectral data, viscosity in three different solvents at three different temperatures. They have observed a little solvent and temperature effect on $[\eta]$. The density (1.3430 – 1.3406 g/cm³) of copolymers was determined by floatation method.



Copolymers possess excellent chemical resistance against water, 10% each of acids, alkalis and salts. They possess moderate to good tensile strength ($10.6 - 79.5 \text{ N/mm}^2$), excellent volume resistivity ($7.5 - 28 \times 10^6 \text{ ohm cm}$), electric strength ($53 - 118 \text{ kV/mm}$) and dielectric constant ($1.3 - 1.58$). Copolymers are thermally stable up to about $349 - 373^\circ\text{C}$ in an N_2 atmosphere and possess high T_g ($136 - 196^\circ\text{C}$). DTA endo/exothermic transitions supported either decomposition or formation of new products. Physical properties of copolymers are improved with increasing terephthalate content.

CHAPTER 2
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SYNTHESIS OF MONOMERS,
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CARDOPOLY (ETHER-SULFONE-SULFONATES) COPOLYMERS
AND
CARDOPOLYETHER SULFONE

CHAPTER- 2

SYNTHESIS OF MONOMERS, CARDO POLY (ETHER-SULFONE-SULFONATES) COPOLYMERS AND CARDO POLYETHER SULFONE

This chapter of the thesis describes the synthesis of bisphenol-C, diphenyl ether disulfonyl chloride, di halo diphenyl sulfone and their polymers. This chapter is further subdivided in to five sections:

SECTION-1: SYNTHESIS OF BISPHENOL-C.

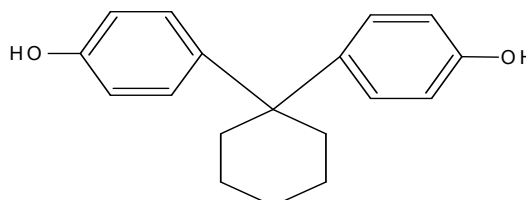
SECTION-2: SYNTHESIS OF 4, 4'-DIPHENYL ETHER DISULFONYL CHLORIDE (DPESC)

SECTION-3: SYNTHESIS OF CARDO CO POLY (ETHER SULFONE - SULFONATES)

SECTION-4: SYNTHESIS OF CARDO POLY (ETHER-SULFONE)

SECTION-1: SYNTHESIS OF BISPHENOL-C

All the chemicals and solvents used were of L.R. grade and purified to their use [1].



1, 1'-Bis (4-hydroxy phenyl) cyclohexane (BC) was synthesized according to reported method [2, 3].

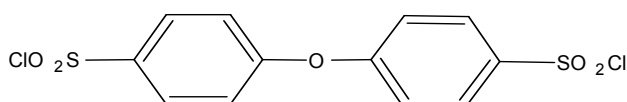
Thus, cyclohexanone (0.5 moles) was treated with phenol (1.0 mole) in the presence of mixture of HCl: CH₃ COOH (2:1 v/v 100:50) as a Friedel-Crafts catalyst at a 55 ° C for 4h. The pink colored product was filtered, washed well with boiling water and treated with 2N NaOH solution. The resinous material was removed by filtration through cotton plug. The yellowish solution obtained was acidified with dilute sulfuric acid, filtered,

1. A. Weissberger and E.S.Proskauer, "Techniques of Organic Solvents", Interscience, New York, 1955
2. M.V.Rao,A.J.Rojivadia, H.H .Parekh and P.H.Parsania, J.Ind. Chem. Soc., 64, 758, 1987
3. H.H Garchar, H.N.Shukla and P.H.Parsania, Ind. Acad. Sci. Chem. Sci.), 103, 149, 1991

washed well with water and dried at 50°C. BC was further recrystallized repeatedly from benzene and methanol-water systems to get pure, white and shining crystals of - 81% yield, m.p. of BC is 186°C.

SECTION-2: SYNTHESIS OF 4, 4'-DIPHENYL ETHER DISULFONYL CHLORIDE (DPESC)

4, 4'-Diphenyl ether disulfonyl chloride here after designated as DPESC was synthesized according to reported method [4].



Thus, 1.5 moles of chlorosulfonic acid containing 0.2 moles of urea as a catalyst was added at 50°-60°C over 1h to 0.5 mole diphenyl ether placed in a round bottomed flask. The mixture was treated at 30°- 40°C with 1.5 moles of chlorosulfonic acid and stirred for 3h. The reaction mixture was poured in to a large quantity of crushed ice and the product was isolated, washed well with 10% sodium bisulfite, distilled water and dried at 50°C. DPESC was recrystallized repeatedly from chloroform-n-hexane system. The yield was ~ 80% and m.p. 122°-126°C.

SECTION-3: SYNTHESIS OF CARDO CO POLY (ETHER- SULFONE-SULFONATES)

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 by product such as H₂O, HCl, ROH, etc. Molecular weight of the polymers depends on the reactivity of the initial compound [5]. In order to get high molecular weight polymer, it is essential to remove the byproduct from the reaction zone and stoichiometry must be maintained. An excess of one of the reactants always results in the formation of low molecular weight polymer.

4. F. G. Bordwell and G. W. Crosby, J. Am. Chem. Soc., **78**, 5367, 1956.
5. V. V. Korshak, V. A. Sergeev, V. K. Shitikov, A. A. Severov, V. F. Durlutsky, and S. G. Djeltakova, Avt. Svudet, U.S.S.R. 172, 489, 1962; Bull. Izobr., 13, **70**, 1965; **C. A.** **63**, 16, 564, 1965

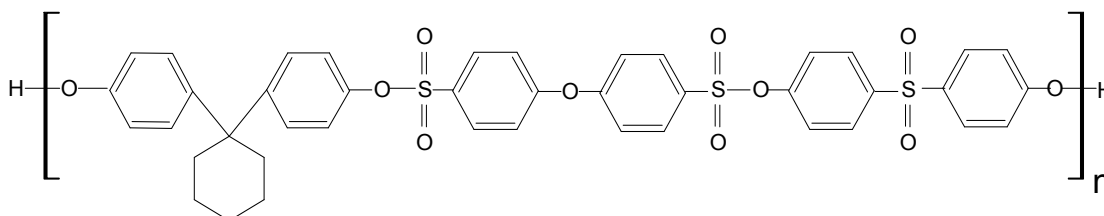
Wittbeker and Morgan [6] showed that interfacial poly condensation is a better technique than that of melt polymerization. In melt polymerization, the polymerization is generally carried out well above 200°C and further this technique is limited to intermediates and polymers those are stable under several 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 Na₂CO₃ and other phase is an organic solvent, generally one of the reactant i.e., dichloride or disulfonyl 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. 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.

Polyether- sulfone-sulfonate copolymers of different compositions are synthesized by interfacial polycondensation as described below.

In to a 500ml three necked round bottomed flask equipped with a high speed mechanical stirrer at 0°C was placed 0.0025 mol BC and 0.0025 mol DHDPs in 50ml water containing 0.025mol NaOH and stirred well. After 5 min 50mg cetyl trimethyl ammonium bromide (CTAB) was added and the resultant emulsion was stirred for 15 min and then 0.005 mol DSDPE in 12.5ml chloroform was added drop wise through a dropping funnel over 10min. and the emulsion was stirred vigorously for 4h, and polymer was isolated from excess of methanol, filtered, washed well with water and finally with methanol, and dried at 50°C. Similarly 25:75 and 75:25 % (BC: DHDPs) compositions were synthesized. The yields were 80-82%. The copolymers are hereafter

designated as PSS-1, PSS-2 and PSS-3 (25:75, 50:50, and 75:25% BC: DHDPS compositions). PSS-1 to PSS-3 was purified repeatedly from chloroform-methanol system. Copolymers are highly soluble in common organic solvents like chloroform, 1, 2-dichloro ethane, dichloromethane, 1, 4-dioxane, THF, DMF, DMSO, etc.



	BC	BS	DPESC
PSS-1	25	75	100
PSS-2	50	50	100
PSS-3	75	25	100

SECTION- 4 : SYNTHESIS OF CARDO POLY ETHER SULFONE

Polyether- sulfones and ketones are well known as engineering plastics and find their usefulness in various fields [7-10]. Polyether sulfones and ketones containing cardo (Latin meaning a loop) groups are novel high performance thermoplastics with high T_g , exceptional mechanical and thermal properties [11-13]. Thermally stable polymers containing rigid backbone generally exhibit high softening temperature and poor solubility [8] but the solubility of such polymers can be enhanced by introducing cardo groups across the backbone chain [9].

Thermally stable linkages such as ether, sulfone, ketone and sulfide lower the softening temperature and increase the solubility. However flexible linkage results in a somewhat lowering of enduse temperature. The presence of cardo groups along the backbone chain not only enhances the solubility but

7. A. Conix and U Laridon , *Angew Chem.*, **72** ,116 ,1960.

8. Y. Shuto and Zasshi Kogoyo Kagaku, **67**, 367, 1964; *Chem. Abst.* **61**, 8419, 1964.

9. D.W. Thomson and G. F .L .Ehler, *J. Polym. Sci. Part A.* **2**, 1051, 1964.

10. J. L. Work and J. E. Herweh , *J. Polym. Sci., Part A1* **6**, 2022, 1968.

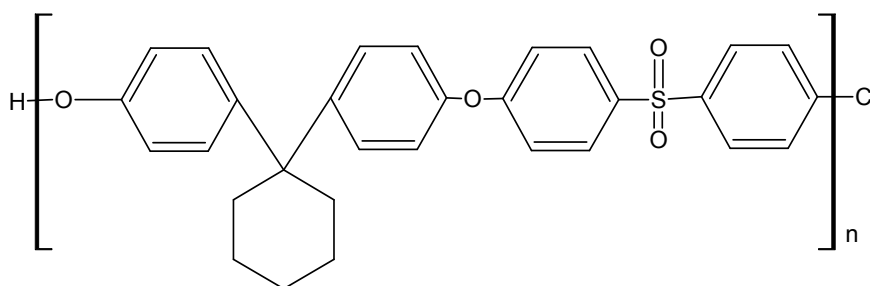
11. Y. Yang, J. Yin and B. Li and G. Zhuang, *J. Appl. Polym. Sci.* **52** 1365, 1994.

12. Y.Han, Y.Yang, B.Li and Z. Feng , *J Appl Polym Sci.*, 56, 979, 1995.

13. Y. Yang, B. Li, Y. Zhang and G. Zhuang, *J Appl. Polym. Sci.* **55**, 63, 1995.

also mechanical and thermal properties [14-15]. In present investigation polyether-sulfone containing cyclohexyl as a cardo group is synthesized by solution polymerization as follows:

Thus, 0.01 mol BC, 0.01 mol DCDPS, 0.02mol anhydrous Na_2CO_3 , 6 ml N, N- dimethyl acetamide and 10 ml chlorobenzene were placed in to a 100 ml round bottomed flask equipped with a mechanical stirrer and a condenser. The temperature of the oil bath was gradually raised to 140°C . After completion of the azeotropic distillation, the mixture was heated at $170\text{-}175^\circ\text{C}$ for varying periods (6-20h). The polymer was isolated from excess of water, filtered, washed well with water to remove traces of N, N-dimethyl acetamide and finally with methanol and dried at 50°C . The effect of reaction time on % yield is reported in Table- 2.1. Similarly reactions were also conducted in other solvents like DMF, DMSO and nitrobenzene to improve the yields and molecular weight of the polymer, but encouraging results were not obtained in these solvent systems. The goodness of different solvent systems was judged on the basis of the viscosity measurements. The polymer is here after designated as PES-C, which is highly soluble in common organic solvents like chloroform, 1, 2-dichloroethane, dichloromethane, 1, 4-dioxane, DMF, DMSO, THF, etc. PES-C possesses film forming property from solution, but it is very difficult to remove film from a glass plate due to powerful adhesion with the glass surface and therefore we could not cast films from the solutions.



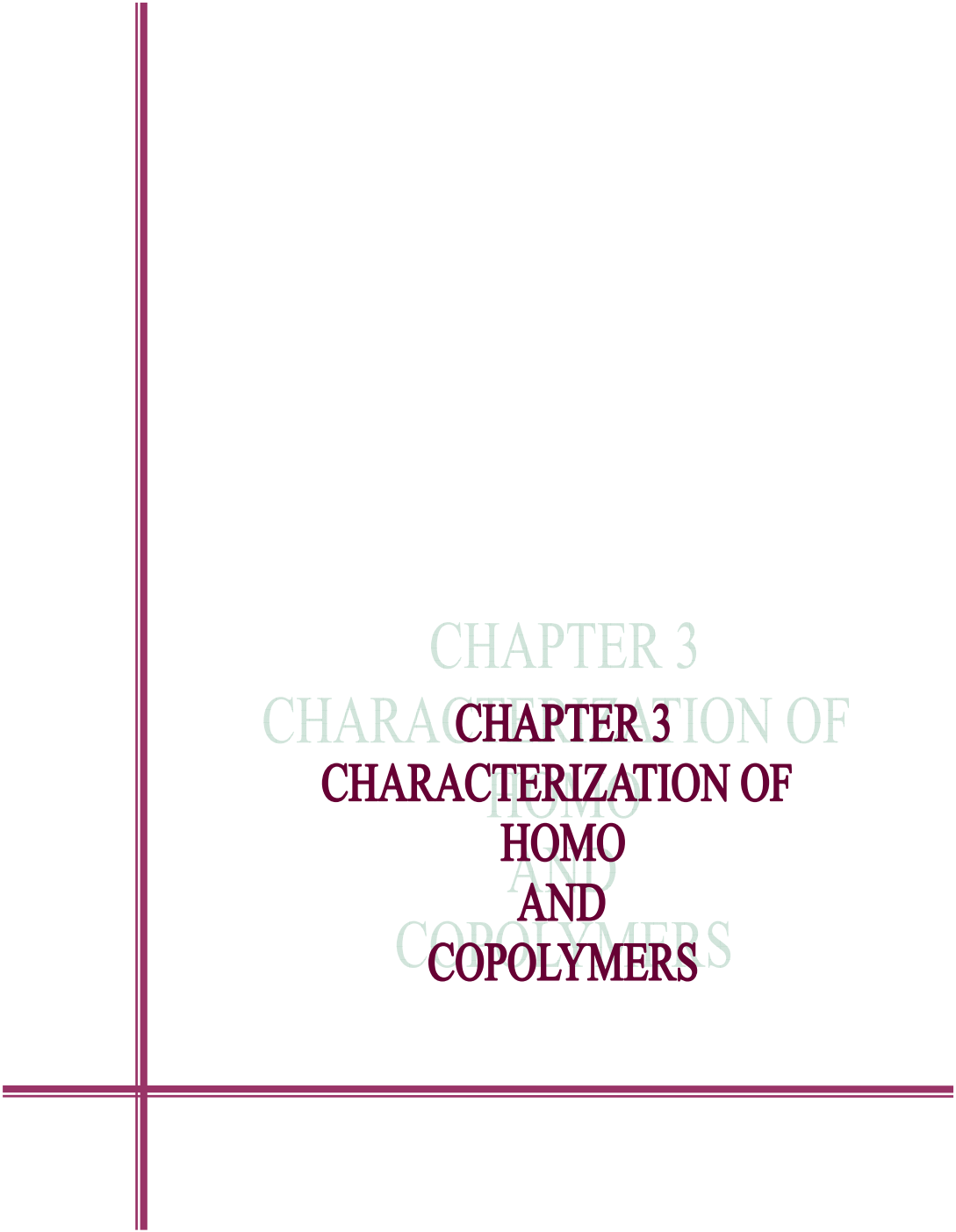
14. J. K. Stille, R. M. Harris and S. S. M. Padaki, *Macromolecules* 14, 486, 1981.

15. G. K. Noren and J. K. Stille, *J Polym. Sci. Part- D5*, 385, 1971.

Table-2.1: Effect of reaction time on % yield and intrinsic viscosity and number average molecular weight data of PES-C

Reaction time, h	% Yield	$[\eta]^*$	Number average molecular weight
6	50.5	0.38	5028
10	57.5	0.37	3885
20	59.4	0.37	3922

* In chloroform at 30°



CHAPTER 3
CHARACTERIZATION OF
CHAPTER 3
CHARACTERIZATION OF
HOMO
AND
COPOLYMERS

CHAPTER-3**CHARACTERIZATION OF HOMO AND COPOLYMERS**

This chapter deals with the characterization of homo and copolymers and it is further subdivided in to nine sections.

SECTION 1: SOLUBILITY OF POLYMERS**SECTION 2: SPECTRAL CHARACTERIZATION OF HOMO AND COPOLYMERS****SECTION 3: PREPARATION OF POLYMER FILMS****SECTION 4: VISCOSITY MEASUREMENTS****SECTION 5: DENSITY MEASUREMENTS****SECTION 6: HYDROLYTIC STABILITY****SECTION 7: ANTI BACTERIAL ACTIVITY OF POLYMERS****SECTION 8: GEL PERMIATION CHROMATOGRAPHY****SECTION 9: END GROUP ANALYSIS BY CONDUCTANCE METHOD****SECTION 1: SOLUBILITY OF POLYMERS**

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 house hold applications.

The solubility of liquids and gases in polymer strongly depends on crystallinity. Crystallinity decreases the solubility of polymers markedly since

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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

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.

Dissolution of a polymer is a slow process and occurring in two stages. First, solvent is slowly imbibed in to the polymer to produce a swollen gel. In the second stage, the gels gradually disintegrate in to a true solution. Only the second stage is materially speed up by agitation. If the polymer is cross linked by primary valance 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 PSS-1 to PSS-3 and PES-C are reported in Table-3.1.

Table-3.1: The solubility of PSS-1 to PSS-3 and PES-C in different solvents at room temperature.

Solvent	Polymer			
	PSS-1	PSS-2	PSS-3	PES-C
Chloroform	S	S	S	S
1,2 - Dichloroethane	S	S	S	S
Dichloromethane	S	S	S	S
1,4 – Dioxane	S	S	S	S
N,N-Dimethylformamide	S	S	S	S
Dimethylsulfoxide	S	S	S	S
Chlorobenzene	IS	IS	IS	IS
Tetrahydrofuran	S	S	S	S
Cyclo hexanone	IS	IS	IS	IS
Acetone	IS	IS	IS	IS
Benzene	IS	IS	IS	IS
Toluene	IS	IS	IS	IS
Nitrobenzene	IS	IS	IS	IS
Methanol	IS	IS	IS	IS
Isopropyl alcohol	IS	IS	IS	IS
n-Propyl alcohol	IS	IS	IS	IS
n-Butanol	IS	IS	IS	IS
Ethanol	IS	IS	IS	IS
Di thyl ether	IS	IS	IS	IS
Carbontetrachloride	IS	IS	IS	IS
Acetophenone	IS	IS	IS	IS

SECTION-2: SPECTRAL CHARACTERIZATION OF HOMO AND COPOLYMERS

This section includes IR and NMR spectral characterization of PSS-1 to PSS-3 and PES-C

[A] IR SPECTRAL CHARACTERIZATION

Information about the structure of a molecule could frequently be obtained from its absorption spectrum. The atomic and electronic configuration of a molecule is responsible for the position of absorption bands. The most structural information of organic molecules could be obtained from their IR spectra. The masses of the atoms and the forces holding them together are of such magnitude that usual vibration of organic molecules interacts with electromagnetic radiation so as to absorb and radiate in the IR region. During the absorption, it is necessary for the molecule to undergo a change in a dipole moment. IR spectroscopy is an excellent method for the qualitative analysis because except for optical isomer, the spectrum of a compound is unique. It is most useful for the identification, purity and gross structural detail. This technique is faster than any other analytical method.

The IR spectra of polymer powder were scanned on a Carl Zeiss Specord FTIR spectrometer. The IR spectra of PSS-1 to PSS-3 and PES-C over the frequency range of 4000-400 cm^{-1} are shown in Figs.-3.1 and 3.2. The characteristic IR absorption frequencies (cm^{-1}) are reported in Table-3.2.

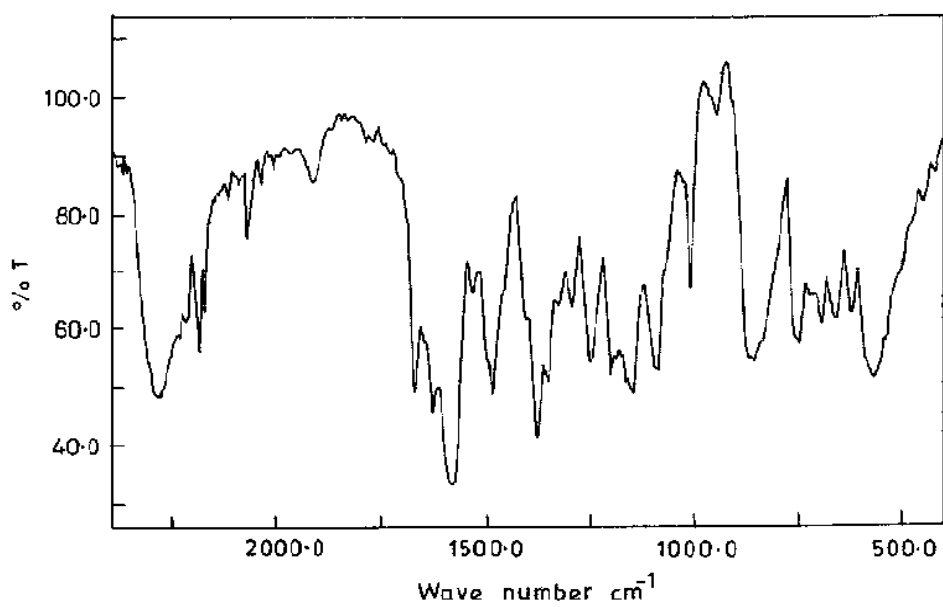
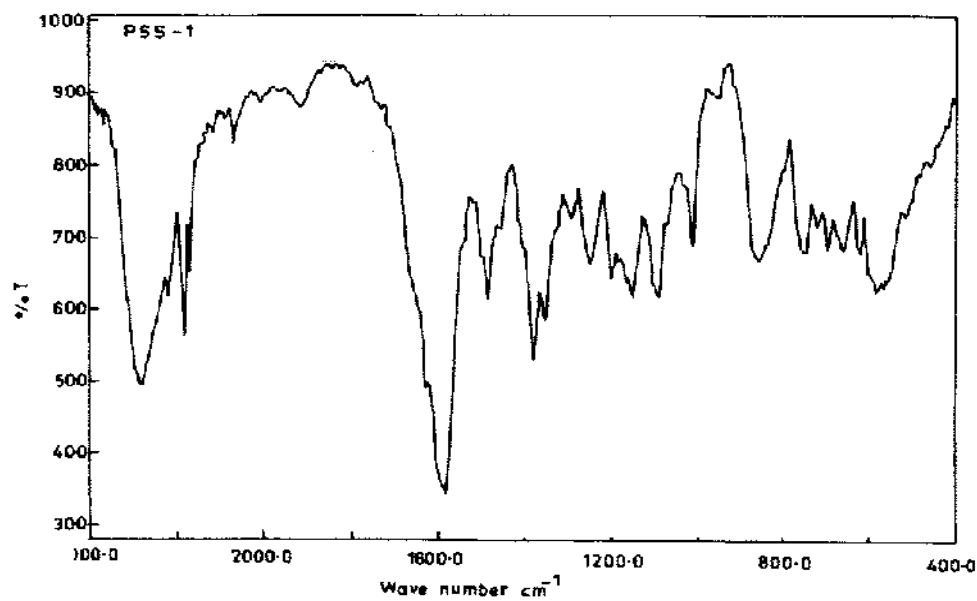


Fig.- 3.1: IR (KBr) Spectra of PSS-1 and PSS-2

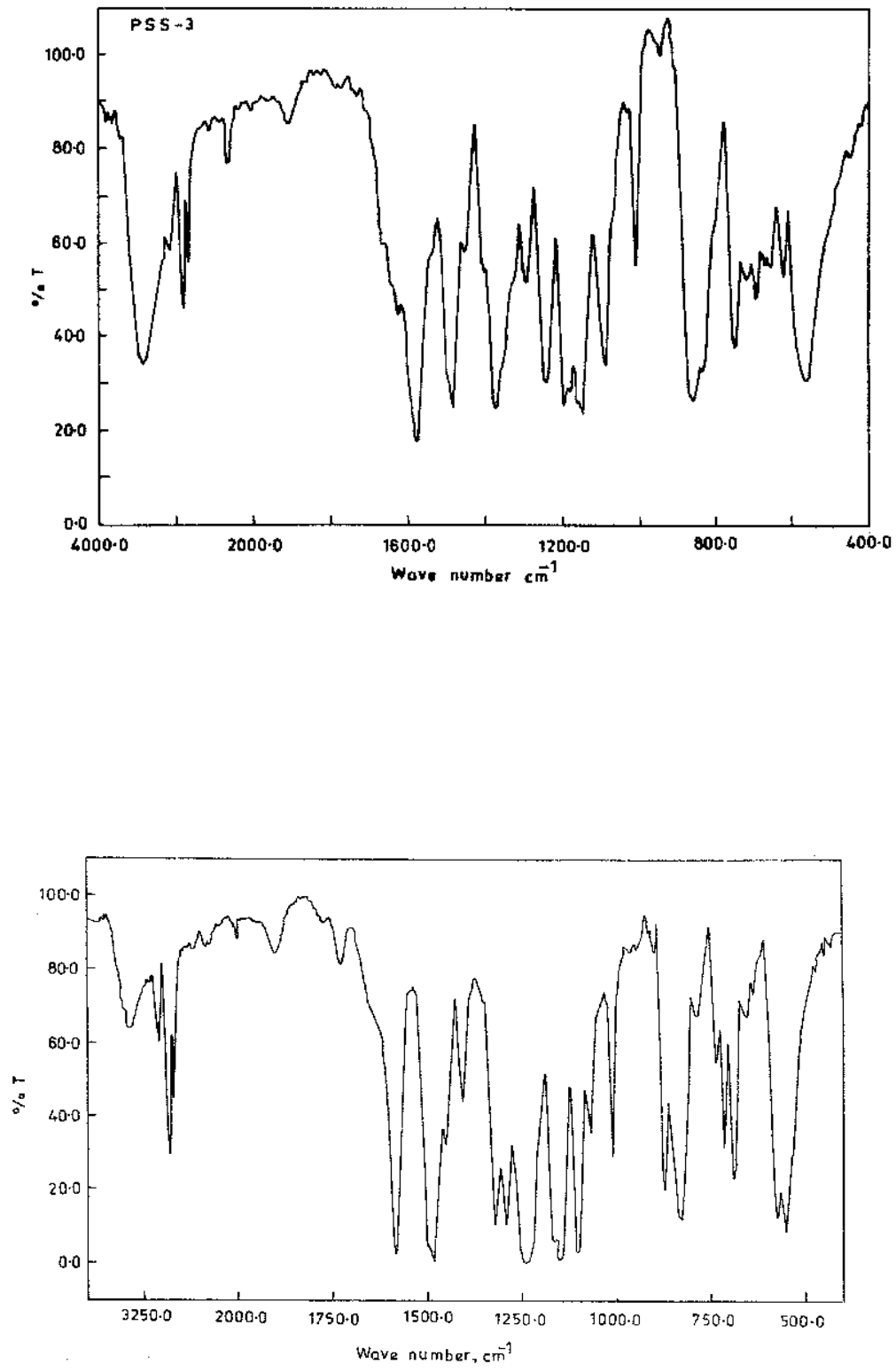


Fig.-3.2: IR (KBr) Spectra of PSS-3 and PES-C

Table-3.2: The characteristic IR absorption bands (cm^{-1}) of co poly (ether-sulfone-sulfonates) (PSS-1 to PSS-3)

Types	Group Vibration mode	Observed IR Frequencies, (cm^{-1})			Expected Frequencies (cm^{-1})
		PSS-1	PSS-2	PSS-3	
Alkane	C-H (str.) ν_{as} ν_{s}	2930.6	2926.8	2930.6	2975-2950
		2857.3	2857.3	2857.3	2880-2860
	C-H (def) asym sym	1455.2	1455.2	-	1470-1435
		1378	1380.9	1378.0	1385-1370
	Aromatic	=C-H (str.)	3074.3	3074.3	3074.3
C=C (str.) (ring str.)		1581.5	1584.4	1581.5	1606 \pm 6, 1579 \pm 6,1520-1480, 1409 \pm 8 (1,4 sub.)
		1467.0	1488.0	1488.0	1616 \pm 8,1577 \pm 8, 1510 \pm 8, 1456 \pm 1(1,2,4 sub)
C-H (i.p.d)		1187.1	-	1187.1	1258 \pm 11, 1175 \pm 6, 1117 \pm 7, 1073 \pm 5 (1,4 sub)
C-H (i.p.d)		1093.6	1094.5	1092.6	1225-1175, 1175-1125, 1070-1000(1,2,4 sub)
Sulfone	S=O (str.) ν_{as} ν_{s}	1152.4	1151.4	1152.4	1200-1145
		1382.9	1380.9	1378.0	1420-1350
	S-O (str.)	559.3	559.3	550.6	700-450
	S-Cl (str.)	625.9	620.4	625.9	700-500

Table-3.3: The characteristic IR absorption bands (cm^{-1}) of polyether sulfone.

Types	Group vibration mode	Observed IR Frequencies, (cm^{-1})	Expected Frequencies (cm^{-1})
Alkane		PES-C	
	C-H (str.) ν_{as} ν_{s}	2933.0	2975-2950
		2858.3	2880-2860
	C-H (def) asym sym	1452.3	1470-1435
		-	1385-1370
Aromatic	=C-H (str.)	3037.7	3080-3030
	C=C (str.) (ring str.)	1585.4	1606 \pm 6, 1579 \pm 6, 1520-1480, 1409 \pm 8(1,4 sub.)
		1452.3	1616 \pm 8, 1577 \pm 8, 1510 \pm 8, 1456 \pm 1(1,2,4 sub)
Ether	C-O-C	1244.0	1190-1210
Hydroxy	-OH (str.)	3402	3400-2800
Sulfone	S=O (str.) ν_{as}	1161.4	1200-1145
Halogen	C-Cl (str.)		800-600

[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 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 number of nuclei in the sample that undergo the transition and can be used for quantitative analysis. NMR spectrometer was invented in 1945 by Felix Bloch (Stanford University) and Edward Purcell. They shared the Nobel Prize (1952) in Physics for their work.

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

-
4. V. M. Parikh, "Absorption Spectroscopy of Organic Molecules", Addison Wesley Pub., p. 243-258, 1978
 5. D. L. Pavia, G. M. Lampan and G. S. Kriz, "Introduction to Spectroscopy", Saunders Publishing, Philadelphia, 46, 1979
 6. R. M. Silverstein, G. C. Bassler and T. C. Morrill, "Spectrometric Identification of Organic Compounds", 6th Ed. John Willey and Sons, New York, 1996
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standard Figs. 3.3 and 3.4 show the NMR spectra of PSS-1 to PSS-3 and PES-C. Different types of protons and their multiplicity along with chemical shifts with J values are reported in Table-3.4.

The integrated area of each signal of homo polymer furnished the knowledge on the agreement of protons with theoretical protons. From Figs.- 3.3 and 3.4, it is clear that NMR spectra of PSS-1 to PSS-3 are very complex and as a result it is difficult to determine their compositions.

UV, IR and NMR spectral techniques [9-13] are well established for the quantitative determination of copolymer composition but due to complex nature and unreliable integrated areas, the composition of copolymers are not determined. The complexity of spectra may also be due to trace amount of homopolymers present in copolymers. Because of high solubility of homo and copolymers in solvent systems studied, it is very difficult to purify the copolymers.

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8. J. R. Ebdon, *Polymer* 15, 782, 1974
 10. V. S. Nithianandan, K. Kaleem, K.V.S. Sreenivasan and K.T. Joseph, *J. Polym. Sci. Polym. Chem.*, 21, 761, 1983
 11. A. Rudian, F. F. O'Driscoll and M. S. Rumack, *Polymer* 22, 740, 1981
 12. G. V. S. Shashidhar, K. Ranga Rao, N. Satyanarayana and E.V. Sundaram, *J. Polym. Sci. Part-C Polym. Lett.*, 28, 157, 1990
 13. R. Ulku and M.B. Bhahatti, *J. Appl. Polym. Sci.*, 32, 58 65, 1986

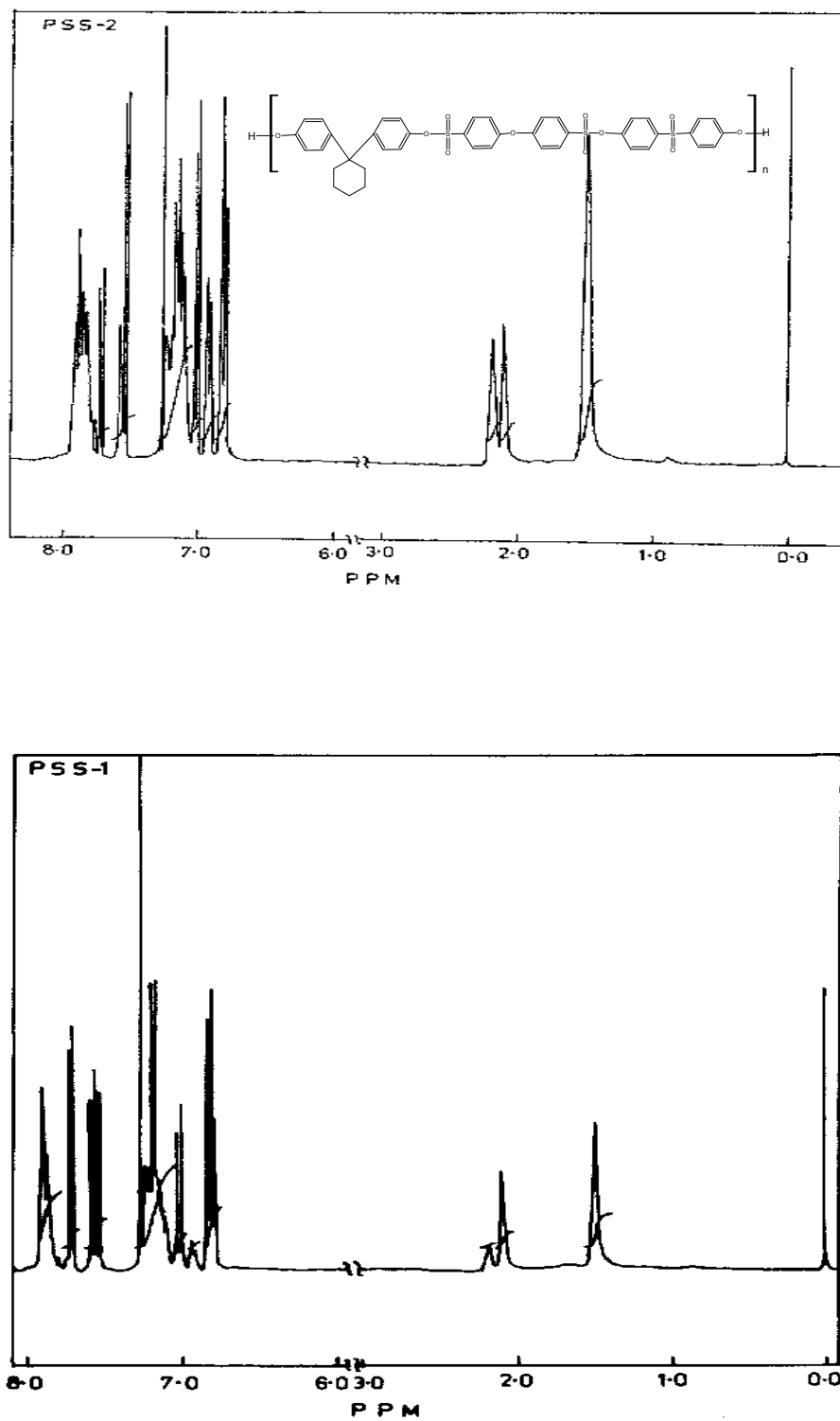


Fig.-3.3: NMR (300MHZ) spectra of PSS-1 and PSS-2 in CDCl₃

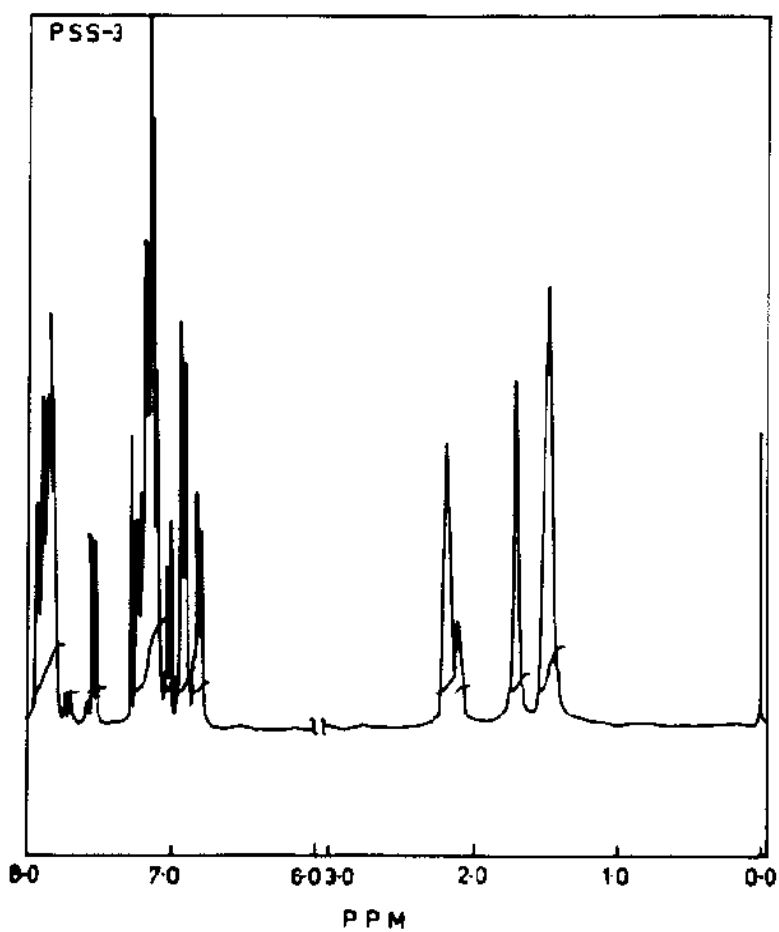
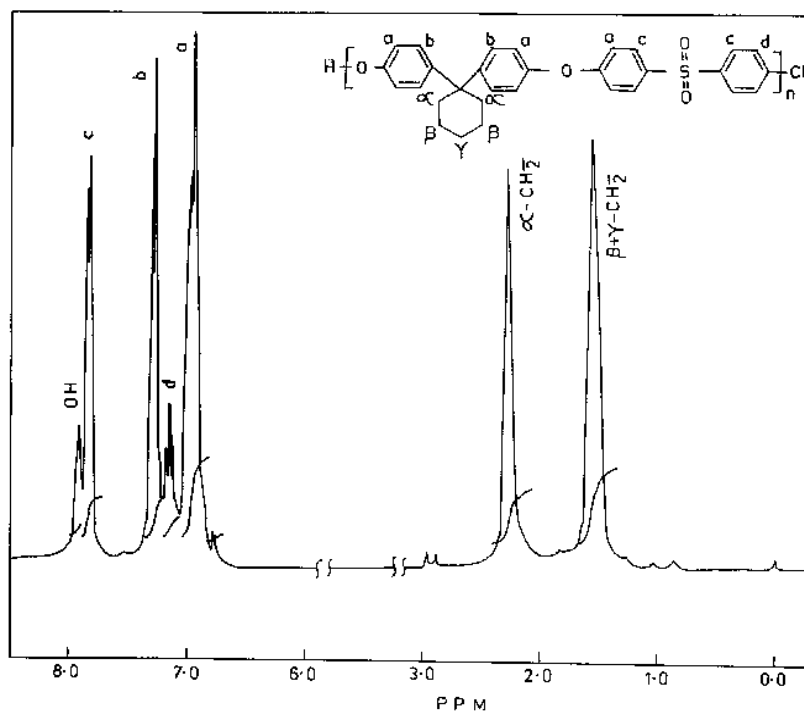


Fig.-3.3: NMR (300 MHz) spectra of PES-C and PSS-3 in CDCl₃

Table-3.4: NMR chemical shifts of PSS-1 to PSS-3 and PES-C

Sample	NMR chemical shifts, ppm
PSS-1	7.91-7.81[m, 4H(a)+2OH(end group)] 7.73-7.68 and 7.58-7.57 [m,4H(e)] 7.23-7.09 [m, 8H(b)] ,7.03-6.98 [m, 2H(c)] 6.95-6.70 [m, 4H(f)] ,6.83-6.76 [m, 4H(d)] 2.17-2.10 [d, 4H(α -CH ₂ -)] 1.50 [s, 6H (β + γ -CH ₂ -)]
PSS-2	7.91-7.78 [m, 4H(a)+2OH end group] 7.72-7.69 and 7.57-7.52 [m, 4H(e)] 7.23-7.09 [m, 8H(b)] , 7.04-6.99 [m, 2H(c)] , 6.92-6.90[m,2H(f)] ,6.83-6.78 [m, 4H(d)] 2.18-2.10 [d, 4H(α -CH ₂ -)] 1.49 [s, 6H(β + γ -CH ₂ -)]
PSS-3	7.91-7.78 [m, 4H(a)+2OH end group] 7.73-7.68 and 7.54-7.51 [m, 4H(e)] 7.23-7.09 [m, 8H(b)], 7.02-6.99 [m, 2H(c)] 6.83-6.78 [m, 4H(d)] 2.09-2.08 [d, 4H(α -CH ₂ -)] 1.46 [s, 6H(β + γ -CH ₂ -)]
PES-C	1.544 (β + γ -CH ₂ -,S) 2.265 (α -CH ₂ , S) 6.926-7.002 (6ArH, m, d) 7.270-7.297(4 ArH, m, b) 7.832-7.857(4 ArH, m, c) 7.974-7.956(1H, m, OH)

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° 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: VISCOSITY MEASUREMENTS

Viscosity Measurement is the simplest and the most widely used technique for routinely determining of molecular weights [14]. The International Union of Pure and Applied chemistry have recommended names for various designations [15]. 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 [16] 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.

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14. W. R. Sorenson and T. W. Campbell, "Preparative Methods of Polymer Chemistry", 2nd Edn. Willey Interscience, New York, p. 43, 1968.
 15. International Union of Pure and Applied Chemistry, J. Polymer Sci, 8, 257, 1952.
 16. L. Ubbelohde, Ins. Pet. London, 19, 376, 1933.

Viscosity measurements of PSS-1 to PSS-3 and PES-C were carried out in four different solvents such as chloroform (CF), 1, 2- dichloroethane (DCE), 1, 4- dioxane (DO) and tetrahydrofuran (THF) at 30° C.

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° C. The viscometer was clamped in a thermostat and a measured quantity of solvent or solution was taken in to 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_0) at a given temperature for a given solvent, the relative viscosity (η_r) and specific viscosity (η_{sp}) were determined according to eqns. 3.1 and 3.2, respectively:

$$\eta_r = t/t_0 \quad \dots 3.1$$

$$\eta_{sp} = (\eta - \eta_0)/\eta_0 = \eta_r - 1 = (t - t_0)/t_0 \quad \dots 3.2$$

The intrinsic viscosity $[\eta]$, can be determined from the joint application of reduced viscosity (η_{sp}/C) and inherent viscosity ($\ln\eta_r/C$) data according to Huggin's [17] and Kraemer's [18] relationships:

$$\eta_{sp}/C = [\eta] + k'[\eta]^2 C \quad \text{Huggin's Eqn.} \quad \dots 3.3$$

$$\ln\eta_r/C = [\eta] - k''[\eta]^2 C \quad \text{Kraemer's Eqn.} \quad \dots 3.4$$

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 $[\eta]$ and k' for polymers in different solvents at 30°C were determined according to Eqn. 3.3 and they are reported in Table- 3.5. The plots of η_{sp}/C against C for PES-C and PSS-1 to PSS-3 in CF, DCE, THF and DO at 30°C are shown in Figs.-3.5 to 3.10

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 $[\eta]$ and the slope of η_{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.

17. M. L. Huggins, J. Am. Chem. Soc., 64, 2716, 1942

18. E. O. Kraemer, Ind. Eng. Chem. 30, 1200, 1938

Table-3.5: The intrinsic viscosities and Huggins constant of polymers in different solvents at 30°C

Polymer	CF			DCE			THF			DO		
	[η]	K'	γ	[η]	K'	γ	[η]	K'	γ	[η]	K'	γ
PSS-1	0.32	1.50	0.925	0.22	0.50	0.960	0.23	0.54	0.931	0.09	2.22	0.750
PSS-2	0.33	0.37	0.995	0.23	0.20	0.921	0.24	0.49	0.971	0.10	0.55	0.9749
PSS-3	0.335	0.37	0.978	0.23	0.09	0.878	0.25	0.37	0.993	0.10	1.5	0.975
PES-C (6-h)	0.38	0.75	0.998	0.205	0.77	0.998	0.22	0.89	0.998	0.14	0.99	0.979
PES-C (10-h)	0.37	1.32	0.997	0.20	0.85	0.980	0.21	0.92	0.980	0.13	2.0	0.993
PES-C (20-h)	0.365	1.26	0.996	0.19	1.37	0.993	0.20	0.99	0.979	0.12	2.2	0.993

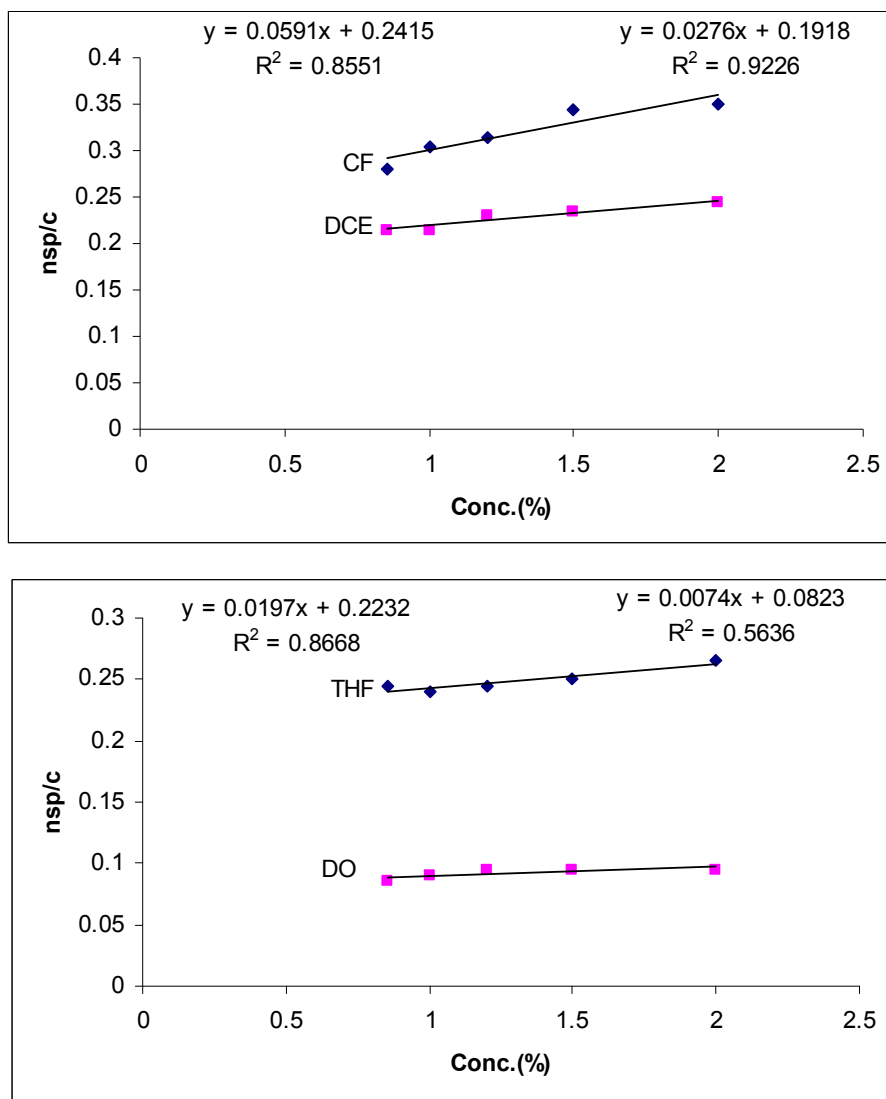


Fig.-3.5: The Plots of η_{sp}/C against C for copolymer (PSS-1) in CF, DCE, THF and DO at 30°C.

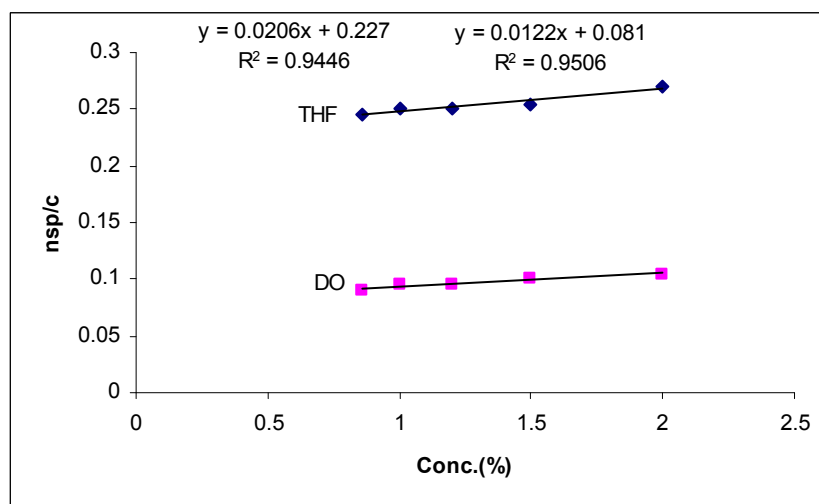
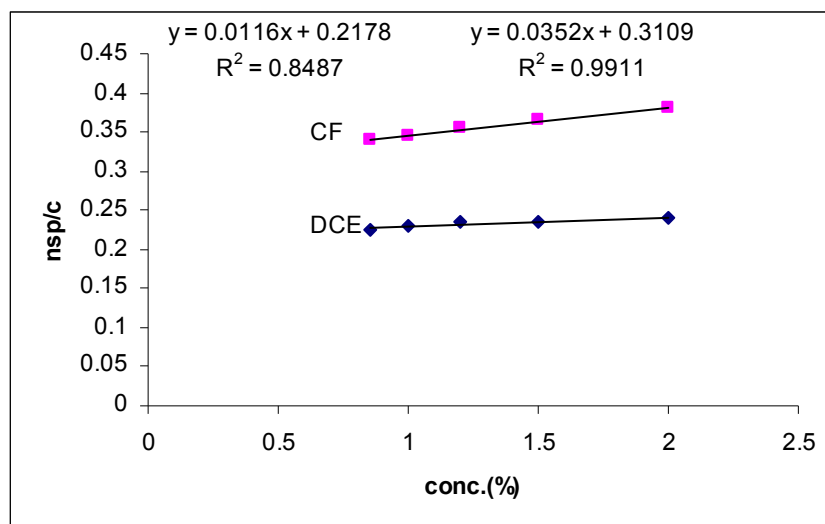


Fig.-3.6: The Plots of η_{sp}/C against C for copolymer (PSS-2) in CF, DCE, THF and DO at 30°C.

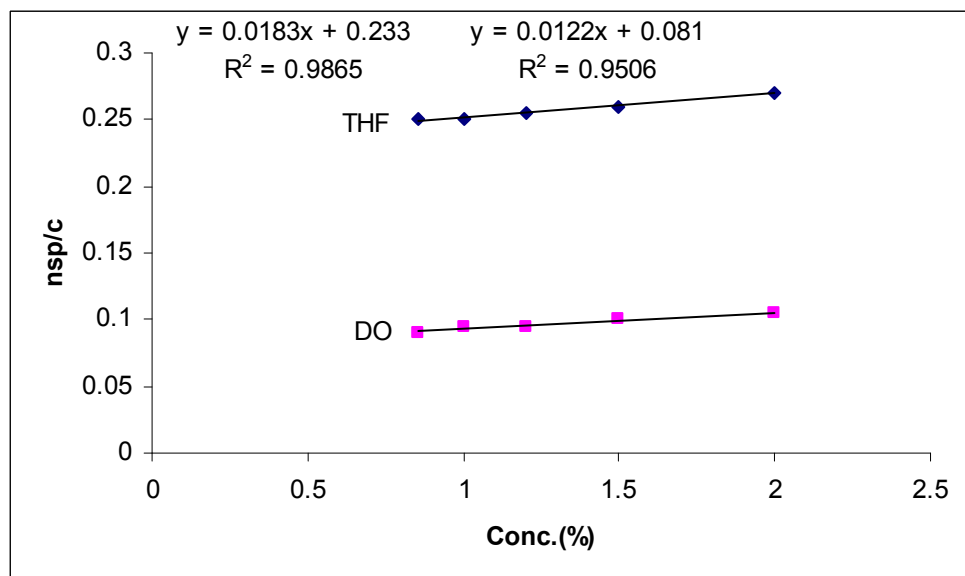
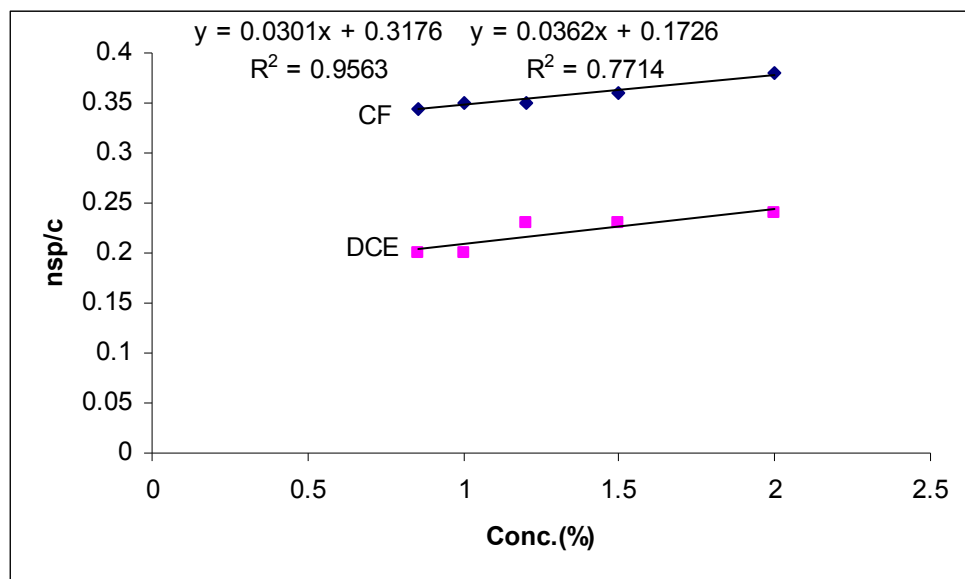


Fig.-3.7: The Plots of η_{sp}/C against C for copolymer (PSS-3) in CF, DCE, THF and DO at 30°C.

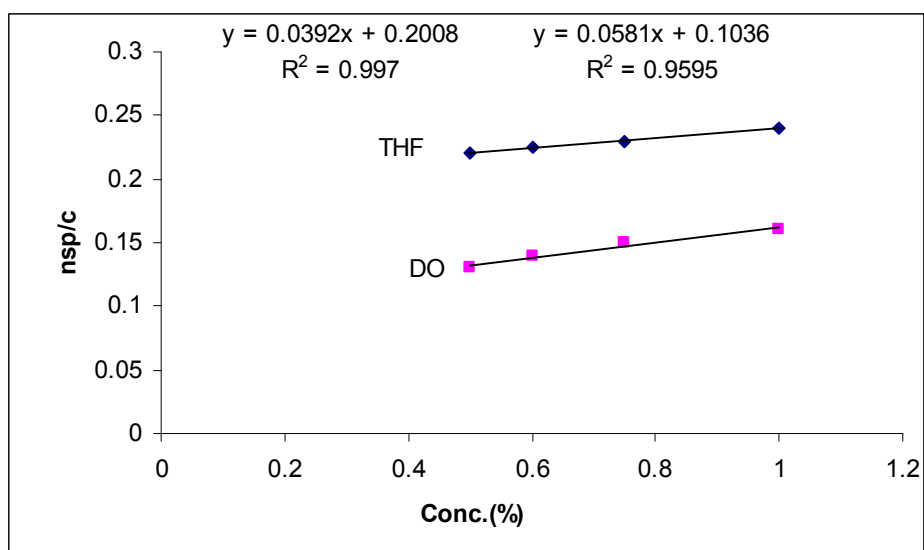
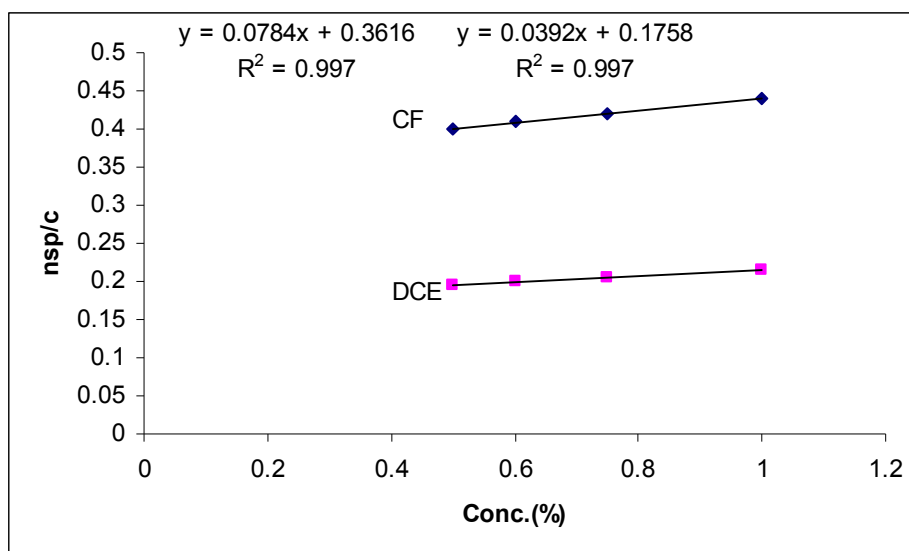


Fig.-3.8: The Plots of η_{sp}/C against C for homopolymer (PES-C, 6h) in C F, DCE, THF and DO at 30°C

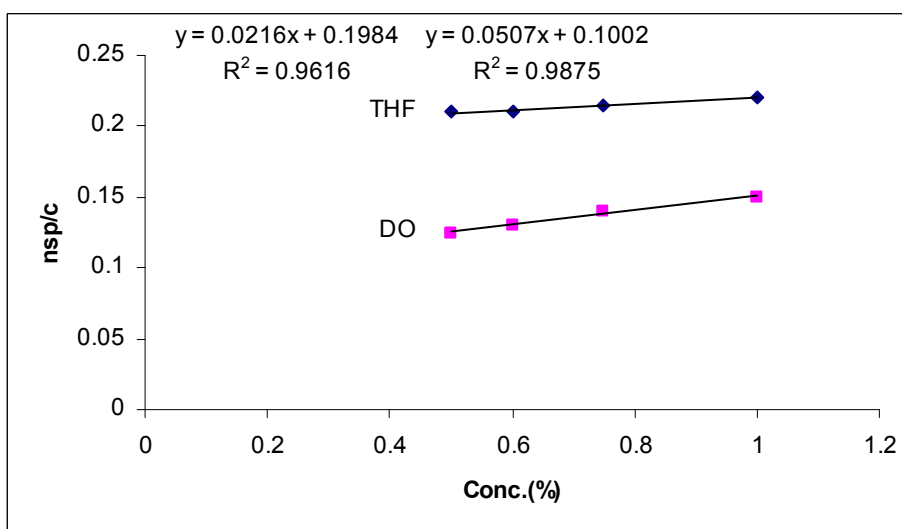
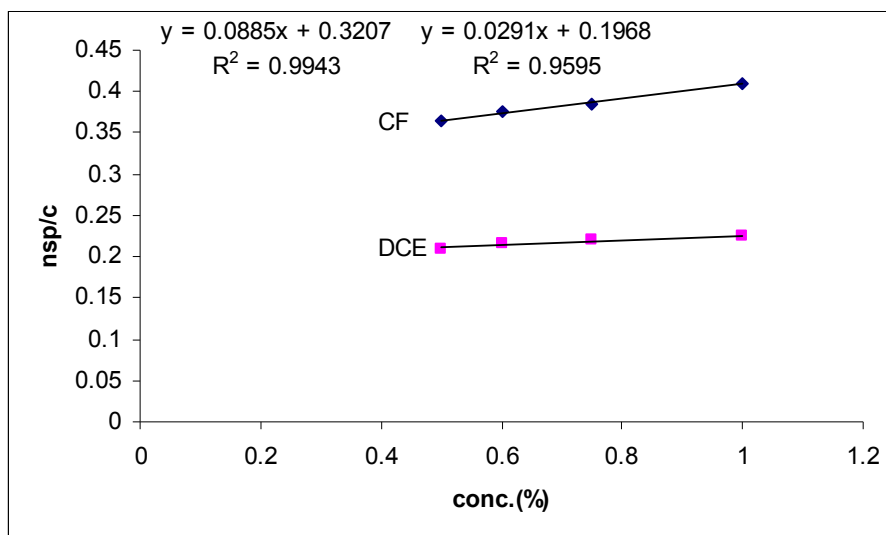


Fig.-3.9: The Plots of η_{sp}/C against C for homopolymer (PES-C, 10h) in CF, DCE, THF and DO at 30°C

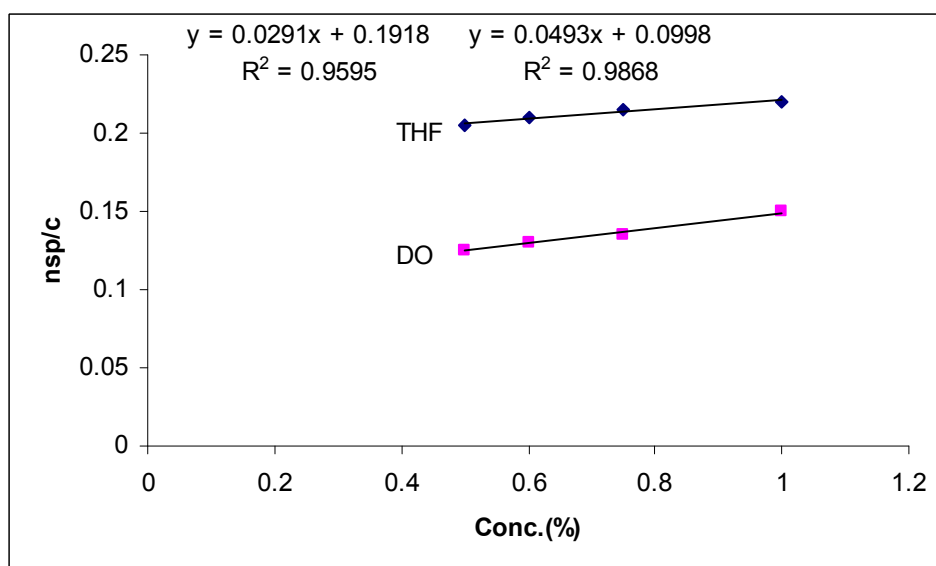
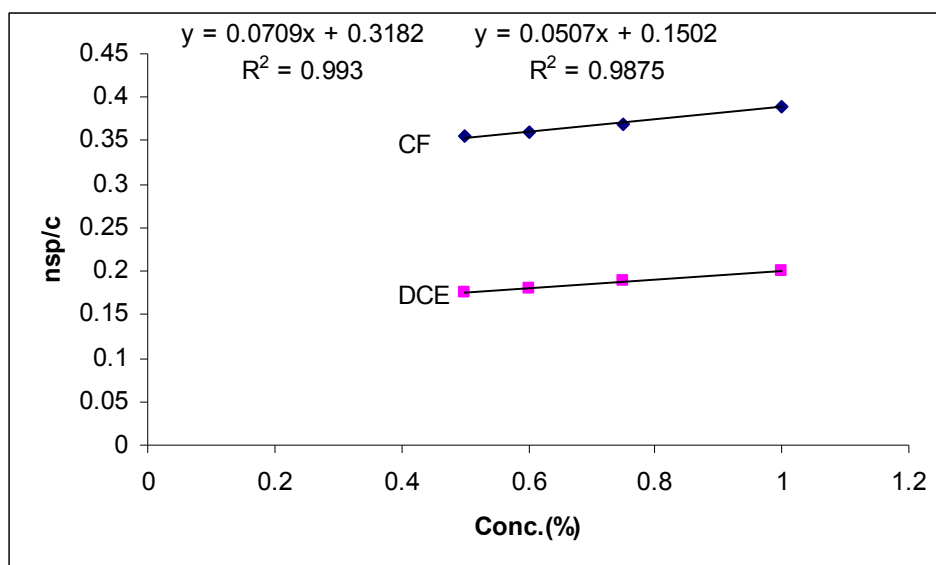


Fig.-3.10: The Plots of η_{sp}/C against C for homopolymer (PES-C, 20h) in CF, DCE, THF and DO at 30°C

From Table-3.4, it is clear that the observed trend in $[\eta]$ is CF>THF>DCE>DO in co poly (ether-sulfone-sulfonates) as well as poly ether sulfone. The magnitudes of $[\eta]$ indicated that the copolymers and homopolymer have moderately high molecular weights and no systematic trend in k' indicated polydisperse nature of the polymers and specific interactions occurring in the solutions.

From Table-3.4 it is evident that $[\eta]$ increased with decreasing bisphenol-C content in the copolymers, while in case of poly ether- sulfone $[\eta]$ decreased with increasing reaction time. No systematic trend in k' is observed with solvent indicating polydisperse nature of the polymers and specific solvent polymer interactions.

SECTION – 5: 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 [19-23]. 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. [24] the density of polymer may be expressed as:

19. H. F. Mark, N. C. Gaylord and N. F. Bikales, "Encyclopedia of Polymer Science and Technology", vol 12, Willey InterScience, New York, 1970.
20. C. Tanford, "Physical Chemistry of Macromolecules", John Willey and Sons, Inc. New York, 1961.
21. V. R. Gowariker, N. V. Vishvanathan and J. Sreedhar, "Polymer Science", Willey Eastern Ltd. ,1986.
22. T.M.Aminabhavi and P.Munk, Macromolecules, 6, 1186, 1979.
23. L.Holiday and W.A.Ghlomeswalker, J Appl. Polym. Sci., 16, 139, 1972.
24. G. L. Slonimskii, A. A. Askadskii and A. I. Kitaigorodkii, Polym. Sci. USSR, A-12 (3) 556, 1970.

1

$$\rho = \frac{KM}{N_A \sum \Delta V_i} \quad \dots \quad \mathbf{3.5}$$

Where K is the packing coefficient, M is the molecular weight of the repeating unit of the polymer, $\sum \Delta V_i$ is the intrinsic volume of the polymer repeat unit and N_A is the Avogadro's number

According to Slonimskii et al. [24] the values of $\sum \Delta V_i$ can be calculated from the knowledge of the volume increments ΔV_i of the atoms and groups of atoms and is reported in Tables 3.6 and 3.7.

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.

$$K = V_{\text{int}} / V_{\text{true}} = N_A \sum \Delta V_i / (M/\rho) \quad \dots \text{3.6}$$

Slonimskii et. al [24] 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.

In addition to intrinsic volume of the repeat unit, the knowledge of packing coefficient K is also necessary for the calculation of the density of polymer. Theoretical density (1.1989g/cm^3) of PES-C was calculated by calculating $\sum \Delta V_i$ (454.58 \AA^3) and $K=0.681$.

EXPERIMENTAL

1. Determination of densities by floatation method

The densities of PSS-1 to PSS-3 films were determined by floatation method by using CCl_4 -n-hexane system at 30°C . 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 averages of six measurements along with the standard deviation are reported in Table-3.8.

According to equation 3.5 the density depends upon M and $\sum \Delta V_i$ 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, which 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 $\Sigma\Delta V_i$.

From Table 3.8, it is clear that the density has decreased with increasing amount of BC content in the polymer chains. Copolymers possess somewhat high density as compared to poly sulfonate (PS) of BC and DSDPE (1.3733 g/cm³). [25]

Determination of density by specific volume method

The densities of PES-C solutions of different concentrations (0.5-4%) in different solvents such as chloroform (CF), 1, 2-dichloroethane (DCE), 1, 4-dioxane (DO) and tetrahydrofuran (THF) were determined at room temperature (32°C) by usual method and fitted to following equation:

$$\frac{1}{W_1\rho_{12}} = \frac{1}{\rho_1} + \frac{W_2}{W_1\rho_2} \quad \dots 3.7$$

Where W_1 and W_2 are weight fractions of solvent and polymer, respectively. ρ_1 , ρ_2 and ρ_{12} are the densities of solvent, polymer and solution, respectively. The least square densities along with correlation coefficient (γ) are reported in Table 3.9. Theoretical density of PES-C was calculated according to Slonimskii et al. [24] and it is reported in the foot note of Table - 3.9.

25. Y. V. Patel and P. H. Parsania, Polymer Testing, 21, 711, 2002

Table-3.8: The densities of copolymers determined by floatation method at 35°C

Polymer	$\rho, \text{g cm}^{-3}$
PSS-1	1.4049±0.0005
PSS-2	1.3897±0.0001
PSS-3	1.3825±0.0001

Table-3.9: Theoretical and experimental densities of PES-C

Solvent	ρ, gcm^{-3}	% Error	Correlation coefficient, γ
CF	1.5128	26.18	0.9999
DCE	1.2886	7.48	0.9999
DO	1.0669	-11.01	0.9999
THF	1.1237	-6.27	0.9989

* $M = 482$, $\Sigma\Delta V_i = 454.58 \text{ \AA}^3$, $K = 0.681$ and $\rho_{\text{cal}} = 1.1989 \text{ gcm}^{-3}$

From Table-3.9, it is clear that experimental and theoretical densities are not in agreement due to solvation phenomena. The polymer-solvent interactions are responsible for the change in apparent molar volume and apparent molecular weight. Relatively large and positive magnitude of % error indicates predominant change in molecular weight over apparent molar volume and vice-versa. Dipole-dipole interactions of opposite type favor solvation. The lone pairs of electrons of ether and sulfone oxygen and π -e⁻s of aromatic rings are electronegative groups and form H-bonding with hydrogen of CF and DCE, while oxygen of THF and DO undergo repulsion with said groups. Thus, Eqn. 3.7 is only applicable to the system in which solvation is minimum i.e. approaching ideal conditions.

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 [26, 27].

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-3.9. Other reagents used for testing plastics for chemical resistance are oleic acid, methanol, acetone, 1, 2-dichloroethane,

26. Raymond B Seymour, "Treatise on Analytical Chemistry"- Interscience publication, New York, Vol III, pp 341-391

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

carbon tetrachloride, heptanes, benzene, toluene, aniline, mineral oil, transformer oil, olive oil, kerosene, gasoline, turpentine, 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 3.10.

Table-3.10: 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 questions. 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 cm² surface area of plastic sample free from extractable substance and it is 20 ml per cm² 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. 3.7

$$\Delta M = [(M_2 - M_1) / M_1] \times 100 \dots 3.7$$

Where ΔM 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. 3.8.

$$\Delta l = (l_2 - l_1 / l_1) \times 100 \quad \dots \text{3.8}$$

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 to 1.5 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-3.11.

In present investigation the hydrolytic stability of PSS-1 to PSS-3 films were determined by the change in weight method [26-27]. 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-3.12.

From Table-3.12, 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 -3.11: Stability characteristic of plastics on exposure to reagents

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

Table- 3.12: Chemical resistance of Copolymers by change in weight method at room temperature

Solution %	% Weight Change								
	After One day	After One week	After One month	After One day	After One week	After One month	After One day	After One week	After One month
	PSS-1			PSS-2			PSS-3		
H ₂ O	-1.30	-0.80	-2.60	0.32	0.60	1.20	0.38	3.86	4.63
HCl	1.02	1.02	1.50	0.64	2.27	1.95	0.36	0.37	0.37
HNO ₃	0.98	0.90	0.00	1.31	1.84	2.10	0.33	5.00	5.30
H ₂ SO ₄	2.18	2.62	3.05	1.92	1.92	1.92	-0.39	-0.40	-0.80
NaCl	1.28	2.10	3.41	0.90	1.81	2.12	-0.83	-1.25	-1.67
NaOH	3.04	3.55	4.06	4.1	5.16	7.74	-0.42	-0.42	-1.28
KOH	2.61	0.70	0.37	0.28	1.4	3.73	1.49	4.40	4.86

SECTION-7: ANTI BACTERIAL ACTIVITY OF POLYMERS

Polymer materials possess some unique characteristics, which exert a profound influence on biological activities [28, 29] in number of cases. The nature, molecular weight, molecular weight distribution of polymers, degree of cross linking, stereo configuration, etc. have significant role on their biological activities.

EXPERIMENTAL

In order to grow different microorganisms, the nutrient agar media was prepared according to reported method [30, 31].

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

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°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°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°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-3.13.

28 M.Ghosh, *Polymer Mater. Sci. Engg.*, ACS. 55, 755, 1986

29 M.Ghosh, *J.Polym. Mater.*, 6, 81, 1989

30 A.L.Bary, "The Antimicrobial Susceptibility Test, Principles and Practices." Illus Lea and Febiger, Philadelphia, pp 180-193, 1976

31 R.Chuickshank, J.P.Duigd, D.P.Marmom and R.H.A.Swain, "Medical Microbiology" Churchill- Livingstone, Edinburgh, London. Vol 2, 1975.

From the Table-3.13, it is clear that copolymers show mild antibacterial and antifungal activities as compared to standard drugs like amoxicillin, ampicillin, ciprofloxacin and erythromycin. The moderate fungal activity might be due to phenolic (-OH) and -Cl end groups.

Table-3.13: A comparative zones of inhibition for standard and polymers against different microorganisms

Sample	Zone of inhibition				
	E.coli	B. mega	B. sub.	P. Vulgeris	A. niger
PSS-1	8	9	8	9	12
PSS-2	9	8	9	9	18
PSS-3	8	8	8	8	19
Amoxicillin	18	19	22	22	18
Ampicillin	17	21	19	23	20
Ciprofloxacin	22	20	21	24	19
Erythromycin	19	20	22	24	18

SECTION-8: GEL PERMEATION CHROMATOGRAPHY

The molecular weights of polymers can be determined by various methods such as chemical method, osmotic pressure measurements, light scattering, ultracentrifugation, viscometry, gel permeation chromatography (GPC), ebulliometry and cryoscopy. Except viscometry and gel permeation chromatography all other methods are absolute methods. GPC method requires calibration by using standard samples of known molecular weight. Viscometry is empirically related with molecular weight. All these methods require solubility of the polymers and involve extrapolation to infinite dilution. For ideal behavior of polymer solutions, θ condition is essential.

Gel permeation chromatography (GPC) is a faster and efficient method for polymer fractionation and provides simultaneous determination of molecular weight distribution curve. It is based on size exclusion principle. In GPC column, the solute travels inside the column from top to the bottom. The solute distributes between stationary and mobile phases. In GPC, the solvent itself acts as both stationary as well as mobile phases. GPC column is filled with a gel material of known size. Usually styragel a cross-linked styrene divinyl benzene copolymer or glass beads having a large number of micro pores of uniform size are used. The beads are hard and incompressible and of different porosity (50 \AA to 1000 \AA). When GPC column is filled with a suitable solvent, the solvent occupies both the void and pore volumes. The solvent phase occupying void volume acts as a mobile phase, while solvent occupying pore volume acts as a stationary phase.

The GPC operates on the principle that polymer molecules in solution separate according to their size and not chemical interaction or chemical retention. The separation is based on the difference in hydrodynamic volumes of polymer molecules of different molecular weights in their dissolved state. When dilute polymer solution is introduced in a solvent stream flowing through the column, the polymer solution along with the solvent starts streaming down the column.

The mobile phase around the beads contains polymer molecules, whereas the stationary phase does not contain polymer molecules. Because

of concentration difference between mobile and stationary phases, the polymer molecules start diffusing in to the stationary phase depending on their size and the pore-size distribution of the gel. Larger molecules can enter only to small extent or completely excluded. The smaller polymer molecule penetrates a larger fraction of the interior of the gel and the larger molecules excluded from entering the pores are washed down the column by the solvent. Thus, the highest molecular weight molecules elute out of the column first. The different molecules with different molecular weights elute according to their molecular size. The lowest molecular weight molecules spend maximum time in the column, while the highest molecular weight molecules spend minimum time in the column and those of intermediate molecular weights diffuse slowly between mobile and stationary phases. As the column is eluted further with a pure solvent, the mobile phase does not contain any molecule whereas the stationary phase contains some molecules. Due to concentration gradient, drives the molecules to diffuse in to the mobile phase. During this diffusion in and out of the pore volume, the smallest molecular weight species are retained in the column for a longer time and hence elute last. The intermediate size molecules elute in between.

Let V_p be the pore volume and V_o be the void volume. The largest molecules, which are excluded from the pores, elute out of the column when V_o volume of the solvent elutes out after the injection of the sample. The smallest molecules diffuse in and out of the pores and elute out at volume of V_o+V_p . The intermediate molecules elute in between V_o and $V_o + V_p$. Thus, elution volume is directly related to molecular size. In practice, a calibration curve of $\log M$ Vs elution volume V_E is prepared by using known molecular weight and narrow molecular weight distribution standard polystyrene samples. Chromatograms of these samples are run and the elution volumes corresponding to the peak maximum are obtained. From the knowledge of V_E and M , a calibration plot is prepared.

From the knowledge of the calibration curve and recorder response from the base line for different elution volumes, it is possible to determine polymer concentration and hence the molecular weight distribution and molecular weights (\overline{M}_w and \overline{M}_n). The height from the base line corresponds to

the product $N_i M_i$ for a given V_E . i.e. the concentration of polymer molecules having molecular weight M_i . The weight average and number average molecular weights can be determined according to following relations:

$$\overline{M}_n = \frac{\sum N_i M_i}{\sum N_i} \quad \dots \text{3.9}$$

$$\overline{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} \quad \dots \text{3.10}$$

The molecular weight distribution is given by the ratio of \overline{M}_w to \overline{M}_n .

Average molecular weights and molecular distribution of PES-C samples were determined by GPC Compact V 3.0 b-61. The experimental details are as under:

Column	:	Shodex KD 804
Column material	:	Styragel
Solvent	:	DMF
Detector	:	RI-71
Sample concentration	:	0.1g/dl
Flow rate	:	1 ml/min.
Injection volume	:	20 μ l

The columns were connected in series. The solvents and solutions were filtered through G-3 funnel. GPC chromatograms of PES-C (10h) and PES-C (20h) are shown in Figs-3.11 and 3.12, respectively. The average molecular weights (\overline{M}_n and \overline{M}_w) and molecular weight distribution ($\frac{\overline{M}_w}{\overline{M}_n}$) derived from eqns. 3.9 and 3.10 are presented in Table-3.14. It is clear from Table-3.14 that molecular weight has increased with reaction time. Moreover both samples are monodisperse. PES-C (6h) could not be analyzed because this sample was beyond the range of the column used.

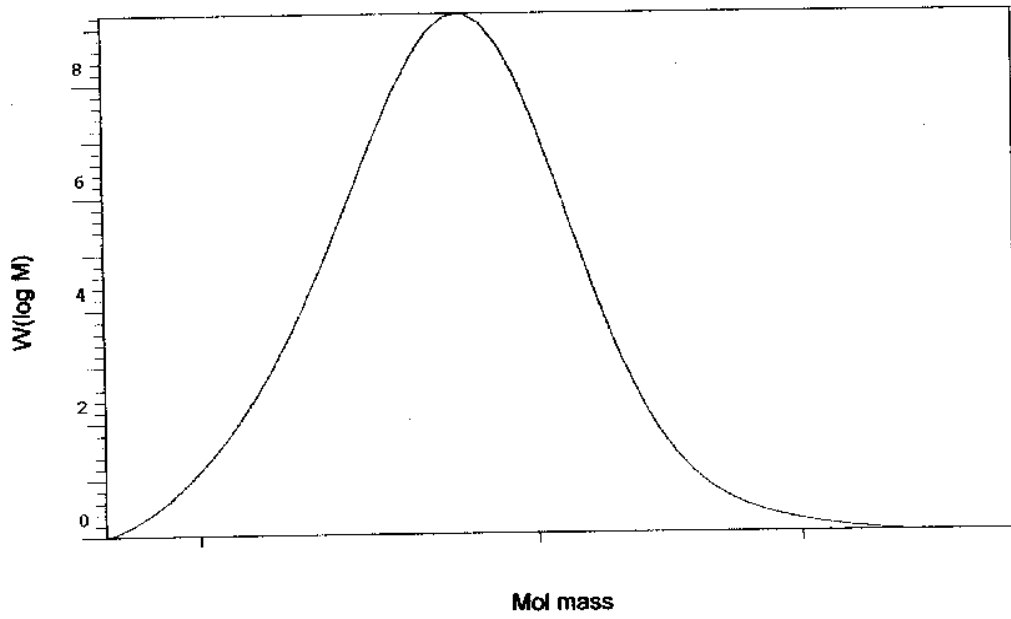


Fig. - 3.11: GPC plot of PES-C (10 h)

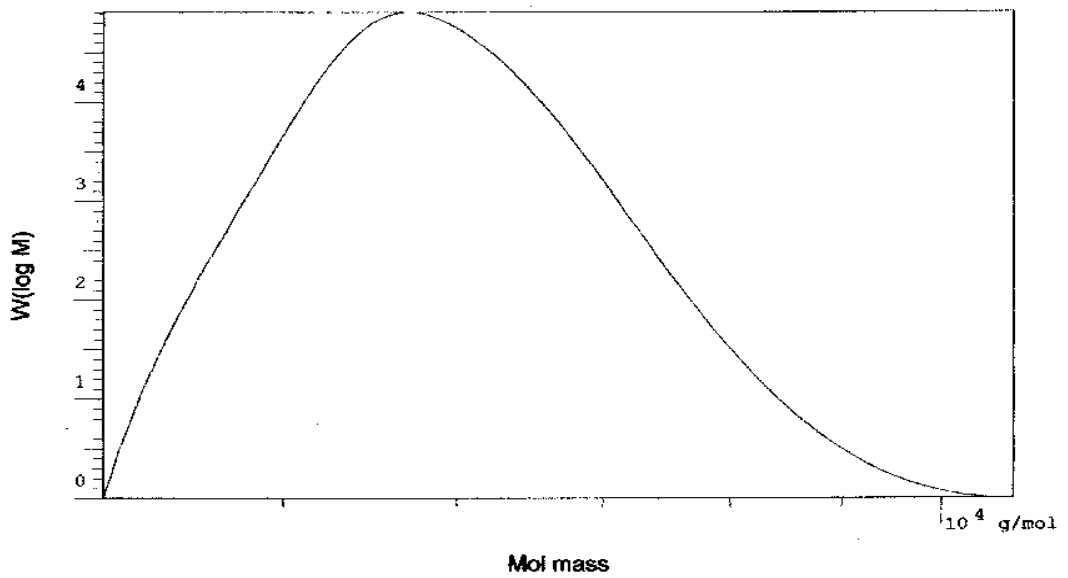


Fig.- 3.12: GPC plot of PES-C (20 h)

SECTION-9: END GROUP ANALYSIS BY CONDUCTANCE METHOD

The end group analysis is a chemical method, which requires that the polymer must contain reactive functional groups at one end or both the ends of the molecule. The functional groups are hydroxyl, carboxyl, amino, aldehydes, ester or methyl. This method becomes insensitive for high molecular weight polymers because the fraction of end groups becomes too small to be measured with precision due to the inability to purify samples and reagents as to lack of sensitivity in the methods. The molecular weight <25000 can be determined precisely by this method.

Usually the total number of functional groups in a given weight of the samples is expressed as a functional group equivalent/100g. From the knowledge of the functional group equivalent and the functionality, the number average molecular weight can be determined according to eqn.3.11:

$$\overline{M}_n = \text{Functionality} / \text{Functional group equivalent} \quad \dots \text{ 3.11}$$

$$\text{Hydroxyl value} = 56.1 \text{ VN/W mg KOH/g} \quad \dots \text{ 3.12}$$

$$\begin{aligned} \text{Hydroxyl equivalent/100g} &= 56.1\text{VN}/100\text{W} \times 100/56.1 \\ &= \text{VN}/10\text{W} \quad \dots \text{ 3.13} \end{aligned}$$

Where V is the volume of KOH consumed, N is the normality of KOH and W is the sample weight in grams. Assuming a functionality of 2, we get

$$\overline{M}_n = 2 \times 100 / \text{Hydroxyl equivalent} \quad \dots \text{ 3.14}$$

The end group analysis can be used precisely only for linear polymers. If the molecular weight is determined by osmometry and the functional group equivalent is determined by end group analysis, then it is possible to determine the functionality of the polymer. Thus,

$$\text{Functionality} = \overline{M}_n \times \text{Functional group equivalent} \quad \dots \text{ 3.15}$$

An attempt was made to determine number average molecular weights by end group analysis. As hydroxyl groups can not be titrated directly with a strong base by using phenolphthalein as an indicator but it can be titrated by conductance measurements. In present case, known concentration of PES-C was prepared in fractionally distilled 1, 4- dioxane. A 50 ml polymer solution

was taken in a 150ml beaker and cell was completed by using conductivity cell with

cell constant $\theta = 1$. The solution was titrated with 0.0468 N methanolic KOH

Table- 3.14: Molecular weights determined by GPC and end group analysis (conductance method)

Polymer	GPC Method			Conductance method \bar{M}_n
	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n	
PES-C(6h)	----	----	----	5028
PES-C(10h)	3704	3743	1.01	3885
PES-C(20h)	5896	6080	1.03	3922

solution and the change in conductance was recorded at various stages of alkali addition. A typical conductance Vs volume of alkali added is shown in Fig-3.13. The end point was determined by extrapolation of two linear branches and hydroxyl value and hydroxyl equivalent of PES-C samples were determined according to Eqn, 3.12 and Eqn. 3.13, respectively. The number average molecular weights of PES-C samples were determined according to Eqn.3.14 and are reported in Table-3.14. From the Table-3.14, it is clear that \bar{M}_n determined by conductance method is not in agreement with that of GPC method, which might be due to very small change in conductance and inaccurate extrapolation of two branches.

CHAPTER 4
CHAPTER 4
THERMO-MECHANICAL
AND ELECTRICAL PROPERTIES OF
CARDIO COPOLY (ETHER-SULFONE-SULFONATES)
COPOLYMERS
AND
CARDIO POLYETHER SULFONE

CHAPTER-4

THERMO – MECHANICAL AND ELECTRICAL PROPERTIES OF CARDO COPOLY (ETHER-SULFONE-SULFONATES) COPOLY-MERS AND CARDO POLYETHER SULFONE

The chapter -4 of the thesis describes the thermal studies of polyether sulfone and thermo-mechanical and electrical studies of co poly (ether-sulfone-sulfonates) and is further subdivided in to two sections.

SECTION-1: THERMAL PROPERTIES OF POLYETHER- SULFONE AND COPOLY (ETHER-SULFONE- SULFONATES)

SECTION-2: MECHANICAL AND ELECTRICAL PROPERTIES OF COPOLY (ETHER-SULFONE-SULFONATES)

SECTION-1: THERMAL PROPERTIES OF POLYETHER - SULFONE AND COPOLY (ETHER-SULFONE-SULFONATES)

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, which may be useful for high temperature applications.

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.

Studies on thermal behavior of polymers are of paramount importance from both scientific and practical point of views [5]. 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 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 [6].

The 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.

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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. J.W.Bain and G.F.Kay, Trans Roy. Soc. Can., **18**, 269, 1924; C.A. **19**, 893, 1925
 6. H.C.Anderson, J.Appl. Polym. Sci., **6**, 484, 1962.

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 [7] 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.

Effect of various operating parameters

1. Atmosphere

The atmosphere associated with any thermal analysis, which is composed of gases that are introduced from outside and those are evolved from the samples. The presence or absence of such gases may have 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 the primary decomposition of gases will tend to be pumped away from the sample before the molecules collide with the surface and undergo secondary reactions. When these molecules collide with inert gas molecules, 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, where as 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 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 rate of temperature rise will cause the process to be displayed to a higher temperature because they will be at the lower temperature for a shorter length of time. The rate of change of the measured parameter will also be greater for faster heating.

Differential Scanning Calorimetry (DSC) and Differential Thermal Analysis (DTA)

Physical transformation [8] 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,

8. E. Heisenberg; *Cellulose Chemie*, 12,159, 1931; *C.A.* **25**, 59, 823, 1931.

random copolymer structure and stereo regularity and identification of composition of a mixture may be studied through melting.

DSC is a method where by 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.

DSC is a method where by the energy necessary to establish a zero transition occurs, the energy input to the sample is compensated by an increased 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 techniques has been used for characterizing unresolved multistep reactions in polymers [9].

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.

DTA is more versatile and gives data of more fundamental nature than TGA. This technique involves recording of difference in temperature between a substance and a reference material against either time or temperature as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a programmed heating rate. Any transition, which the polymer sample undergoes, will result in absorption or liberation of energy by the sample with a corresponding deviation of its temperature from that of the reference. In DTA, as soon as the sample reaches the temperature of the change of its state (chemical or physical), the differential signal appears as a peak.

The number, position, shape and nature(exothermic or endothermic)of the DTA peaks give informations about glass transition temperature, crystalline rearrangement, melting, curing, polymerization, crystallization, decomposition of polymer, etc.

Thermo Gravimetric Analysis (TGA)

Different polymers decompose over different range of temperatures yielding different proportion of volatile and residues. Thermogravimetry is a useful analytical technique for recording weight loss of a test sample as a function of the temperature or time, which may be useful 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 namely

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 sample starts losing weight at a very slow rate up to a particular temperature and thereafter, the rate of loss becomes large over narrow range of temperature. After this temperature the loss in weight levels off. TGA curves are characteristic for given polymers because of unique sequence of physico-chemical reactions, which occur over definite temperature ranges and at the rates that are function of the polymer structures.

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 the evaluation of volatile products in the formation of heavier reaction products. Pyrolysis of many polymers yields TG curves, which follow relatively simple sigmoidal curves. In such a case weight of sample decreases slowly as reaction begins and then decreases rapidly over a comparatively narrow range of temperature and finally levels off as the reaction gets 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 [10, 11].

10. D.W.Levi, L.Reich and H.T.Lee, *Polym. Engg. Sci.*, 5, 135, 1965.

11. H.L.Friedman, U.S.Dept. Com., Office. Tech. 24 pp, 1959; C.A. **55**, 26, 511, 1961.

Reich and Levi [12] have described several temperature characteristics for qualitative assessment of relative thermal stability of polymers:

1. Initial decomposition temperature (T_0)
2. Temperature for 10% weight loss (T_{10})
3. Temperature for maximum rate of decomposition (T_{\max})
4. Half volatilization temperature (T_s)
5. Differential decomposition temperature
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 the two 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. 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.

$$\frac{dC}{dt} = k f(C) \quad \dots \mathbf{4.1}$$

Where C = Degree of conversion, t = time; k=rate constant,

f(C) = temperature independent function of C

The constant k is generally assumed to have the Arrhenius form

$$k = A e^{-E_a/RT} \quad \dots \mathbf{4.2}$$

C is defined as the conversion with respect to initial material

$$C = 1 - \frac{W}{W_0} \quad \dots \mathbf{4.3}$$

where W_0 = Initial weight of the material and W= weight of the material at any time.

12. L. Reich and D. W. Levi, *Macromol. Rev. Eds. Peterlin Goodman Willey Interscience*, New York, 173, 1968

The residual weight fraction is given by

$$\frac{W}{W_0} = (1-C)$$

and the rate of conversion is given by

$$\frac{dC}{dt} = - (1/W_0) \frac{dW}{dt} \quad \dots \mathbf{4.4}$$

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

$$f(C) = (1-C)^n \quad \dots \mathbf{4.5}$$

Where n = order of the reaction

Upon substituting Eqns. 4.2 and 4.5 in to Eqn. 4.1

$$\frac{dC}{dt} = A e^{-E_a/RT} (1-C)^n$$

OR

$$\frac{dC}{dT} = \left(\frac{A}{\beta} \right) (e^{-E_a/RT}) (1-C)^n \quad \dots \mathbf{4.6}$$

Where β = Rate of heating

Methods of single heating rate

1. Freeman-Carroll [13] and Anderson-Freeman methods [14]

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

$$\frac{\Delta \ln(dC/dt)}{\Delta \ln(1-C)} = n - \frac{E_a}{R} \left[\frac{\Delta(1/T)}{\Delta \ln(1-C)} \right] \quad \dots \mathbf{4.7}$$

A plot of L.H.S. against $\Delta(1/T) / \Delta \ln(1-C)$ would yield a straight line with slope equal to $-E/R$ and the intercept equal to n. Using Eqn. 4.7 Anderson-Freeman derived the Eqn. 4.8

13. E. S. Freeman and B. Carroll; J. Phys. Chem., **62**, 394, 1958.

14. D. A. Anderson and E. S. Freeman; J. Polym. Sci., **54**, 253, 1961.

$$\Delta \ln \left(\frac{dC}{dt} \right) = n \Delta \ln (1-C) - \frac{E_a}{R} \Delta \left(\frac{1}{T} \right) \quad \dots 4.8$$

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

2. Sharp-Wentworth method [15]

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

$$\log \left[\frac{dC/dt}{1-C} \right] = \log (A / \beta) - \frac{E_a}{2.303R} \frac{1}{T} \quad \dots 4.9$$

where C = fraction of polymer decomposed at temperature T ,
 β = rate of heating, A = Frequency factor and E_a = the activation energy of the process. The plot of $\log [(dC/dt)/(1-C)]$ against $1/T$ would be a straight line, with slope equal to $-(E_a/2.303 R)$ and the intercept equal to $\log (A/\beta)$.

3. Chatterjee method [16]

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

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

where W_1 and W_2 are the sample weights.

4. Horowitz -Metzger method [17]

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

$$\ln \left[\ln(1-C)^{-1} \right] = \frac{E_a}{RT_s^2} \theta \quad \dots 4.11$$

15. J. H. Sharp and S.A. Wentworth; *Anal. Chem.*, **41**, 2060, 1969.

16. P. K. Chatterjee; *J. Polym. Sci.*, **A-3**, 4235, 1965.

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

Where, C= fraction of the compound decomposed at time t, Ea= activation energy, Ts= Temperature at which the rate of decomposition is maximum and $\theta = T - T_s$

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

$$\ln E - \ln (RT_s^2) = \ln A - \ln \beta - \frac{E}{RT_s^2} \quad \dots \text{4.12}$$

$$A = \frac{k_b T}{h} e^{\Delta S / R} \quad \dots \text{4.13}$$

where k_b is Boltzmann constant.

Use of multiple heating rates

I. Anderson [18] method

Anderson [18] and Friedman [19] have developed the methods based on multiple heating rates. These methods are based on the fact that as the heating rate increases, TG curve tends to shift to higher temperature range, since at lower temperature decomposition occurs for a shorter time interval range, since at lower temperature decomposition occurs for a shorter time interval.

The relation is

$$\ln R_t = \ln A + n \ln (1-C) - \frac{E_a}{RT} \quad \dots \text{4.14}$$

where $R_t = \beta dC / dT$

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

$$\frac{E_a}{RT_o} = \ln A + n \ln (1-C) \quad \dots \text{4.15}$$

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

18. H. C. Anderson, J. Polym. Sci., **C6**, 175, 1964.

19. H. L. Friedman, J. Polym. Sci., **C6**, 183, 1964.

II Friedman method [19]

Friedman [19] has developed the following Eqn. 4.16:

$$\ln\left(\frac{dC}{dt}\right) = \ln A + n \ln(1-C) - \frac{E_a}{RT} \quad \dots \mathbf{4.16}$$

According to Eqn. 4.16, the plot of $\ln(dC/dt)$ against $1/T$ for various constant values of C at each heating rate would be a straight line with slope equal to $-E_a/R$ and

$$\text{Intercept} = \ln A + n \ln(1-C) \quad \dots \mathbf{4.17}$$

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.

III Ozawa method [20]

Ozawa has developed the following Eqn. 4.18:

$$\log \int_0^c \frac{dC}{(1-C)^n} \approx \log \frac{AE_a}{RT} - \log \beta - 2.315 - 0.4567 \left(\frac{E}{RT} \right) \quad \dots \mathbf{4.18}$$

The plot of $\log \beta$ 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 DTA-TGA thermograms of PSS-1 to PSS-3 and PES-C were scanned on a Mettler TS system at the heating rate of $15^\circ \text{C}/\text{min}$ in an N_2 atmosphere.

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 [21]. Differential thermal methods find wide spread use

20. T. Ozawa; Bull. Chem. Soc. Jap., **38**, 1881, 1965.

21. C. D. Doyle, WADD Tech. Rept., 1, 60, 1960.

in determining the compound of naturally occurring and manufactured products [22-24].

Poly ether- sulfone-sulfonates

Thermo-mechanical and electrical properties of polymers are very important for their end use applications. Thermal analysis of polymers provides insight of bond strength and molecular architecture and useful tool for polymer processing. TG-DTA thermograms of PSS-1 to PSS-3 at the heating rate of 15°C/ min. in an N₂ are shown in Figs. 4.1 to 4.3. DTA transitions, initial decomposition temperature (IDT), decomposition range, % weight loss and temperature of maximum weight loss (T_{max}) are reported in Table 4.1. From Table 4.1, it is evident that there is no change in glass transition temperature (T_g) is observed with change in copolymer composition (234-235°C). An exothermic transition at higher temperature (559-571°C) is due to further decomposition of copolymer chains and confirmed by rapid weight loss in corresponding T_g thermograms of a copolymer. Thus, copolymers possess fairly high T_g and it is slightly high as compared to PS (226°C) [25] and thermal stability decreased (369°C) on copolymerization.

From Figs.4.1 to 4.3 and Table 4.1, it is observed that the copolymers are thermally stable up to about 350°C and followed two steps degradation. It is interesting to note that % weight loss and T_{max} have slightly decreased with increasing BC composition in the copolymer. 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] (Eqns. 4.8, 4.12 and 4.13).The detail calculation schemes are reported in Tables 4.2 to 4.5. The least square values of kinetic parameters along with correlation coefficient (γ) are reported in Table 4.5. From Table 4.6, it is observed that PSS-1 has followed second order degradation kinetics, while PSS-2 and PSS-3 have followed first order kinetics.

22 W. W. Wendlandt, "Thermal Methods of Analysis", 2nd Ed. Wiley, New York, 1974.

23. T. Meisel and K. Seytold, Crit. Rev. Anal. Chem., **12**, 267, 1981.

24. R. C. Mackenzie, Ed., "Differential Thermal Analysis", Vols. 1&2, Academic Press, N. Y. 1970; W. W. Wendlandt Anal. Chem., **54**, 97 R, 1982; **56**, 250R, 1984.

25. Y. V. Patel and P. H. Parsania, *Polym. Testing* **21**, 711, 2002.

The activation energy for second step is greater than that of first step for all the three copolymers and it is decreased with increasing amount of BC in the copolymer indicating rigid nature of DHDPS moiety.

Different magnitudes of kinetic parameters suggested different degradation mechanism. In accordance with theory, high magnitude of E_a supported high magnitude of A in case of all the three copolymers. The values of ΔS^* for both the steps are determined at respective T_{max} and is also reported in Table 4.5. The large and positive magnitudes of ΔS^* for PSS-1 has confirmed less ordered transition state than individual polymer molecules, while large and negative magnitudes of PSS-2 and PSS-3 confirmed highly ordered transition state. Thermal stability of copolymers under investigation is comparable with other polysulfonates based on bisphenol-C derivatives (325°-379°C) [25-31] and polysulfonates containing rigid moieties (> 300°C) [32-37].

The ether, sulfone and sulfonate linkages are weak points in the copolymer chains and hence selective degradation occurs on heating.

The degradation may result in the formation of free radicals, which may further undergo recombination and degrade at high temperatures. The degradation process is a complex process and involves a variety of reactions such as fragmentation of chain segment, branching, networking, re arrangement, etc. Small amount of residual weight suggested the formation of low molecular weight substances on degradation.

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26. J.A.Desai, P.A.Krishnamoorthy, P.H.Parsania, *J. Macromol. Sci. Pue and Appl.Chem.* **A-34**, 1171, 1997
 27. M.M.Kamani, P.H.Parsania, *J. Polym. Mater.* **12**, 223, 1995
 28. A.R.Shah, P.H.Parsania, *J. Polym. Mater.* **14**, 171, 1997
 29. Falguni D. Karia, P.H.Parsania, *J Polym. Mater.* **16**, 161, 1999
 30. Y.V.Patel and P.H.Parsania, *Eurp. Polym. J.* **38**, 1827, 2002
 31. E.P.Goldberg, F. Scardiglia, US Patent. 3, 217, 055, 1966, C.A. **66**, 3,015, 1967
 32. R.J.Schlott, E.P.Goldberg, F. Scardiglia, D.F.Hoeg, *Advan. Chem. Ser.No.* 91, 703, 1969; C.A. **72**, 21,966, 1970
 33. Borg Warner Corporation, British Patent. 1,051,202 1965; C.A. **64**, 8,417, 1966
 34. E.P.Goldberg, F.Scardiglia, U.S.Patent. 3, 262, 914 1966; C.A. **65**, 15, 539, 1966
 35. Borg Warner Corporation, Fr. Patent. 1, 521, 342, 1968; C.A. **70**, 115, 696, 1969
 36. General Electrical Company, Neth. Appl. Pattend. 6, 600, 874, 1966; C.A. **66**, 19, 036, 1967
 37. E.P.Goldberg, F.Scardiglia, British Patent. 1, 151, 599, 1969; C.A. **71**, 30, 834, 1969

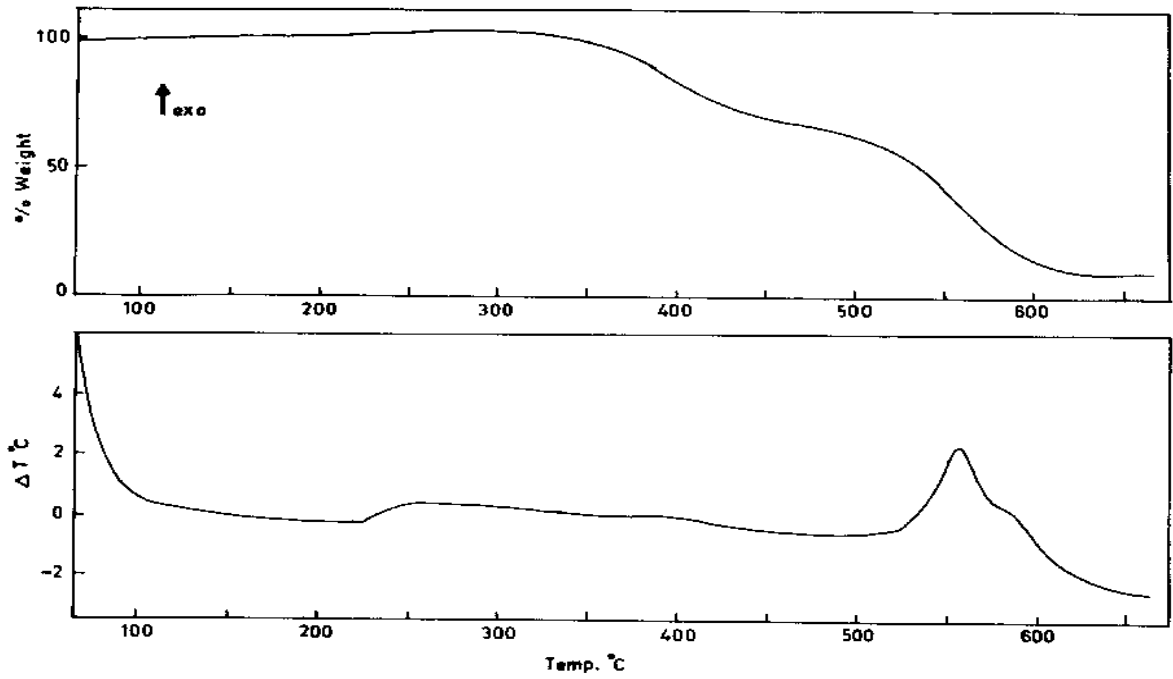


Fig.-4.1 DTA-TG thermograms of PSS-1 at the heating rate of 15°C/min. in an N₂ atmosphere

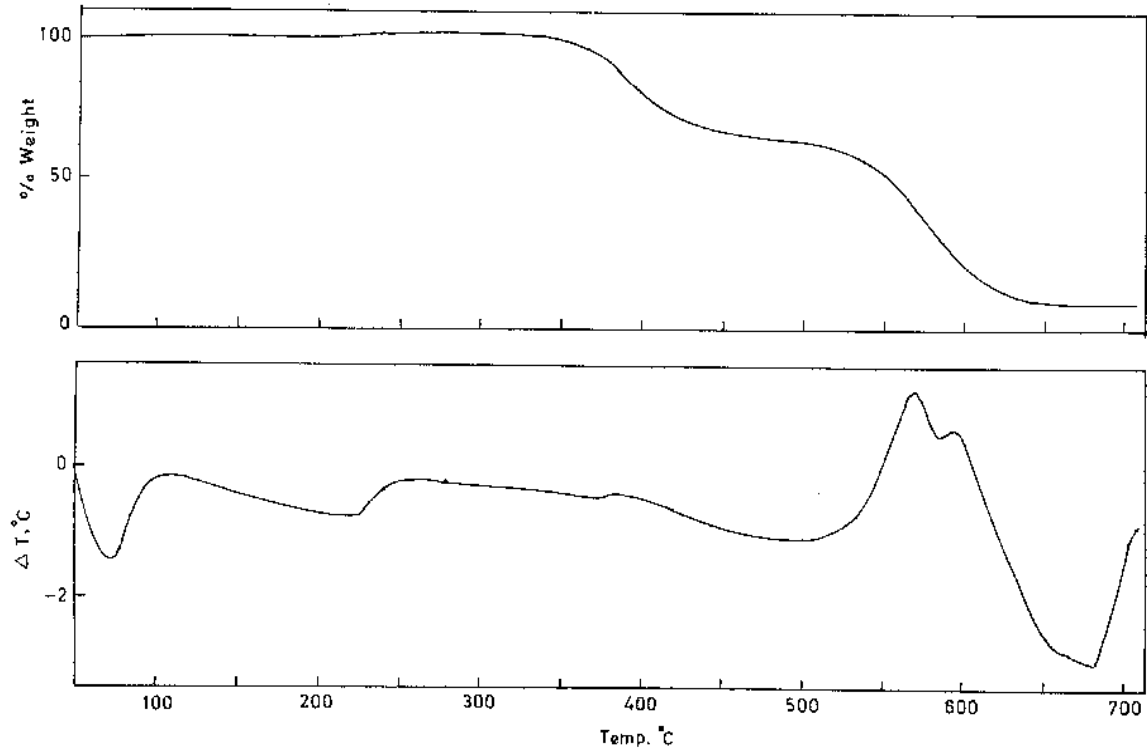


Fig.- 4.2 DTA-TG thermograms of PSS-2 at the heating rate of 15°C/min. in an N₂ atmosphere

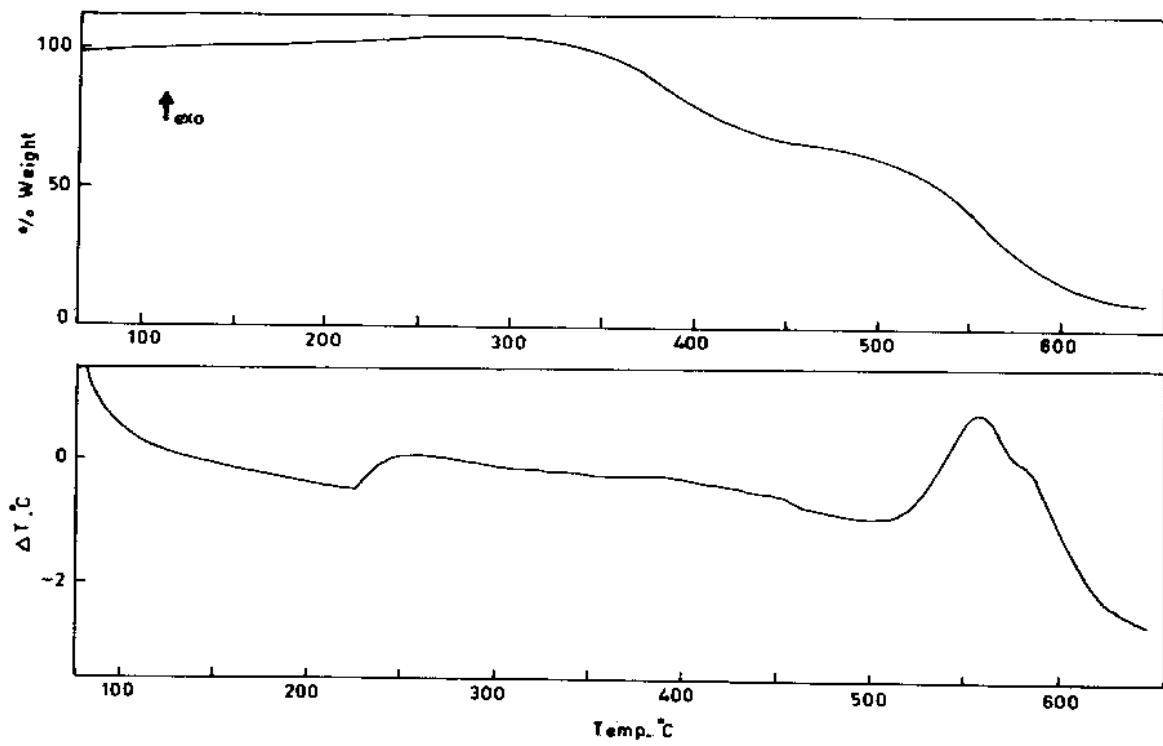


Fig. - 4.3 DTA-TG thermograms of PSS-3 at the heating rate of 15°C/min. in an N₂ atmosphere

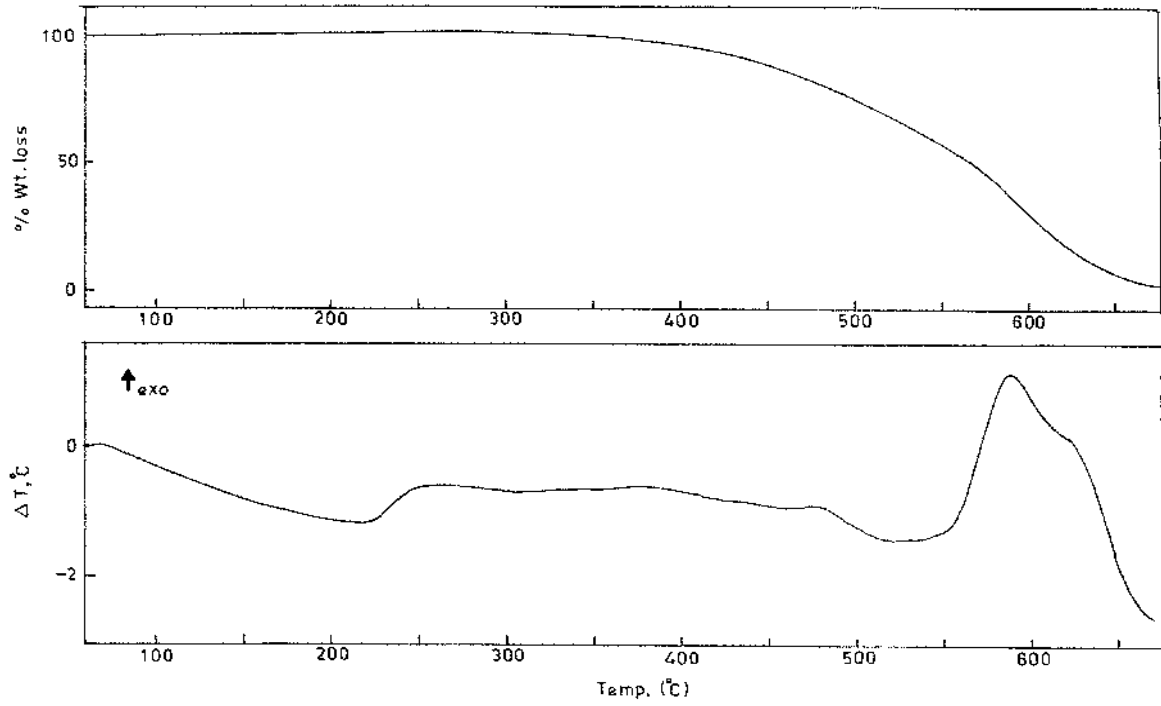


Fig.- 4.4 DTA-TG thermograms of PES-C at the heating rate of 15°C/min. in an N₂ atmosphere

Table-4.1: DTA and TGA data of PSS-1 to PSS-3

Polymer	DTA		TGA			
	Transition	Temp., °C	IDT, °C	Decomp n. °C	% Wt. Loss	T _{max} °C
PSS-1	Endo	235.1	350	350-440	30.4	396
	Exo	559.1	510	510-630	56.2	559.3
PSS-2	Endo	234.1	350	350-425	28.5	392.8
	Exo	570.9	540	540-640	48.6	570.4
PSS-3	Endo	233.7	350	350-430	27.1	388.0
	Exo	560.5	510	510-620	47.8	560.8

Poly ether sulfone

For end use applications, the knowledge of thermal properties of polymers is very essential since it provides informations about characteristic degradation pattern, molecular architecture and degradation mechanism. Thermal stability of polymers is useful in designing specific applications. TG-DTA thermograms of PES-C at the heating rate of 15⁰C/min in nitrogen atmosphere are shown in Fig.4.4. DTA thermogram of PES-C showed T_g at 234⁰C and exothermic decomposition transitions at 485⁰ and 591.4⁰C, which are supported by weight loss in TG thermogram over that temperature ranges. PES-C is thermally stable up to about 350⁰C and involved apparently single step decomposition reaction with 93.6 % weight loss up to 640⁰C.

Actually, it is a two-step decomposition reaction. The temperature of maximum weight loss is observed at 596⁰ C. PES-C possesses some what high T_g as compared to polyether sulfones of bisphenol-A (trade name Udel, T_g 190⁰C) and 4, 4'-dihydroxydiphenyl (Radel, T_g 220⁰C). Due to overlapping of two steps, kinetic parameters are not determined. The ether and sulfone linkages in the chain are weak points, which degrade selectively to form free radicals. These free radicals may further under go recombination to form new products, which may degrade at higher temperatures, but DTA thermograms did not show formation of any compound. Thus, the formation of a new compound is ruled out on the basis of DTA observations and the decomposition at higher temperatures

might be due to further decomposition of fragmented pieces in to low molecular weight hydrocarbons. The degradation of polymers is a complex process and involve a variety of reactions such as chain cleavage, rearrangement of chain segments, decomposition of chain segments, cross linking, branching reaction, etc.

In accordance with theory, high magnitude of E_a supported high magnitude of A in case of all the three copolymers. The values of ΔS^* for both the steps are determined at respective T_{max} and is also reported in Table 4.5. The large and positive magnitudes of ΔS^* for PSS-1 has confirmed less ordered transition state than individual polymer molecules, while large and negative magnitudes of PSS-2 and PSS-3 confirmed highly ordered transition state.

The ether, sulfone and sulfonate linkages are weak points in the copolymer chains and hence selective degradation occurs on heating. The degradation may result in the formation of free radicals, which may further undergo recombination and degrade at high temperatures. The degradation process is a complex process and involves a variety of reactions such as fragmentation of chain segment, branching, networking, rearrangement, etc.

Small amount of residual weight suggested the formation of low molecular weight substances on degradation.

Table-4.2: The calculation scheme for PSS-1by Freeman-Anderson method

1/T	% wt. loss	dw/dt	Active Wt.	InW	In dw/dt	$\Delta \ln W$	$\Delta \ln dw/dt$
PSS-1 STEP-1							
1.57	98.34	3.40	28.26	3.341	1.223	0.040	-0.172
1.56	97.21	4.04	27.13	3.300	1.396	0.051	-0.170
1.55	95.85	4.79	27.77	3.249	1.566	0.063	-0.153
1.54	94.28	5.58	24.20	3.186	1.719	0.075	-0.129
1.53	92.53	6.35	22.45	3.111	1.848	0.089	-0.102
1.52	90.62	7.03	20.54	3.022	1.950	0.105	-0.075
1.51	88.58	7.58	18.49	2.917	2.025	0.124	-0.045
1.5	86.42	7.93	16.34	2.793	2.070	0.147	-0.013
1.49	84.18	8.04	14.10	2.646	2.084	0.175	0.023
1.48	81.91	7.85	11.83	2.471	2.060	0.211	0.069
1.47	69.66	7.32	9.58	2.260	1.991	0.258	0.132
1.46	77.48	6.41	7.40	2.001	1.859	0.323	0.233
1.45	75.43	5.08	5.35	1.678	1.625	0.414	0.436
PSS-1 STEP-2							
1.24	55.30	7.30	46.18	3.832	1.989	0.086	-0.242
1.23	51.47	9.31	42.26	3.746	2.231	0.116	-0.187
1.22	46.81	11.23	37.70	3.629	2.418	0.150	-0.114
1.21	41.56	12.59	32.44	3.479	2.533	0.190	-0.037
1.20	35.95	13.06	26.83	3.290	2.570	0.237	-0.049
1.19	30.29	12.44	21.17	3.052	2.521	0.295	0.158
1.18	24.87	10.62	15.75	2.757	2.363	0.367	0.333

Table-4.3: The calculation scheme for PSS-2 by Freeman-Anderson method

1/T	% wt. loss	dw/dt	Active Wt.	lnW	ln dw/dt	$\Delta \ln W$	$\Delta \ln dw/dt$
PSS-2 STEP-1							
1.56	94.97	4.73	24.51	3.199	1.553	0.059	-0.142
1.55	93.56	5.46	23.10	3.140	1.698	0.075	-0.131
1.54	91.88	6.23	21.42	3.064	1.830	0.093	-0.104
1.53	89.97	6.99	19.52	2.971	1.934	0.113	-0.072
1.52	87.88	7.43	17.42	2.857	2.006	0.137	-0.040
1.51	85.65	7.74	15.19	2.720	2.046	0.165	-0.007
1.50	83.33	7.80	12.87	2.554	2.054	0.200	0.023
1.49	80.99	7.62	10.53	2.354	2.030	0.244	0.053
PSS-2 STEP-2							
1.21	49.22	7.94	42.74	3.755	2.072	0.098	-0.145
1.20	45.22	9.18	38.74	3.656	2.217	0.123	-0.088
1.19	40.74	10.03	34.26	3.534	2.306	0.150	-0.039
1.18	35.96	10.44	29.48	3.383	2.345	0.182	0.006
1.17	31.05	10.37	24.57	3.201	2.339	0.221	0.049
1.16	26.16	9.87	19.69	2.980	2.290	0.272	0.092

Table-4.4: The calculation scheme for PSS-3 by Freeman-Anderson method

1/T	% wt. loss	dw/dt	Active Wt.	lnW	ln dw/dt	$\Delta \ln W$	$\Delta \ln dw/dt$
PSS-3 STEP-1							
1.57	94.46	4.93	23.19	3.143	1.595	0.061	-0.071
1.56	93.07	5.29	21.80	3.082	1.666	0.071	-0.056
1.55	91.58	5.60	20.31	3.011	1.723	0.081	-0.043
1.54	89.99	5.85	18.71	2.929	1.766	0.093	-0.029
1.53	88.31	6.02	17.04	2.835	1.796	0.107	-0.016
1.52	86.57	6.13	15.30	2.728	1.813	0.124	-0.004
1.51	84.79	6.15	13.52	2.604	1.817	0.143	0.009
1.50	82.98	6.09	11.71	2.460	1.807	0.167	0.024
1.49	81.18	5.95	9.91	2.293	1.783	0.197	0.034
PSS-3 STEP-2							
1.24	51.44	6.61	39.58	3.678	1.889	0.080	-0.117
1.23	48.38	7.43	36.52	3.598	2.006	0.099	-0.096
1.22	44.94	8.19	33.07	3.498	2.102	0.121	-0.068
1.21	41.14	8.76	29.28	3.377	2.170	0.149	-0.035
1.20	37.07	9.08	25.21	3.227	2.206	0.182	0.000
1.19	32.84	9.07	20.98	3.043	2.205	0.226	0.040
1.18	28.59	8.71	16.73	2.817	2.164	0.278	0.086
1.17	24.52	7.98	12.66	2.538	2.077	0.343	0.144
1.16	20.84	6.90	8.98	2.195	1.932	0.411	0.225

Table-4.5: The calculation scheme for PES-C by Freeman-Anderson method

1/T	% wt. loss	dw/dt	Active Wt.	lnW	ln dw/dt	Δ lnW	Δ ln dw/dt
PES-C STEP-1							
1.37	87.44	3.38	85.34	4.446	1.217	0.015	-0.082
1.36	86.13	3.67	84.03	4.431	1.300	0.017	-0.073
1.35	84.70	3.95	82.60	4.414	1.373	0.018	-0.063
1.34	83.18	4.20	81.08	4.395	1.436	0.020	-0.053
1.33	81.55	4.43	79.45	4.375	1.489	0.022	-0.042
1.32	79.83	4.63	77.73	4.353	1.532	0.023	-0.033
1.31	78.02	4.78	75.92	4.329	1.566	0.025	-0.023
1.30	76.13	4.90	74.03	4.304	1.589	0.026	-0.015
1.29	74.10	4.98	72.07	4.277	1.605	0.028	-0.009
PES-C STEP-2							
1.18	46.46	7.57	44.36	3.792	2.024	0.093	-0.119
1.17	42.50	8.53	40.40	3.699	2.144	0.114	-0.091
1.16	38.12	9.35	36.02	3.584	2.235	0.148	-0.046
1.15	33.15	9.75	31.05	3.435	2.281	0.161	0.005
1.14	28.51	9.73	36.41	3.274	2.276	0.206	0.058
1.13	23.59	9.18	21.49	3.067	2.217	0.247	0.110
1.12	18.89	8.22	16.79	2.820	2.107	0.290	0.152
1.11	14.65	7.06	12.55	2.530	1.954	0.321	0.166

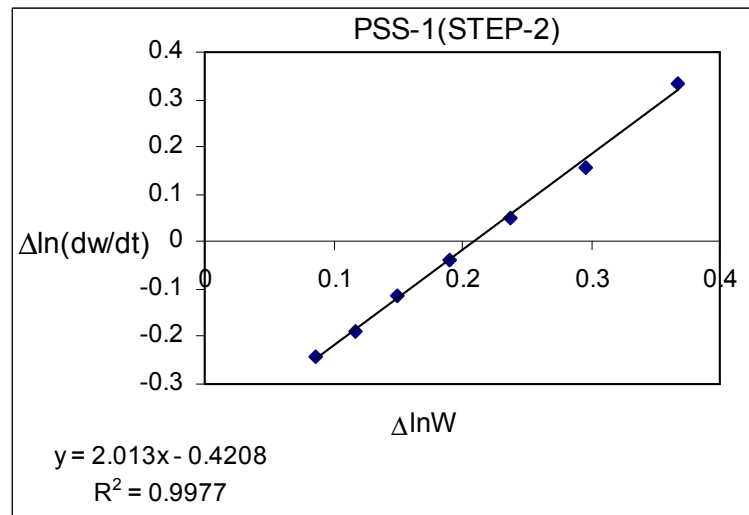
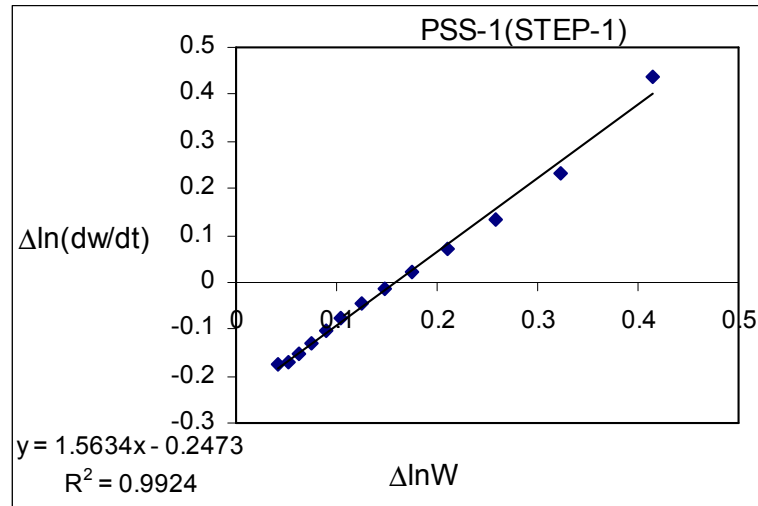


Fig.4.5 The Freeman-Anderson plots of PSS-1

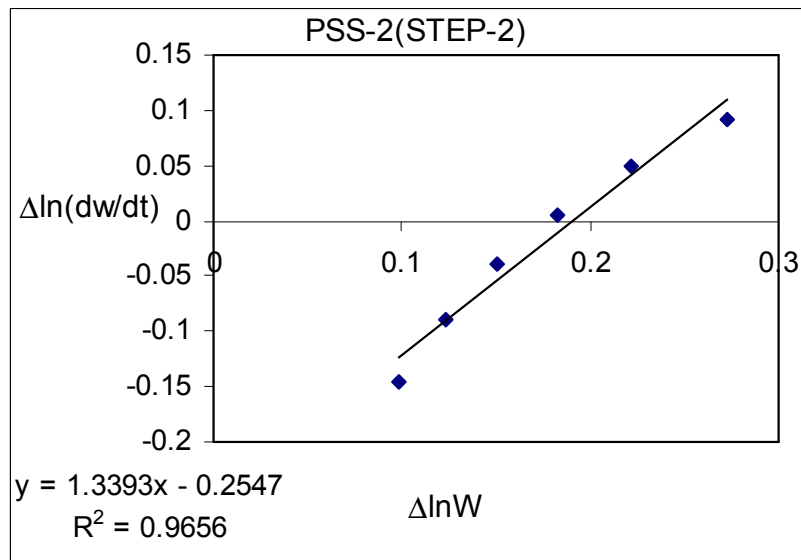
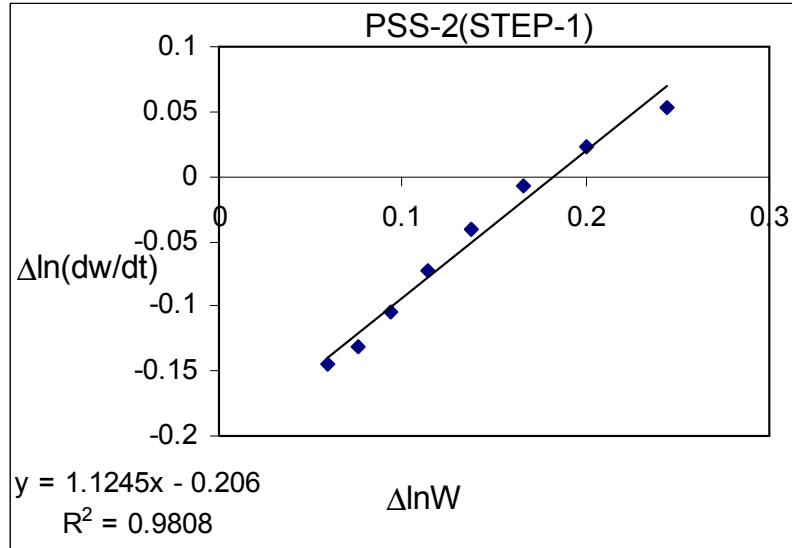


Fig.4.6 The Freeman-Anderson plots of PSS-2

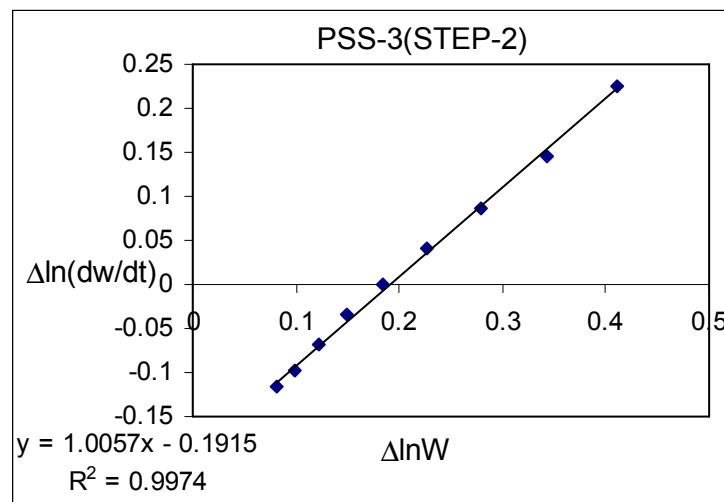
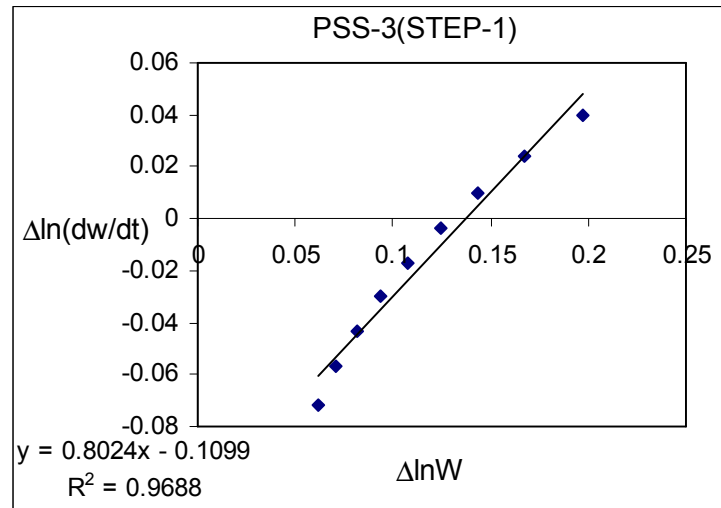


Fig.4.7 The Freeman-Anderson plots of PSS-3

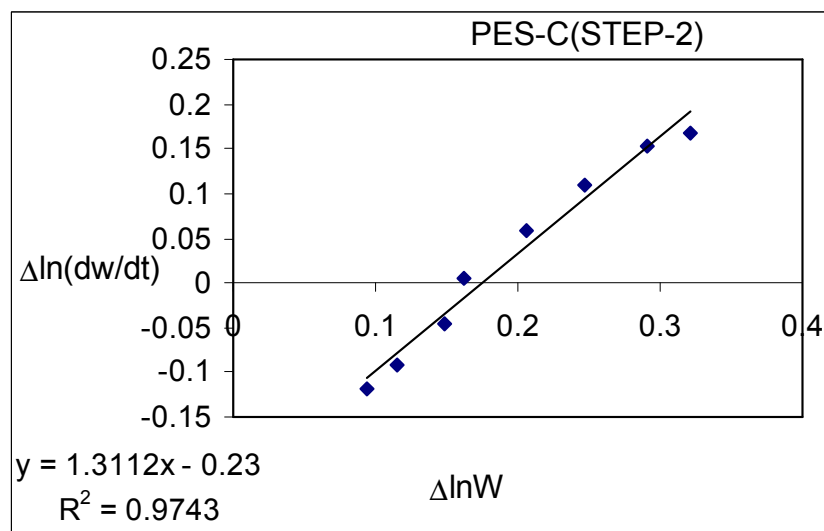
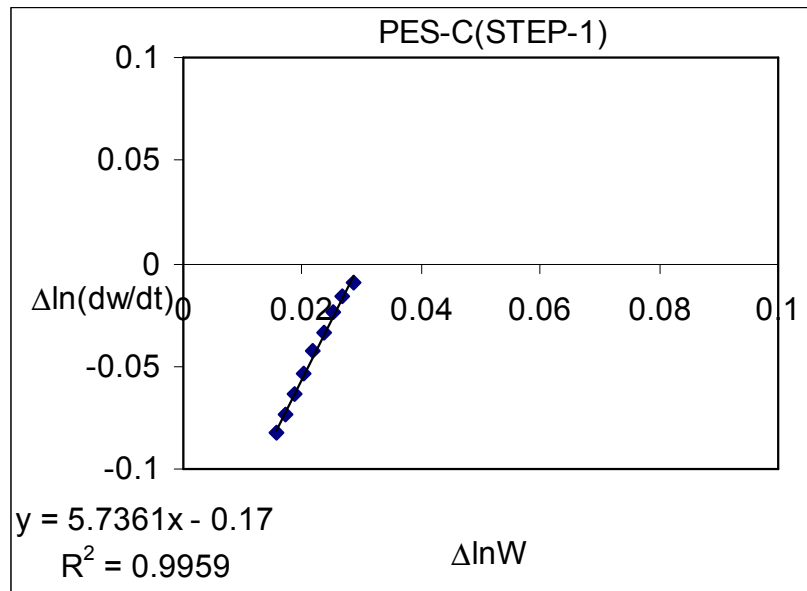


Fig.4.8 The Freeman-Anderson plots of PES-C

Table-4.6: The kinetic parameters of PSS-1 to PSS-3 derived according to Freeman- Anderson method

Polymer	n	Ea, kJ	A, S ⁻¹	ΔS*	γ
PSS-1	1.56	205.6	1.56X10 ¹⁴	20.1	0.9962
	2.01	349.9	1.39X10 ²⁰	132.2	0.9988
PSS-2	1.12	171.3	3.20X10 ¹¹	-31.3	0.9904
	1.34	211.8	1.1810 ¹¹	-41.6	0.9826
PSS-3	0.80	91.4	1.05X10 ⁵	-155.4	0.9846
	1.00	159.2	6.48X10 ⁷	-103.9	0.9987

SECTION-2: MECHANICAL AND ELECTRICAL PROPERTIES OF CARDO COPOLY (ETHER-SULFONE-SULFONATES)

INTRODUCTION

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 [38-41].

The mechanical behavior of a polymer is divided in to 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.

38. A.Krause, A.Lange, M.Ezrin, "Plastics Analysis Guide, Chemical and Instrumental Methods", Harver Pub, New York, 1983

39. T.R.Crompton, "The Analysis of Plastics", Pergamon Press, Oxford, 1984

40. R.P.Brown, "Physical Testing of Rubbers", Applied Science, London, 1979

EXPERIMENTAL

Tough and transparent films of polysulfonates 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° 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.

MEASUREMENTS

The mechanical testing (tensile strength) was made on Instron Universal Testing Machine, Model No. 1185 (IS: 11298-Pt2-1987) at a testing speed of 50 mm/min by using 15mm wide strips.

RESULTS AND DISCUSSION

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 aero plane 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.

Mechanical properties

The mechanical properties of polymers can be divided in to three types:

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

41. P.Ghosh, "Polymer Science and Technology of Plastics and Rubbers", Tata McGraw Hill Publishing Co. Ltd, New Delhi, 1982.

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.

In the present investigation, the tensile strength of PSS-1 and PSS-2 films was determined according to Eqn. 4.19:

$$\text{Tensile strength (kg/cm}^2\text{)} = \frac{\text{Load at break (g)} \times 10}{\text{Thickness in mm}} \quad \dots 4.19$$

The tensile strength data of PSS-1(89 μ m) and PSS-2(107 μ m) films are reported in Table-4.7 along with some useful plastics [41] and cardo polysulfonates [25-27, 29-31]. From Table 4.6, it is clear that PSS-1 and PSS-2 possess good to comparable tensile strength with other polysulfonates and ABS. Due to brittle nature of PSS-3 film tensile strength is not determined. From Table 4.6, it is clear that the PSS-1 and PSS-2 films have almost identical tensile strength, which supports moderate molecular weights of the polymers as supported by low intrinsic viscosities of copolymers.

ELECTRICAL PROPERTIES OF CARDO POLY (ETHER-SULFONE-SULFONATES)

INTRODUCTION

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 in to 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.

EXPERIMENTAL

The electric strength measurements were made on a high voltage tester (Allied Electricals) in an air using 25/75 mm brass electrodes according to ASTM D-149-92 method. The volume resistivity measurements were made on high resistance meter (Hewlett-Packard) at 500-volt dc and after charging for 60 sec according to ASTM D -257-92 method and dielectric measurements were made on a Schering Bridge Tettex Switzerland according to ASTM D-150-92 method.

RESULTS AND DISSCUSION

(1) Volume resistivity

A good insulating material is one that offers a high electrical resistance under a variety of condition. 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 [42] as the ratio of the potential gradient that is the electric field strength E , in a specimen to the current density J .

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:

Table-4.7: Tensile strength of poly (ether-sulfone-sulfonates), some useful plastics [41] and cardo polysulfonates

Polymer	Tensile strength, MPa	Polymer	Tensile strength, MPa
Nylon-66	62-82.7	PSBB [26]	19.71
PMMA	48.3-75.8	PSBT [26]	16.71
UF-R	70	PSMBS [27]	1.70
PPO-PS Blend	66.2	PSBD [29]	7.70
PC	55.2-65.5	PSMD[29]	10.10
PF-R	50	PS-1 [25]	21.1
PS	50	PS-2 [25]	6.2
PVC	49	PS-4 [25]	9.9
PP	32	PS-7 [31]	38.4
Teflon	13.8-34.5	PS-9 [31]	1.1
Cellulose acetate	13.1-62	PSS-1	19.7
ABS	0.24-0.43	PSS-2	18.1

$$\gamma_v = 1/\rho_v \quad \dots \quad \mathbf{4.20}$$

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 :

$$d_m = (d_1 + d_2) / 2$$

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:

$$R_v = \rho_v \cdot 4t / \pi (d_m)^2 \quad \dots \quad \mathbf{4.21}$$

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 measurements of ρ is the Ohm m. From Eqn. 4.21

$$\rho_v = 0.785 R_v (d_m)^2 / t \quad \dots \quad \mathbf{4.22}$$

Most high polymeric materials [43] 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

42. O.M.Kazarnovasky, "Testing of Electrical Insulating Materials", Mir Pub.Moscow, 1982

43. 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 [43-45] 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.

(2) 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} [43]. In some cases voltages for lower than the breakdown voltage give rise to a surface discharge that does not penetrate deep in to the bulk of a material.

This is a surface or creeping, breakdown occurring at a surface breakdown voltage. Breakdown voltage is dependent on the duration and the

44. R.F.Field, "How Humidity Affects Insulation, Part-I, D.C.Phenomena", General Radio Experimenter, Vol. 20, 1945

45. R.F.Field, "The Formation of Ionized Water Films on Dielectrics under Condition of High Humidity", J. Appl. Phys. Vol.5, 1946.

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 [39-42].

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 [43].

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,

$$E_{br} = U_{br} / t \quad \dots 4.23$$

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 [42].

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.

(3) Dielectric constant

Dielectric constant ϵ' is defined as the ratio of capacitance C of a condenser filled with the dielectric to capacitance C_0 of the same condenser with air as the dielectric:

$$\epsilon' = C / C_0 \quad \dots 4.24$$

The dielectric constant is measured in alternating field and depends on frequency and temperature. The mechanical analog of dielectric constant is the stiffness modulus. Most of the non polar polymers have dielectric constant of about 2-3. Introduction of polar and H-bonding considerably increases the dielectric constant of the polymer up to 10-12 and

at the same time, introduction of polar groups increases the leakage current and the electrical energy is dissipated as heat. The dissipation factor $\tan \delta$ is a measure of the hysteresis in charging and discharging a dielectric. It is related to the dielectric loss ϵ''

$$\tan \delta = \epsilon'' / \epsilon'$$



The use of polymers in engineering as dielectrics is becoming increasing by important choice of the dielectric for each concrete case depends on its dielectric and other physical properties over a wide range of temperatures and electric field frequencies. Investigation of dielectric properties is one of the most convenient and sensitive methods of studying polymer structures.

The observed electrical strength, volume resistivity and dielectric constant of PSS-1 and PSS-2 are listed in Table-4.7 along with some useful plastics [41] and cardo polysulfonates [25, 26, 29, 31]. From Table-4.7 it is clear that copolymers possess excellent to good electrical properties as compared to some useful plastics and other polysulfonates. It is interesting to note that volume resistivity, electric strength and dielectric constant decreased with change in

copolymer composition. Electric strength and volume resistivity have decreased with increase in bisphenol-C composition. Electric strength has improved 4 to 5 times due to incorporation of di hydroxy diphenyl sulfone (DHDPS) moiety in PS chain (7.4 kV/mm). Decreasing amount of DHDPS in PS results caused decrease in volume resistivity drastically. Thus, electrical properties especially electric strength and ϵ have improved on copolymerization.

Tablel-4.8: Electrical properties of cardo poly (ether-sulfone-sulfonates), some useful plastics [41] and cardo poly sulfonates

Polymer	Electric strength kV/mm	Volume resistivity Ohm cm	Dielectric constant
Acrylics	17.7 – 21.6	$> 10^{14}$	2.2 - 3.2
Cellulose acetate	10.2 -14.4	$10^{12} - 10^{13}$	3.2 – 7.0
Cellulose acetate butyrate	9.8 – 15.7	$10^{10} - 10^{13}$	3.2 - 6.2
Nylon-6	17.3 – 20.0	$10^{12} -10^{13}$	3.0 - 5.0
PF-R	7.9 – 16.7	$10^9 -10^{12}$	4.0 - 7.0
PVC	55.1	10^{13}	3.0 – 3.5
Polyacetals	18.3	6×10^{14}	3.7
Cellulose propionate	11.8 – 17.7	$10^{12} -10^{15}$	3.4 - 3.6
PSBB [26]	13.5	8.8×10^{11}	-
PSBT [26]	17.9	7.2×10^{14}	-
PSBD [29]	27.1	5.5×10^{15}	-
PSMD [29]	27.5	5.8×10^{15}	-
PS – 1 [25]	7.4	2.1×10^{16}	-
PS – 2 [25]	11.0	4.8×10^{16}	-
PS – 3 [25]	16.2	1.1×10^{14}	-
PS – 7 [31]	16.2	5.7×10^{16}	-
PS – 9 [31]	25.0	1.0×10^{17}	-
PSS -1	37.8	8.8×10^{16}	1.34
PSS – 2	29.5	1.5×10^{14}	1.29



CHAPTER 5
ACOUSTICAL PROPERTIES
CHAPTER 5
ACOUSTICAL PROPERTIES
OF
POLYETHERSULFONE

CHAPTER-5

ACOUSTICAL PROPERTIES OF POLYETHERSULFONE IN DIFFERENT SOLVENTS AT DIFFERENT TEMPERATURES

This chapter of the thesis describes the sound velocity, density and viscosity measurements of PES-C in different solvents such as chloroform (CF), 1,2-dichloro ethane (DCE), tetrahydrofuran (THF) and 1,4-dioxane (DO) at three different temperatures: 30°, 35°, and 40°C and evaluation of their acoustical parameters.

INTRODUCTION

In recent years, ultrasonic has become the subject of extensive research in different fields of sciences namely consumer industries, medical field, engineering, process industries, etc. [1-3]. It is also found most suitable to investigate various organic compounds (liquids), polymers, etc. [4, 5]. Ultrasonic studies in aqueous and non aqueous electrolytic solutions have led to new insight in to ion- solvent interactions [6-11] and valuable informations about the ionic interactions and the nature and the strength of interactions insight in to ion- solvent interactions [6-11] and valuable informations about the ionic interactions and the nature and the strength of interactions.

Ultrasonic velocity offers a rapid non- destructive method for the characterization of materials. Elastic constants of an isotropic material can be determined ultrasonically when both longitudinal and transverse wave velocity are known. The measurements of ultrasonic velocity have been going on for the past several years. Some of the extensively used methods [12-14] include

1. M. Woldan, J. Phys. Chem. 269, 628, 1988.
2. W. Bell and R. A. Pethrick, Polymer; 23, 369, 1982.
3. R. A. Pethrick, J. Macromol. Chem. C9, 91, 1973
4. R.T. Bayer and S.V. Locher, "Physical Ultrasonics" Academic Press, New York, 1969
5. Ch. J. Burton, Acoust. Soc. Amer., 20, 86, 1948
6. S. Granaba and B.R. Rao, Indian J. Pure and Appl. Phys. 7, 468, 1969
7. N. Saraswathi, D.E. Kappikas and S. Sundrajana, Indian J. Pure and Appl. Phys. 12, 509, 1974
8. S.K. Maiti, A.K. Chattopadhyay and S.C. Lahiri, Electro Chem. Acta, 25, 1487, 1980
9. S. Prakash, N. Prasad and O. Prakash, Acoustic, 32, 279, 1975
10. S. Prakash, N. Prasad, and O. Prakash, J. Chem. Engg. Data, 22(1), 51, 1977
11. Iswarya Bhat and H.R. Shivkumar, Indian J. Chem., 37(A), 252, 1998
12. H.J. McSkimin, J. Acoust. Soc. Am. 33, 12, 1961
13. K. Ishazaki, I.L. Spain and P. Bolsaitis, J. Acoust. Soc. Am. 59, 716, 1976
14. Papadakis, J. Acoust. Soc. Am. 59, 716, 1976.

light diffraction method, sing around method, the pulse echo superposition [12,13] , the pulse echo overlap [14] and the faster digital techniques using pulse echo method [15,16].

Non-destructive testing of ultrasonic involves incorporation of physical principles for determining flaws, dimensional variations, micro structural features and the mechanical properties of worked materials without impairing their usefulness. The non-destructive applications of ultrasonic for determining structural integrity, micro structural features and mechanical properties of worked materials.

Non-destructive testing of ultrasonic involves incorporation of physical principles for determining flaws, dimensional variations, micro structural features and the mechanical properties of worked materials without impairing their usefulness. The non-destructive applications of ultrasonic for determining structural integrity, micro structural features and mechanical properties of worked materials.

Ultrasonic non-destructive and evaluation(NDTE) plays a major role in the present day life assessment program of nuclear installation, chemical industries, gas pipe lines, etc. during preservice and in service inspection/conditions. Typical casting defects are non-metallic inclusions, porosity, shrinkage, cavities, cold shut, hot tear (shrink crack) cold or stress crack, blow holes or in homogeneity. All these defects can be tested ultrasonically by proper selection of probes (normal or angle) frequency and attenuation.

In recent years ultrasonic testing and evaluation techniques are widely used for obtaining information about micro structural and mechanical properties of metals [17-21] and wide applications have been found in medical and biological fields. The use of ultrasound for breaking kidney stones is well

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established in the medical field. The effect of sonic vibrations on the people suffering from other diseases of kidneys is not known.

The ultrasonic technique provides a powerful effective and reliable tool to investigate properties of polymer solutions. Among the ultrasonic measurements, the ultrasonic velocity measurements are easy to carry out with less instrumentation and much reliability. Propagation of ultrasonic wave in polymer -polymer solution forms the basis for the qualitative characterization. The studies of ultrasonic wave propagation in solids provide valuable informations [22, 23] on the structure of solids the intra and intermolecular interactions and behavior of polymeric chain in an ultrasonic field [24].

A review of literature [25-28] on acoustical studies on polymer solutions reveals that ultrasonic velocity measurements are used to understand the nature of molecular interactions. In recent years, an extensive use of polymeric materials in technology has necessitated the study of molecular interactions of polymers with solvents. Knowledge of acoustical properties of any solutions gives information about interactions occurring in the solutions like excess volume; the isentropic compressibility also throws the light on the nature and degree of molecular interactions in the binary mixtures.

In the solution, a coiled up polymer molecule unfolds and expands because of the natural repulsion between similar charged groups in their chain. The extent of expansion and unfolding depends on the intensity of the repulsive force and the characteristics of the polymer chain, which are generally manifested in the results of viscosity, light scattering, osmotic pressure and other measurements. It is presumed that the molecular properties such as degree of extension of the polymer chain may be related to

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the compressibility data, obtained by sound velocity measurements.

The literature survey on sound velocity measurements revealed that the most of the work has been confined mainly on liquids and liquid mixtures but in case of polymers it has been confined mainly on addition polymers [29-35].

Recently sound velocity measurements on condensation polymers in protic or aprotic solvents are carried out by Parsania et.al. [36-52] and investigated the influence of solvent, concentration, temperature and the nature of the substituents on the structure of polymers and molecular interactions in the solutions under investigations.

With a view to understand the influence of solvents on the structure and molecular interactions occurring in the solutions, the present chapter reports the effects of temperature, concentration and solvent on sound velocity and thermodynamic parameters of PES-C polymer solutions.

EXPERIMENTAL

The solvents and polymers used in the present study were purified by appropriate methods prior to their use. The densities (ρ), viscosities (η) and

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sound velocities(U) were measured by means of specific gravity bottle, Ubbelohde suspended level viscometer and multi frequency interferometer operating at 2 MHz (Mittal Enterprises, Delhi), respectively. All the measurements were carried out at three different temperatures: 30° , 35° , $40^\circ \pm 0.1^\circ \text{C}$

(1) Density measurements

The densities of pure solvents were measured by means of specific gravity bottle at three different temperatures: 30° , 35° and 40°C by determining the weights of distilled water, solvents and solutions.

The density (ρ) was calculated according to Eqn. 5.1 with an accuracy of $\pm 0.0001 \text{ g/cm}^3$:

$$\rho \text{ (g / cc)} = \frac{\text{Wt.ofsolvent/solution}}{\text{Wt.ofwater}} \quad \dots 5.1$$

(2) Viscosity measurements

The method for determining the dynamic viscosity or coefficient of viscosity of liquids relies on stoke's law.

In present investigation, suspended level viscometer developed by Ubbelohde was used. The viscometer was washed with chromic acid, distilled water, acetone and then dried at 50°C in an oven. Viscometer was suspended in a thermostat at $30^\circ\text{C} \pm 0.1^\circ\text{C}$ and measured quantity of the distilled water / solvent / solution was placed into the viscometer reservoir by means of a pipette and thermally equilibrated for about 10 min. The efflux time of liquid between two marks was measured by means of digital stopwatch with an accuracy of $\pm 0.01 \text{ sec}$. Three replicate measurements on each liquid were made and the arithmetic mean was considered for the purpose of calculations. Using the flow times (t) and known viscosity of standard (water) sample, the viscosities of solvents and solutions were determined according to Eqn. 5.2.:

$$\frac{\eta_1}{\eta_2} = \frac{t_1 \rho_1}{t_2 \rho_2} \quad \dots 5.2$$

Where η_1 , ρ_1 , t_1 and η_2 , ρ_2 , t_2 are the viscosities, densities and flow times of standard and unknown samples, respectively.

(3) Sound velocity measurements

Ultrasonic interferometer (F-81) (Mittal Enterprises, New Delhi) was used in the present investigation. The working of interferometer was tested by measuring the sound velocity of pure solvents: benzene, n-hexane, cyclohexane and carbon tetrachloride and comparing the results with literature data. The advantage of this instrument is that the quantity of sample needed for measurement is small (15-20 ml).

The measuring cell (2 MHz) with quartz crystal was filled with the solvent/solution and then micrometer was fixed. The circulation of water from the thermostat (at 30°, 35° and 40°C) was started and the experimental liquid in the cell is allowed to thermally equilibrate. The high frequency generator was switched on and the micrometer was rotated very slowly so as to obtain a maximum or minimum of the anode current. A number of maximum readings of anode current (n) were counted. The total distance (d) traveled by the micrometer for $n=20$ was read. The wave length (λ) was determined according to Eqn. 5.3 :

$$\lambda = \frac{2d}{n} \quad \dots 5.3$$

The sound velocity (U) of solvents and solutions were calculated from the wave length (λ) and frequency (F) according to Eqn. 5.4:

$$U = \lambda \cdot F \quad \dots 5.4$$

RESULTS AND DISCUSSION

The density (ρ), viscosity (η), sound velocity (U) and pooled precision standard deviation (Sp) data of pure solvents: chloroform (CF), 1,2-dichloroethane (DCE) and tetrahydrofuran (THF), dioxane (DO) and polymer (PES-C) solutions (0.5 to 4%) at three temperatures: 30°, 35° and 40° C are determined according to Eqns. 5.1 to 5.4, respectively and are reported in Tables- 5.1 to 5.4 : The plots of ρ against C and η against C and U against C are shown in Figs. 5.1 to 5.12, respectively. From Figs. 5.1 to 5.4, it is clear the density of PES-C solutions increased linearly with concentration and

decreased linearly with temperature. The observed trend in ρ is CF>DCE>DO>THF. Viscosity of PES-C solutions increased linearly (Figs. 5.5, 5.7 and 5.8) with C except DCE system Fig.5.6) and decreased linearly with T. In DCE system above 2% concentration η showed curvature at all the three temperatures studied. The observed trend in η is DO>DCE> CF> THF. Ultrasonic velocity (U) increased linearly with C and decreased linearly with T (Figs.5.9 to 5.12). The observed trend in U is DO>THF>DCE>CF. The linear least square equations and regression coefficients (R^2) are presented in respective figures. A good to excellent correlation between ρ and C ($R^2=0.9004-0.9962$) to excellent correlation between η and C ($R^2=0.951-0.9794$) and U and C ($R^2=0.8185-0.9896$). The increase in ρ, η and U with C indicated increase in cohesion forces due to powerful polymer-solvent interactions. The decrease in ρ, η and U with T supported decrease in cohesion forces. The changes in ρ and U with C are not appreciable as compared to η because macromolecular motion is affected by polymer-solvent and polymer-polymer interactions. The nonlinear increase in η above 2% in DCE system indicated structural modification due to polymer-solvent interactions [53-56]. The increase in temperature of the system results in to increase in kinetic energy and volume expansion, which are responsible for the decrease in η and ρ and increase in intermolecular free length.

With a view to understand the effect of solvent and temperature on molecular interactions occurring in the solutions, various acoustical parameters were calculated according to following standard relationships:

1. Isentropic compressibility

Isentropic compressibility (κ_s) can be evaluated according to Newton and Laplace:

$$\kappa_s = \frac{1}{U^2 \rho} \quad \dots 5.5$$

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Table-5.1: The density (ρ), viscosity (η), sound velocity (U) and pooled precision standard deviation (Sp) data of polymer (PES-C) solutions in chloroform (CF) at three different temperatures: 30°, 35° and 40°C.

Conc. %	Density ρ , kg / m ³	Viscosity η . 10 ³ PaS	Ave. Dist. d.10 ³ , m	Wave length λ .10 ³ ,m	U ms ⁻¹ (F=2MHz)	Sp
PES-C + CF at 30° C						
0	1461.1	0.608	4.795	0.4795	959	0.003
0.5	1465.3	0.632	4.828	0.4828	965.6	
1	1467.2	0.698	4.836	0.4836	967.2	
1.5	1469.1	0.731	4.845	0.4845	969	
2	1470.5	0.774	4.857	0.4857	971.4	
3	1472	0.830	4.868	0.4868	973.6	
4	1473	0.851	4.883	0.4883	976.6	
PES-C + CF at 35° C						
0	1458.9	0.571	4.737	0.4737	947.4	0.002
0.5	1464	0.637	4.757	0.4757	951.4	
1	1466.1	0.638	4.777	0.4777	955.4	
1.5	1467.9	0.684	4.794	0.4794	958.8	
2	1469.2	0.726	4.801	0.4801	960.2	
3	1470.7	0.764	4.810	0.4810	962	
4	1471.7	0.801	4.813	0.4813	962.6	
PES-C + CF at 40° C						
0	1456.8	0.546	4.606	0.4606	921.2	0.002
0.5	1462.8	0.574	4.668	0.4668	933.6	
1	1465	0.607	4.677	0.4677	935.4	
1.5	1467	0.648	4.686	0.4686	937.2	
2	1468.1	0.696	4.694	0.4694	938.8	
3	1469.2	0.734	4.706	0.4706	941.2	
4	1470.5	0.779	4.729	0.4729	945.8	

Table-5.2: The density (ρ), viscosity (η), sound velocity (U) and pooled precision standard deviation (Sp) data of polymer (PES-C) solutions in 1,2-dichloro ethane (DCE) at three different temperatures: 30°, 35° and 40° C .

Conc. %	Density ρ , kg / m ³	Viscosity $\eta \cdot 10^3$ PaS	Ave. Dist. $d \cdot 10^3$, m	Wave length $\lambda \cdot 10^3$, m	U ms ⁻¹ (F=2MHz)	Sp
PES-C + DCE at 30° C						
0	1240	0.711	5.843	0.5843	1168.6	0.002
0.5	1245.1	0.769	5.875	0.5875	1175	
1	1246.9	0.802	5.864	0.5864	1172.8	
1.5	1249	0.826	5.880	0.5880	1176	
2	1250.9	0.845	5.884	0.5884	1176.8	
3	1252.4	0.864	5.903	0.5903	1180.6	
4	1253.9	0.878	5.993	0.5993	1198.6	
PES-C + DCE at 35° C						
0	1238.5	0.674	5.856	0.5856	1171.2	0.003
0.5	1244	0.731	5.866	0.5866	1173.2	
1	1245.2	0.765	5.874	0.5874	1174.8	
1.5	1247.7	0.786	5.881	0.5881	1176.2	
2	1249.6	0.808	5.886	0.5886	1177.2	
3	1251.1	0.834	5.904	0.5904	1180.8	
4	1252.6	0.843	5.912	0.5912	1182.4	
PES-C + DCE at 40° C						
0	1237.1	0.653	5.588	0.5588	1117.6	0.003
0.5	1234.8	0.714	5.686	0.5686	1137.2	
1	1244.1	0.753	5.691	0.5691	1138.2	
1.5	1246.2	0.770	5.707	0.5707	1141.4	
2	1248.6	0.790	5.708	0.5708	1141.6	
3	1250.1	0.812	5.735	0.5735	1147	
4	1251.3	0.829	5.723	0.5723	1144.6	

Table-5.3: The density (ρ), viscosity (η), sound velocity (U) and pooled precision standard deviation (Sp) data of polymer (PES-C) solutions in tetrahydrofuran(THF) at three different temperatures: 30°, 35° and 40° C .

Conc. %	Density ρ , kg / m ³	Viscosity $\eta \cdot 10^3$ PaS	Ave. Dist. $d \cdot 10^3$, m	Wave length $\lambda \cdot 10^3$, m	U ms ⁻¹ (F=2MHz)	Sp
PES-C + THF at 30° C						
0	883.5	0.468	6.316	0.6319	1263.2	0.003
0.5	890.6	0.504	6.294	0.6294	1258.8	
1	891.5	0.523	6.299	0.6299	1259.8	
1.5	892.8	0.547	6.303	0.6303	1260.6	
2	894.4	0.579	6.319	0.6319	1263.8	
3	896.3	0.607	6.333	0.6333	1266.6	
4	898.8	0.635	6.335	0.6335	1267	
PES-C + THF at 35° C						
0	881.5	0.447	6.156	0.6156	1231.2	0.002
0.5	889.5	0.473	6.177	0.6177	1235.4	
1	890.1	0.500	6.180	0.6180	1236	
1.5	891.2	0.523	6.203	0.6203	1240.6	
2	892.8	0.554	6.187	0.6187	1237.4	
3	894.6	0.578	6.208	0.6208	1241.6	
4	897.1	0.602	6.224	0.6224	1244.8	
PES-C + THF at 40° C						
0	877.8	0.427	6.059	0.6059	1211.8	0.003
0.5	887.6	0.456	6.071	0.6071	1214.2	
1	888.3	0.480	6.088	0.6088	1217.6	
1.5	889.4	0.509	6.096	0.6096	1219.2	
2	891.1	0.535	6.104	0.6104	1220.8	
3	892.9	0.563	6.108	0.6108	1221.6	
4	895.1	0.593	6.122	0.6122	1224.4	

Table-5.4: The density (ρ), viscosity (η), sound velocity (U) and pooled precision standard deviation (Sp) data of polymer (PES-C) solutions in 1, 4-dioxane (DO) at three different temperatures: 30°, 35° and 40°C.

Conc. %	Density ρ , kg / m ³	Viscosity η . 10 ³ PaS	Ave. Dist. d.10 ³ , m	Wave length λ .10 ³ ,m	U ms ⁻¹ (F=2MHz)	Sp
PES-C + DO at 30° C						
0	1025	1.080	6.605	0.6605	1321	0.002
0.5	1038.7	1.100	6.627	0.6627	1325.4	
1	1039.8	1.113	6.637	0.6637	1327.4	
1.5	1040.8	1.130	6.644	0.6644	1328.8	
2	1041.8	1.140	6.651	0.6651	1330.2	
3	1043.1	1.166	6.661	0.6661	1332.2	
4	1044.5	1.174	6.669	0.6669	1333.8	
PES-C + DO at 35° C						
0	1023	1.025	6.528	0.6528	1305.6	0.002
0.5	1037.1	1.052	6.554	0.6554	1310.8	
1	1038.1	1.076	6.572	0.6572	1314.4	
1.5	1039.3	1.082	6.597	0.6597	1319.4	
2	1040.2	1.101	6.616	0.6616	1323.2	
3	1041.4	1.119	6.628	0.6628	1325.6	
4	1042.5	1.139	6.654	0.6654	1330.8	
PES-C + DO at 40° C						
0	1020.9	1.006	6.518	0.6518	1303.6	0.003
0.5	1033.5	1.0323	6.526	0.6526	1305.2	
1	1036.4	1.052	6.543	0.6543	1308.6	
1.5	1037.9	1.066	6.546	0.6546	1309.2	
2	1038.9	1.088	6.562	0.6562	1312.4	
3	1039.8	1.091	6.572	0.6572	1314.4	
4	1041.5	1.117	6.594	0.6594	1318.8	

2. Isentropic compressibility

Isentropic compressibility (κ_s) can be evaluated according to Newton and Laplace:

$$\kappa_s = \frac{1}{U^2 \rho} \quad \dots \text{5.5}$$

3. Specific acoustical impedance

$$Z = U\rho \quad \dots \text{5.6}$$

4. Rao's molar sound function

Rao's molar sound function (R) can be evaluated by employing a method suggested by Bagchi et al. [57]:

$$R = \frac{M}{\rho} U^{1/3} \quad \dots \text{5.7}$$

The apparent molecular weight (M) of the solution can be calculated according to Eqns. 5.8:

$$M = M_1W_1 + M_2W_2 \quad \dots \text{5.8}$$

Where W_1 and W_2 are weight fractions of solvent and polymer, respectively. M_1 and M_2 are the molecular weights of the solvent and polymer repeat unit, respectively. The weight fractions and apparent molecular weights of polymer (PES-C) solutions are reported in Tables 5.5 to 5.8.

5. Van der Waals constant

Van der waals constant (b) [58] can be calculated according to Eqn.5.9

$$b = \frac{M}{\rho} \left[1 - \left[\frac{RT}{MU^2} \right] \left[\sqrt{1 + \frac{MU^2}{3RT}} - 1 \right] \right] \quad \dots \text{5.9}$$

Where R (8.314 JK⁻¹ mol⁻¹) is the gas constant and T (°K) is the absolute temperature.

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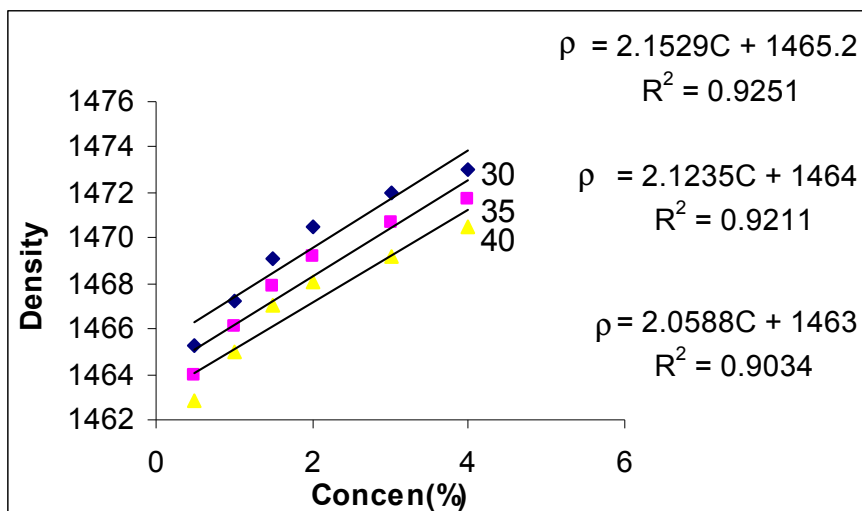


Fig 5.1: The plots of density (ρ) against concentration (%) at 30°, 35° and 40°C for PES-C in chloroform

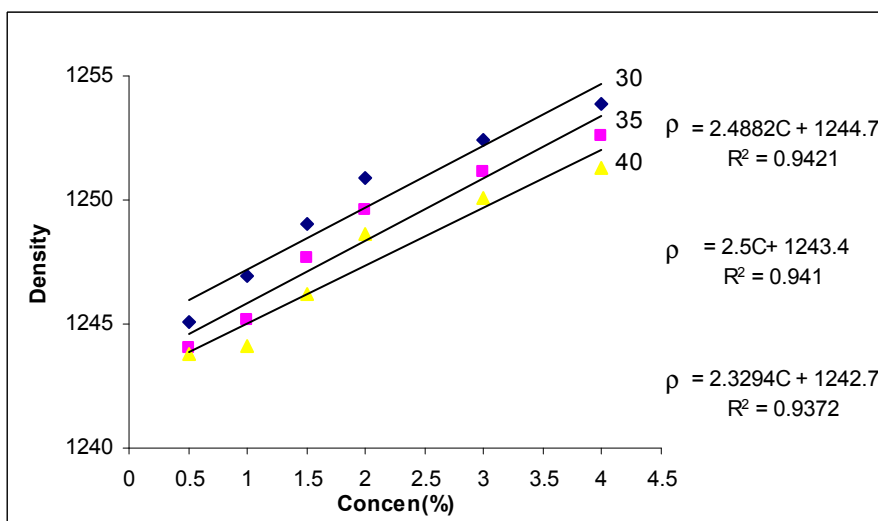


Fig 5.2: The plots of density (ρ) against concentration (%) at 30°, 35° and 40°C for PES-C in 1, 2- dichloroethane.

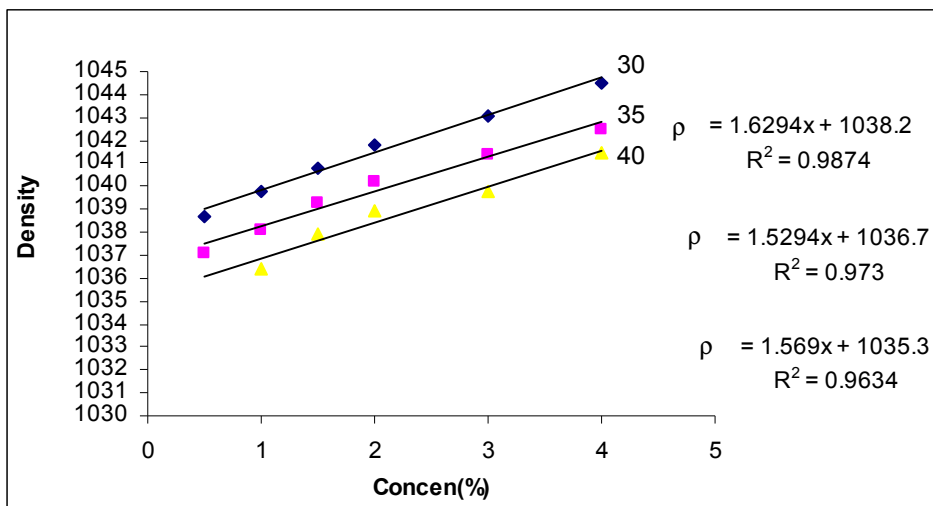


Fig 5.3: The plots of density (ρ) against concentration (%) at 30°, 35° and 40°C for PES-C in 1, 4-dioxane.

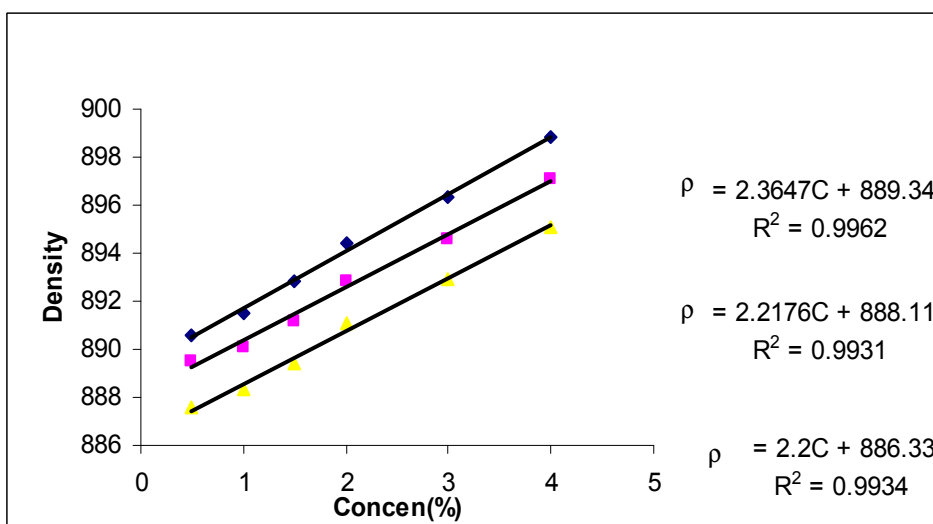


Fig 5.4: The plots of density (ρ) against concentration (%) at 30°, 35° and 40°C for PES-C in THF

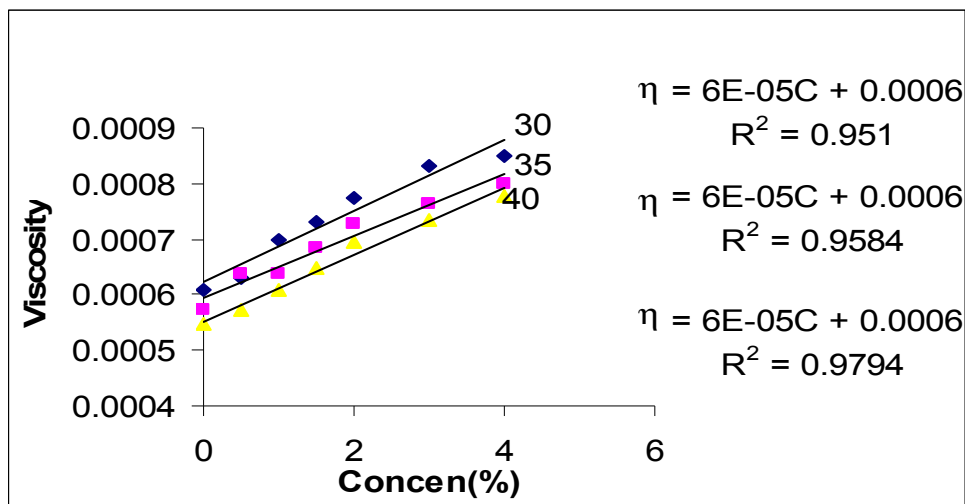


Fig 5.5: The plots of viscosity (η) against concentration (%) at 30°, 35° and 40°C for PES-C in chloroform

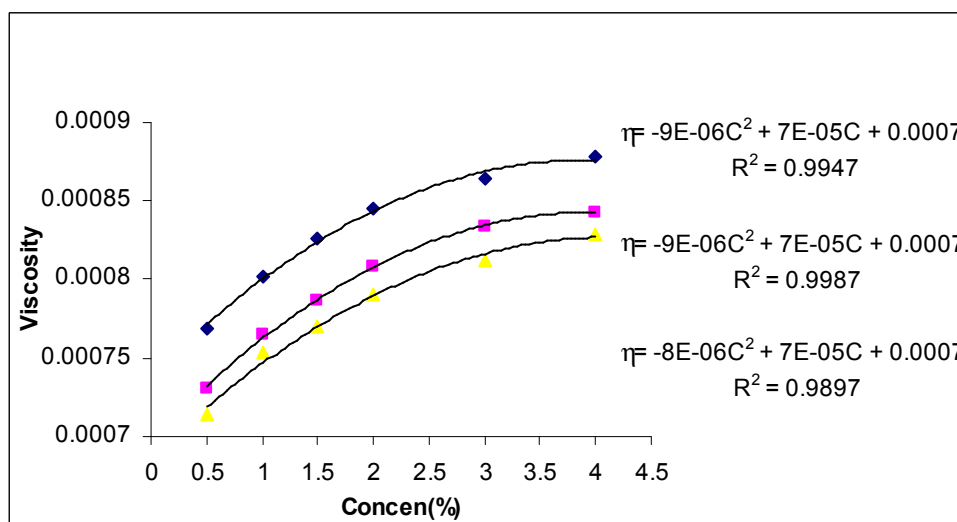


Fig 5.6: The plots of viscosity (η) against concentration (%) at 30°, 35° and 40°C for PES-C in 1, 2 dichloroethane

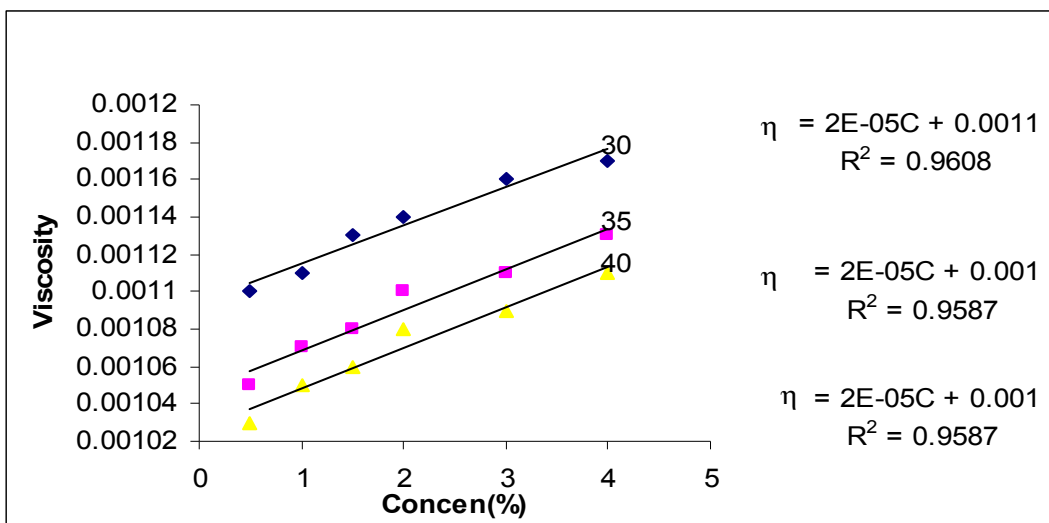


Fig 5.7: The plots of viscosity (η) against concentration (%) at 30°, 35° and 40°C for PES-C in 1, 4-dioxane.

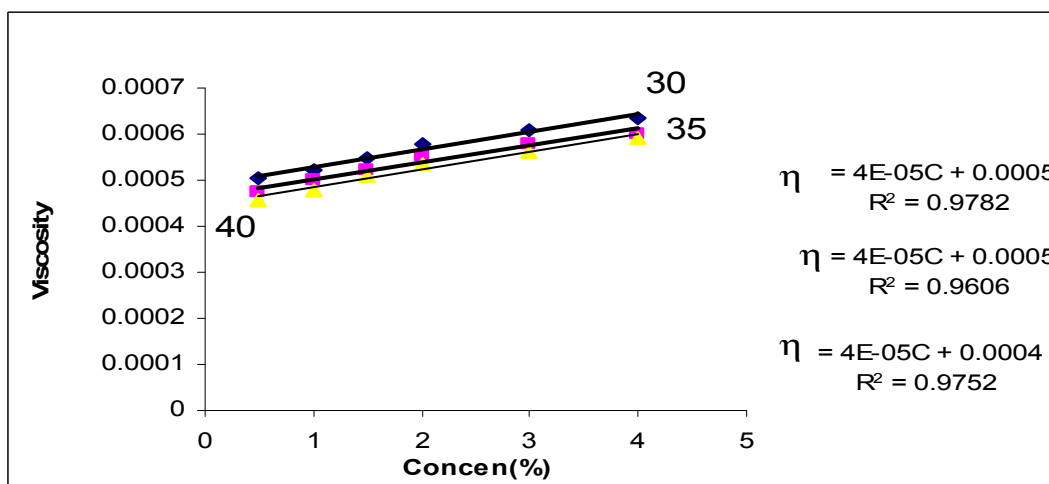


Fig 5.8: The plots of viscosity (η) against concentration (%) at 30°, 35° and 40°C for PES-C in THF.

Table-5.5: The apparent molar weights of the solutions (M) and the number of grams of solute in 100 g of chloroform solution (X) at 30°, 35° and 40°C

Conc., %	W ₁	W ₂	M, kg	X	Sn
PES-C + CF at 30° C					
0	1.0000	0.0000	0.1193	-	-
0.5	0.9966	0.0034	0.1206	0.3412	0.84
1	0.9932	0.0068	0.1218	0.6815	1.32
1.5	0.9898	0.0102	0.1230	1.0210	1.99
2	0.9864	0.0136	0.1243	1.3600	2.15
3	0.9796	0.0204	0.1267	2.0380	2.66
4	0.9728	0.0271	0.1292	2.7155	3.05
PES-C + CF at 35° C					
0	1.0000	0.0000	0.1193	-	-
0.5	0.9966	0.0034	0.1206	0.3415	1.17
1	0.9932	0.0068	0.1218	0.6820	1.29
1.5	0.9898	0.0102	0.1230	1.0218	1.94
2	0.9864	0.0136	0.1243	1.3612	1.88
3	0.9796	0.0204	0.1267	2.0398	2.52
4	0.9728	0.0271	0.1292	2.7179	2.98
PES-C + CF at 40° C					
0	1.0000	0.0000	0.1193	-	-
0.5	0.9966	0.0034	0.1206	0.3418	0.45
1	0.9932	0.0068	0.1218	0.6825	0.78
1.5	0.9898	0.0102	0.1230	1.0224	1.17
2	0.9864	0.0136	0.1243	1.3623	1.37
3	0.9796	0.0204	0.1267	2.0419	1.89
4	0.9728	0.0271	0.1292	2.7201	2.25

Table-5.6: The apparent molar weights of the solutions (M) and the number of grams of solute in 100g of DCE solution (X) at 30°, 35° and 40°C.

Conc.,%	W ₁	W ₂	M, kg	X	Sn
PES-C + DCE at 30° C					
0	1.0000	0.0000	0.0989	-	-
0.5	0.9960	0.0040	0.1005	0.4015	1.32
1	0.9920	0.0080	0.1020	0.8019	3.11
1.5	0.9880	0.0120	0.1035	1.2009	4.68
2	0.9840	0.0159	0.1050	1.5988	4.03
3	0.9760	0.0239	0.1081	2.3954	5.32
4	0.9681	0.0319	0.1118	3.1900	5.36
PES-C + DCE at 35° C					
0	1.0000	0.0000	0.0989	-	-
0.5	0.9960	0.0040	0.1005	0.4019	2.52
1	0.9920	0.0080	0.1020	0.8030	3.44
1.5	0.9880	0.0120	0.1035	1.2022	5.17
2	0.9840	0.0159	0.1050	1.6005	5.02
3	0.9760	0.0239	0.1081	2.3978	6.31
4	0.9681	0.0319	0.1119	3.1933	6.16
PES-C + DCE at 40° C					
0	1.0000	0.0000	0.0989	-	-
0.5	0.9960	0.0040	0.1005	0.4019	0.49
1	0.9920	0.0080	0.1020	0.8037	0.95
1.5	0.9880	0.0120	0.1035	1.2036	1.44
2	0.9840	0.0159	0.1051	1.6017	1.64
3	0.9760	0.0239	0.1081	2.3998	2.37
4	0.9681	0.0319	0.1120	3.1966	2.66

Table-5.7: The apparent molar weights of the solutions (M) and the number of grams of solute in 100g of THF solution (X) at 30°, 35° and 40°C.

Conc.,%	W ₁	W ₂	M, kg	X	Sn
PES-C + THF at 30° C					
0	1.0000	0.0000	0.0721	-	-
0.5	0.9944	0.0056	0.0744	0.5614	0.65
1	0.9888	0.0112	0.0767	1.1217	1.26
1.5	0.9832	0.0168	0.0789	1.6801	1.90
2	0.9776	0.0223	0.0812	2.2361	2.44
3	0.9665	0.0334	0.0858	3.3470	3.36
4	0.9555	0.0445	0.0903	4.4503	4.15
PES-C + THF at 35° C					
0	1.0000	0.0000	0.0721		-
0.5	0.9944	0.0056	0.0744	0.5621	2.40
1	0.9888	0.0112	0.0767	1.1234	4.38
1.5	0.9832	0.0168	0.0790	1.6831	6.60
2	0.9776	0.0223	0.0812	2.2401	5.93
3	0.9665	0.0334	0.0858	3.3534	10.3
4	0.9555	0.0445	0.0903	4.4588	10.1
PES-C + THF at 40° C					
0	1.0000	0.0000	0.0721		
0.5	0.9944	0.0056	0.0744	0.5633	2.53
1	0.9888	0.0112	0.0767	1.1257	3.59
1.5	0.9832	0.0168	0.0790	1.6865	5.41
2	0.9776	0.0223	0.0813	2.2441	6.14
3	0.9664	0.0336	0.0858	3.3598	7.91
4	0.9555	0.0445	0.0904	4.4687	9.59

Table-5.8: The apparent molar weights of the solutions (M) and the number of grams of solute in 100g of DO solution (X) at 30°, 35° and 40°C.

Conc.,%	W ₁	W ₂	M, kg	X	Sn
PES-C + DO at 30° C					
0	1.0000	0.0000	0.0881	-	-
0.5	0.9952	0.0048	0.0900	0.4813	1.34
1	0.9904	0.0096	0.0918	0.9617	2.24
1.5	0.9856	0.0144	0.0937	1.4411	3.37
2	0.9808	0.0192	0.0956	1.9197	4.01
3	0.9712	0.0287	0.0994	2.8760	5.46
4	0.9617	0.0383	0.1031	3.8295	6.44
PES-C + DO at 35° C					
0	1.0000	0.0000	0.0881	-	-
0.5	0.9952	0.0048	0.0900	0.4821	1.24
1	0.9904	0.0096	0.0919	0.9632	1.92
1.5	0.9856	0.0144	0.0937	1.4432	2.89
2	0.9808	0.0192	0.0956	1.9227	2.97
3	0.9712	0.0288	0.0994	2.8807	3.82
4	0.9616	0.0384	0.1032	3.8369	4.64
PES-C + DO at 40° C					
0	1.0000	0.0000	0.0881	-	-
0.5	0.9952	0.0048	0.0900	0.4837	1.82
1	0.9904	0.0096	0.0918	0.9648	2.37
1.5	0.9855	0.0145	0.0937	1.4452	3.57
2	0.9807	0.0193	0.0956	1.9251	4.33
3	0.9711	0.0289	0.0994	2.8851	5.34
4	0.9616	0.0384	0.1032	3.8406	6.38

6. Relaxation strength

The relaxation strength (r) [59] can be calculated according to Eqn.

5.10:

$$r = 1 - \left(\frac{U}{U_{\infty}} \right)^2 \quad \dots \quad 5.10$$

7. Internal pressure

Internal pressure (π) can be evaluated according to Suryanarayana and Kuppuswamy [60]:

$$\pi = bRT \left(\frac{K\eta}{U} \right)^{1/2} \frac{\rho^{2/3}}{M^{7/6}} \quad \dots \quad 5.11$$

Where $R=8.3143 \text{ JK}^{-1} \text{ mol}^{-1}$ is the gas constant and $b=2$, is the packing factor and $K=4.28 \times 10^9$ is a constant. The internal pressure (π) depends on temperature, density, ultrasonic velocity and specific heat at a constant pressure.

8. Classical absorption coefficient

The classical absorption coefficient $(\alpha/f^2)_{cl}$ has its origin in the viscosity of the medium and it is proposed by Subrahmanyam et al. [61]:

$$\left(\frac{\alpha}{f^2} \right)_{cl} = \frac{8\pi^2\eta}{3U^3\rho} \quad \dots \quad 5.12$$

9. Viscous relaxation time

The resistance offered by viscous force in the flow of sound wave appears as a classical absorption associated with it is the viscous relaxation time (τ):

$$\tau = \frac{4\eta}{3\rho U^2} \quad \dots \quad 5.13$$

59. G.K.Johri and R.C.Mishra, *Acustica*, **57**, 292, 1985

60. C.V.Suryanarayana and J.Kuppuswamy, *J. Acoust Soc. (India)*, **9(1)**, 4, 1981

61. T. V. S. Subrahmanyam, A. Viswanadhasharma and K. Subbarao, *J. Acoust. Soc.* **7(1)**, 1, 1979

10. Solvation number

The solvation number (S_n) can be evaluated according to Passynsky [62] method. The number of grams of solvent (n) connected in the apparent solvation of 1 g of solute assuming that the solvent molecules participating in the solvation are effectively incompressible due to strong localized electronic fields, is expressed as:

$$n = \left[1 - \frac{\kappa_s(100 - X)}{\kappa_{s1}X} \right] \quad \dots \quad 5.14$$

Where X is the number of grams of solute in 100 g of the solution. The Solvation number (S_n) can be expressed as:

$$S_n = \frac{M_2}{M_1 \left(1 - \frac{\kappa_s}{\kappa_{s1}} \right) \left(\frac{100 - X}{X} \right)} \quad \dots \quad 5.15$$

Where M_1 and M_2 are the molecular weights of solvent and polymer repeat unit, respectively.

11. Apparent molar volume

Apparent molar volume [63] can be calculated according to Eqn.5.16:

$$\phi_{V2} = \frac{M}{\rho_1} \left[1 - \frac{(100)}{C} (\rho - \rho_1) \right] \quad \dots \quad 5.16$$

Where, M is the molecular weight of polymer repeat unit and ρ_1 and ρ are the densities of solvent and polymer solution, respectively.

12. Apparent molar compressibility

Apparent molar compressibility [63] can be calculated according to Eqn. 5.17:

$$\phi \kappa_s = M_2 \kappa_{s1} \left[\frac{100}{C} \left(\frac{\kappa_s}{\kappa_{s1}} - \frac{\rho}{\rho_1} \right) + \frac{1}{\rho_1} \right] \quad \dots \quad 5.17$$

62. A. Passynsky, Acta Phys. Chem. USSR, 22, 317, 1943

63. P. R. Chowdhury, Indian J. Chem., 7, 692, 1969.

Where C is the concentration in dl/g and κ_{s1} and κ_s are the isentropic compressibility of solvent and polymer solution, respectively.

13. Free volume

Free volume [64] can be calculated according to Eqn. 5.18:

$$V_f = \left[\frac{MU}{K\eta} \right]^{3/2} \quad \dots 5.18$$

14. Inter molecular free path length

Intermolecular free path length (L_f) can be evaluated according to Eqn. 5.19, as proposed by Jacobson [65]:

$$L_f = K.(\kappa_s)^{1/2} \quad \dots 5.19$$

where $K = (93.875 + 0.375T) \times 10^{-8}$ is a constant and temperature dependent.

Using experimental data on ρ , η and U various acoustical parameters such as isentropic compressibility (κ_s), specific acoustical impedance (Z), Rao's molar sound function (R), Van der waals constant (b), relaxation strength (r), internal pressure (π), classical absorption coefficient (α/f^2)_{cl}, viscous relaxation time (τ), free volume (V_f), inter molecular free length (L_f) and solvation number (S_n), etc are determined according to Eqn. 5.5 to 5.19 and correlated with concentration (C).

The plots of various acoustical parameters against concentration (C) are presented in Figs.5.13 to 5.56. The linear least square equations and regression coefficients (R^2) are presented in respective figures. From Figs. 5.13 to 5.56, it is clear that a good to excellent correlation is observed except few cases where polynomial correlation is observed.

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64. C. V. Surayanarayana and J. Kuppasami, J. Acoust. Soc. India, 4, 75, 1976
 65. B. Jacobson, Nature, 173, 772, 1954

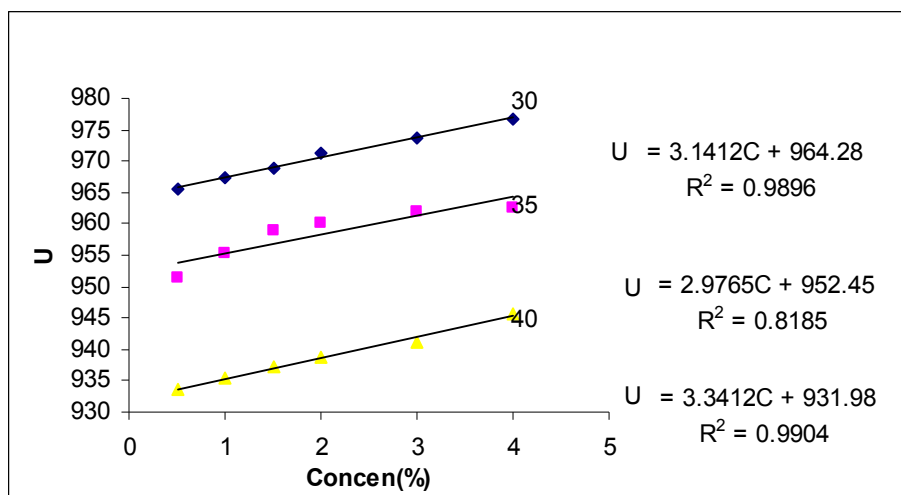


Fig 5.9: The plots of sound velocity (U) against concentration (%) at 30°, 35° and 40°C for PES-C in chloroform

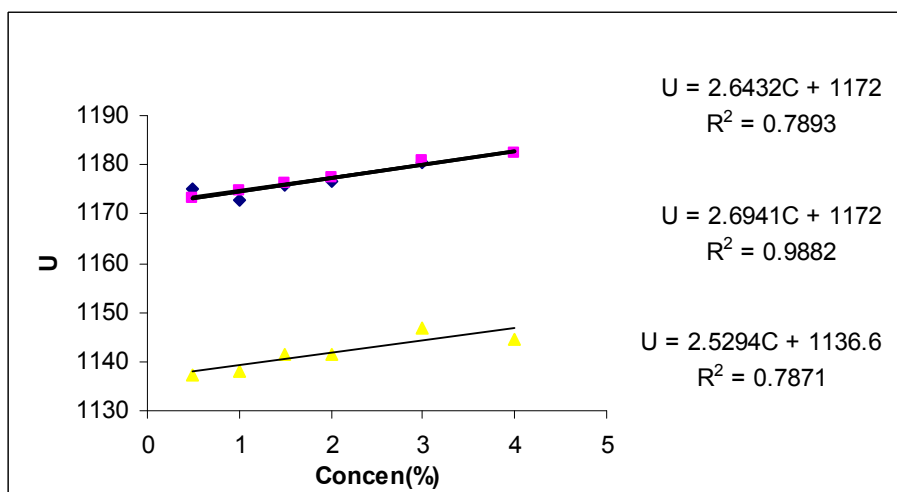


Fig 5.10: The plots of sound velocity (U) against concentration (%) at 30°, 35° and 40°C for PES-C in 1, 2- dichloro ethane

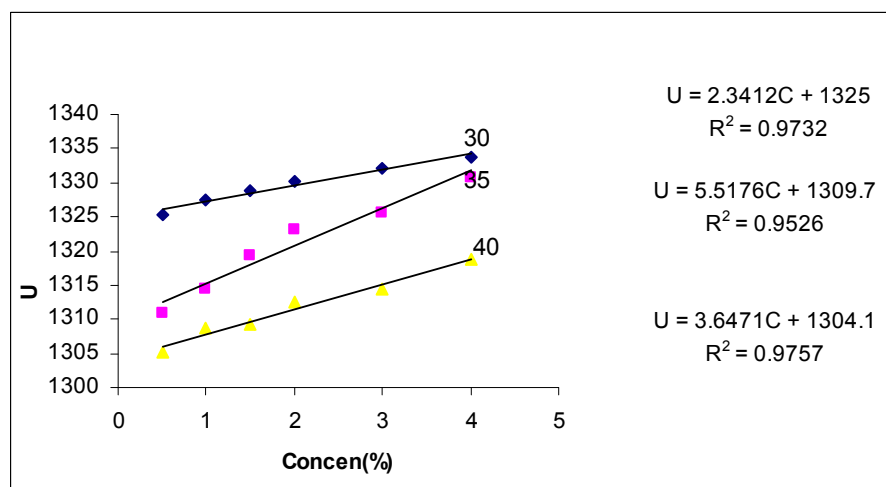


Fig 5.11: The plots of sound velocity (U) against concentration (%) at 30°, 35° and 40°C for PES-C in 1, 4-dioxane.

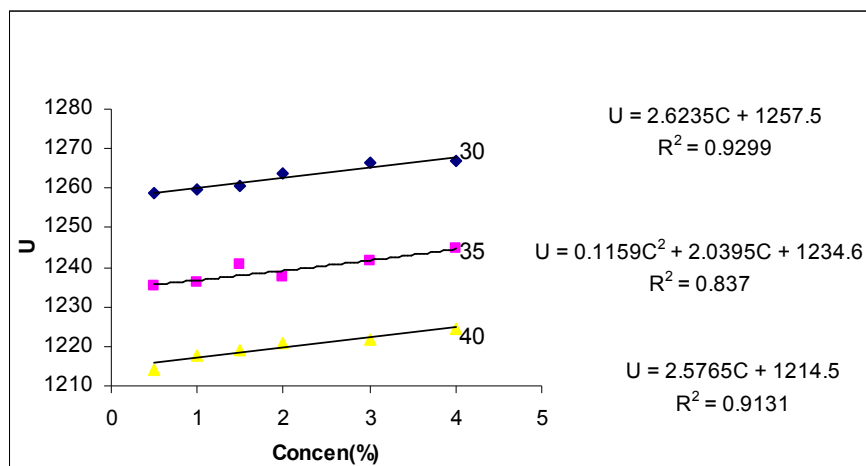


Fig 5.12: The plots of sound velocity (U) against concentration (%) at 30°, 35° and 40°C for PES-C in THF.

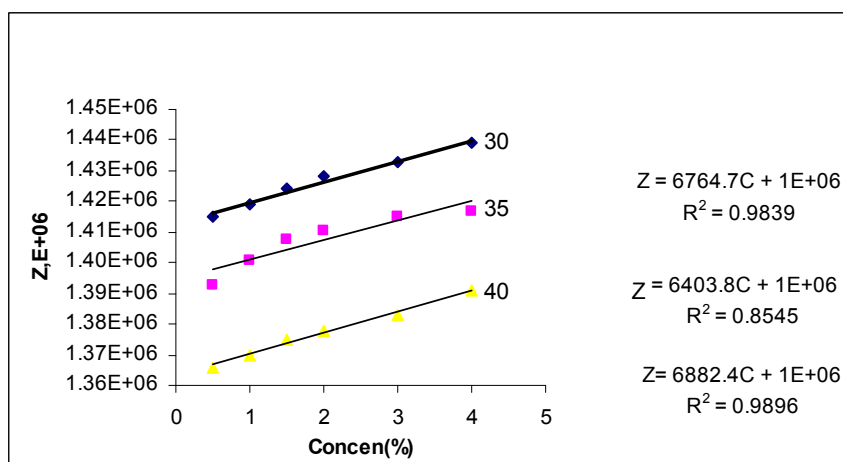


Fig 5.13: The plots of specific acoustical impedance (Z) against concentration (%) at 30°, 35° and 40°C for PES-C in chloroform

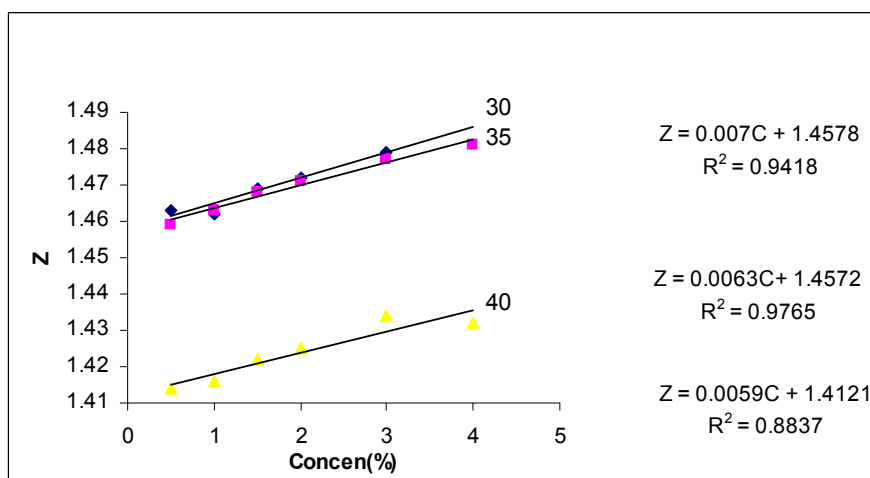


Fig 5.14: The plots of specific acoustical impedance (Z) against concentration (%) at 30°, 35° and 40°C for PES-C in 1,2, dichloro ethane

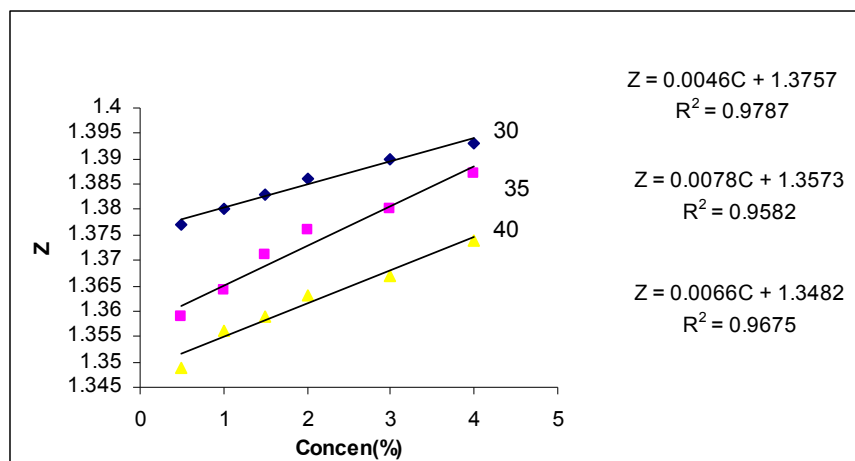


Fig 5.15: The plots of specific acoustical impedance (Z) against concentration (%) at 30°, 35° and 40°C for PES-C in 1,4-dioxane

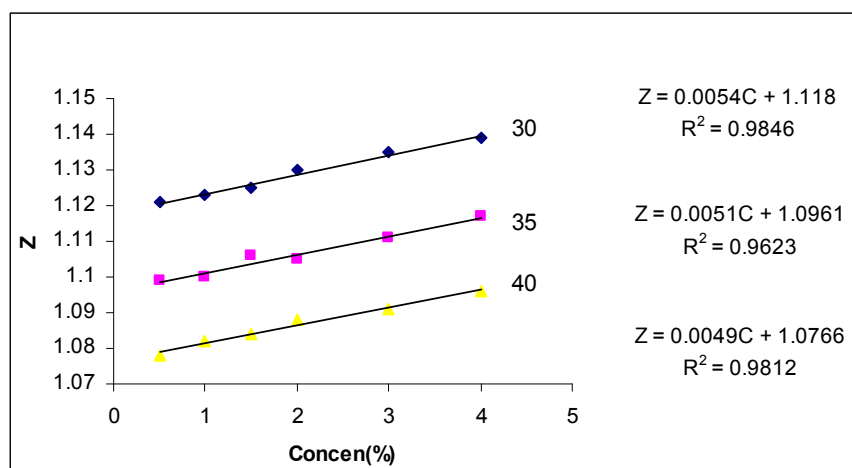


Fig 5.16: The plots of specific acoustical impedance (Z) against concentration (%) at 30°, 35° and 40°C for PES-C in THF

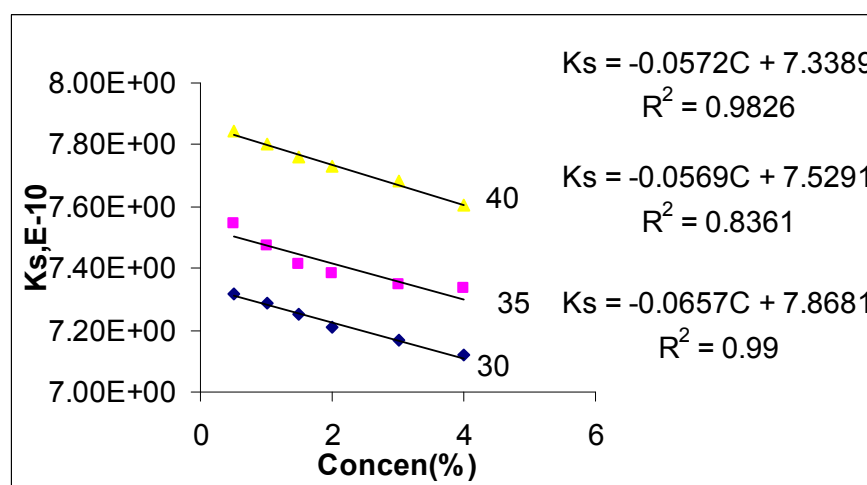


Fig 5.17: The plots of isentropic compressibility (κ_s) against concentration (%) at 30°, 35° and 40°C for PES-C in chloroform

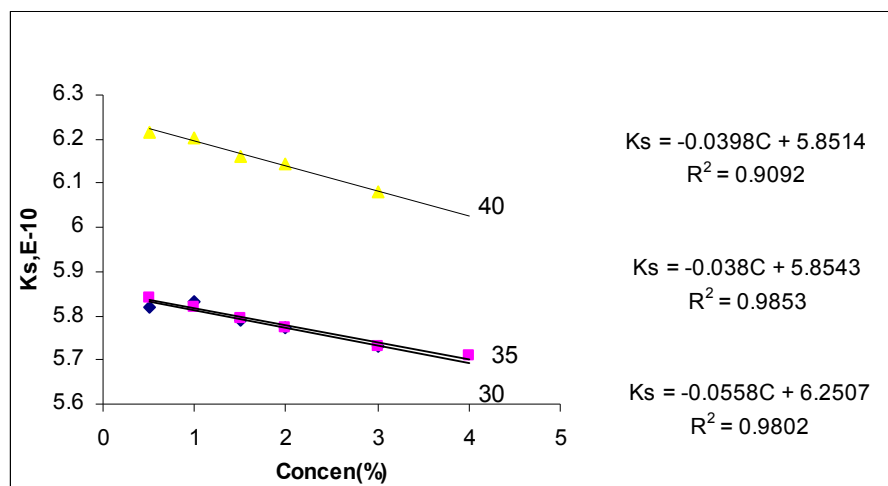


Fig 5.18: The plots of isentropic compressibility (κ_s) against concentration (%) at 30°, 35° and 40°C for PES-C in 1- 2, dichloroethane

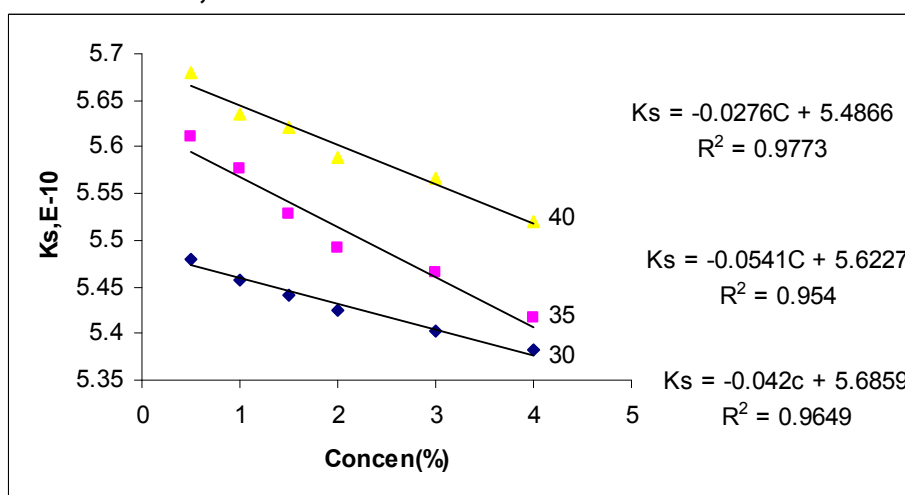


Fig 5.19: The plots of isentropic compressibility (κ_s) against concentration (%) at 30°, 35° and 40°C for PES-C in 1, 4- dioxane

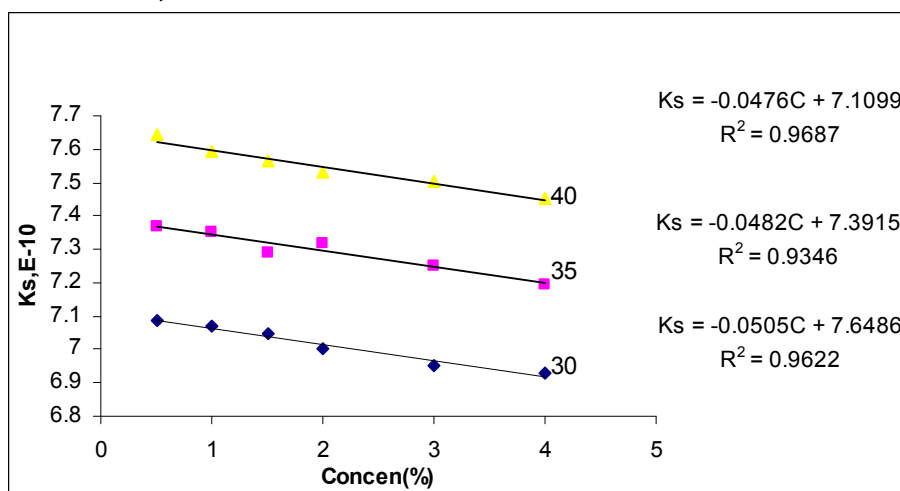


Fig 5.20: The plots of isentropic compressibility (κ_s) against concentration (%) at 30°, 35° and 40°C for PES-C in THF

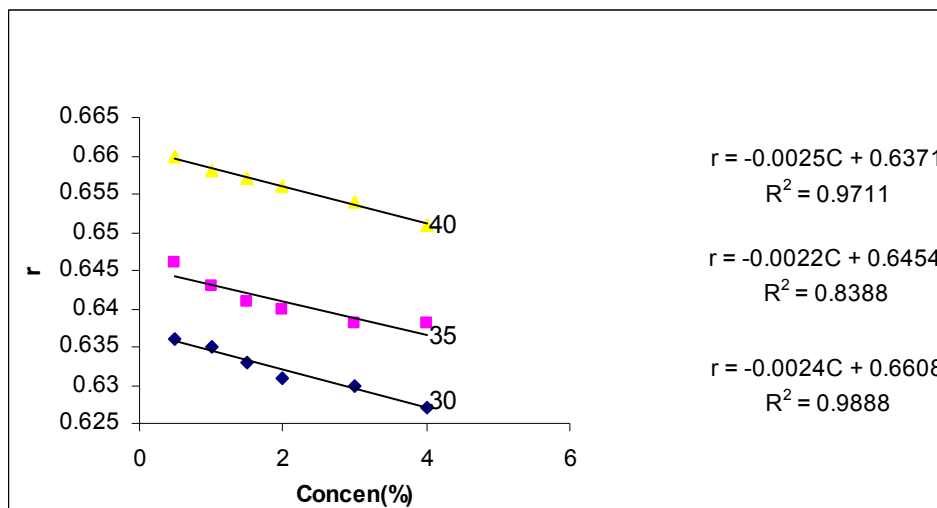


Fig 5.21: The plots of relaxation strength (r) against concentration (%) at 30°, 35° and 40°C for PES-C in chloroform

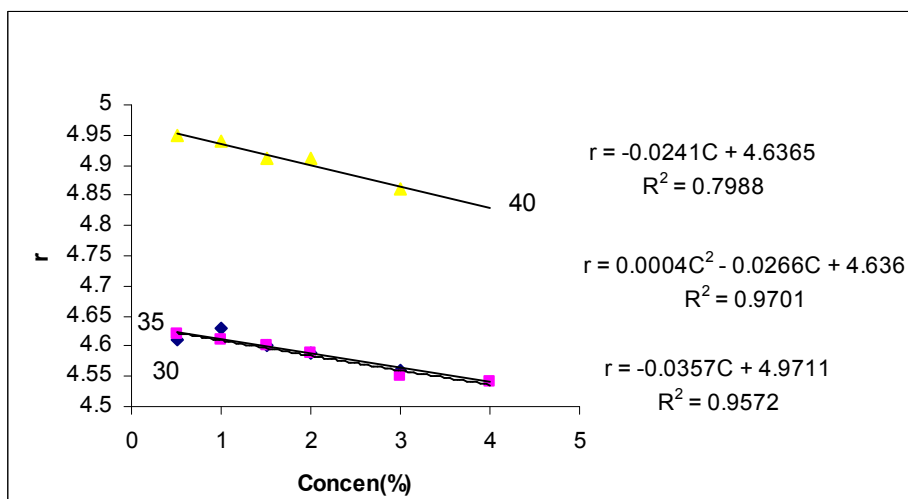


Fig 5.22: The plots of relaxation strength (r) against concentration (%) at 30°, 35° and 40°C for PES-C in 1,2-dichloroethane.

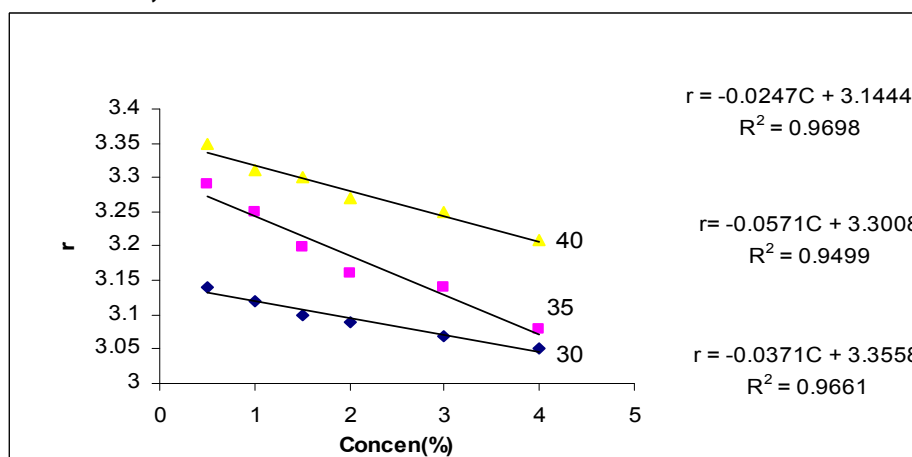


Fig 5.23: The plots of relaxation strength (r) against concentration (%) at 30°, 35° and 40°C for PES-C in 1,4-dioxane

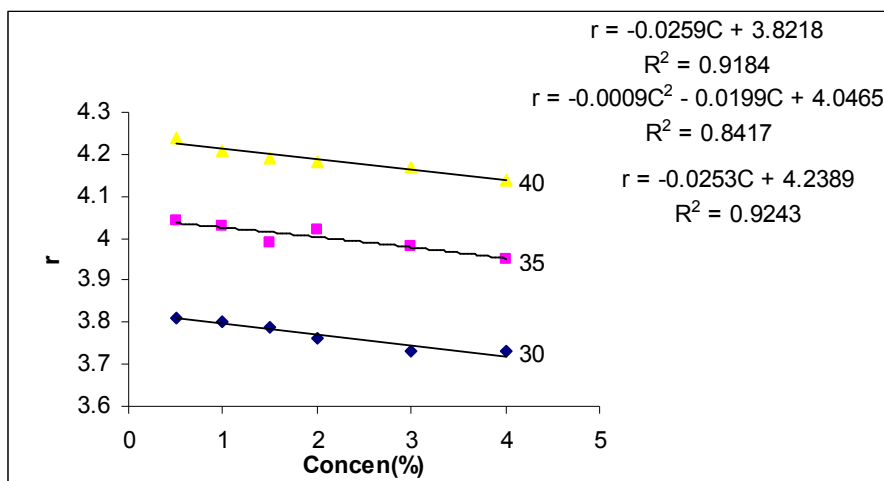


Fig 5.24: The plots of relaxation strength (r) against concentration (%) at 30°, 35° and 40°C for PES-C in THF.

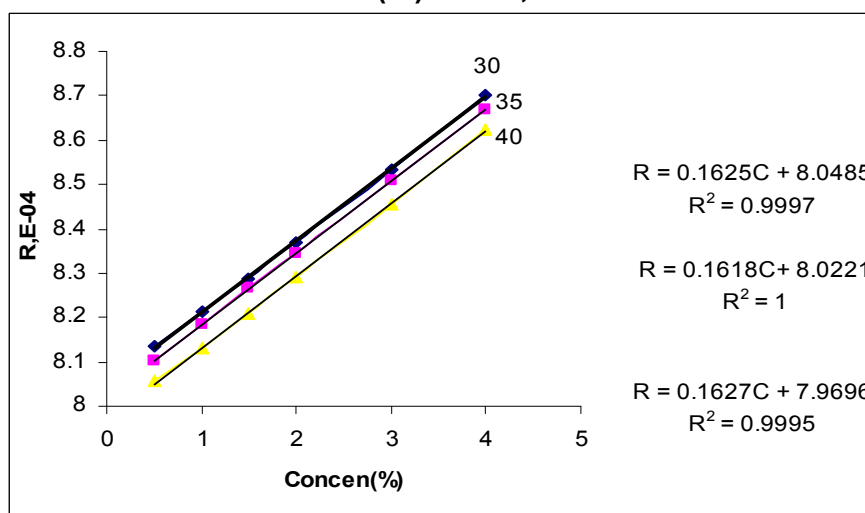


Fig 5.25: The plots of Rao's molar sound function(R) against concentration (%) at 30°, 35° and 40°C for PES-C in chloroform.

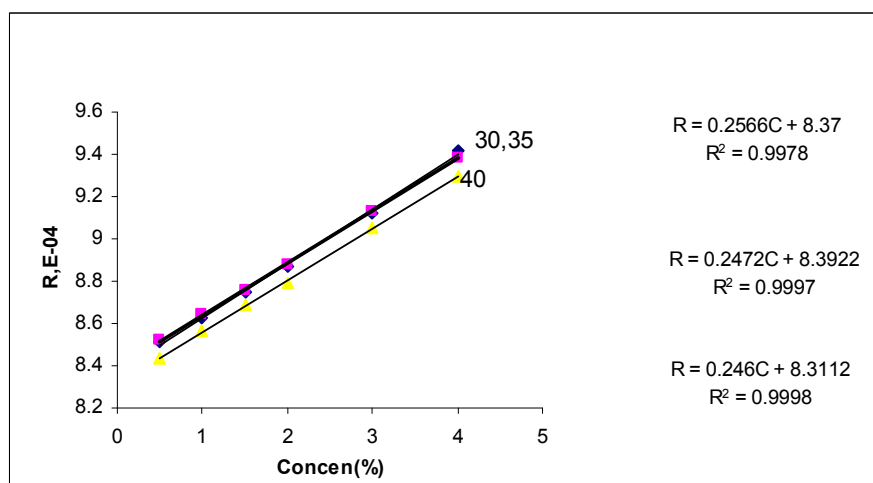


Fig 5.26: The plots of Rao's molar sound function(R) against concentration (%) at 30°, 35° and 40°C for PES-C in 1, 2-dichloroethane

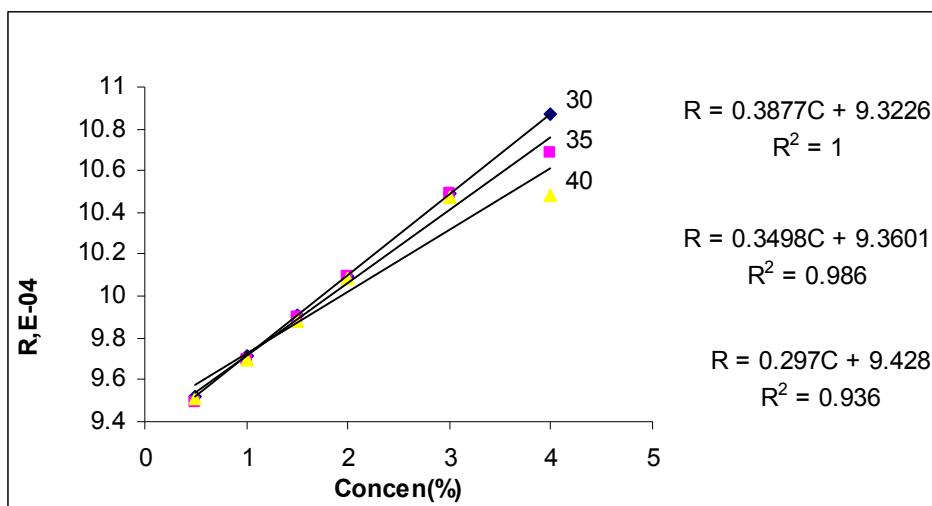


Fig 5.27: The plots of Rao's molar sound function(R) against concentration (%) at 30°, 35° and 40°C for PES-C in 1, 4-dioxane

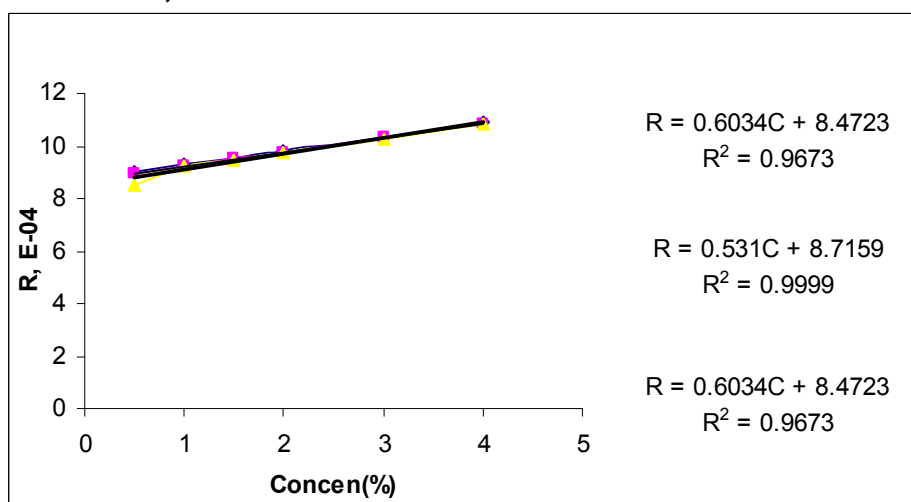


Fig 5.28: The plots of Rao's molar sound function(R) against concentration (%) at 30°, 35° and 40°C for PES-C in THF.

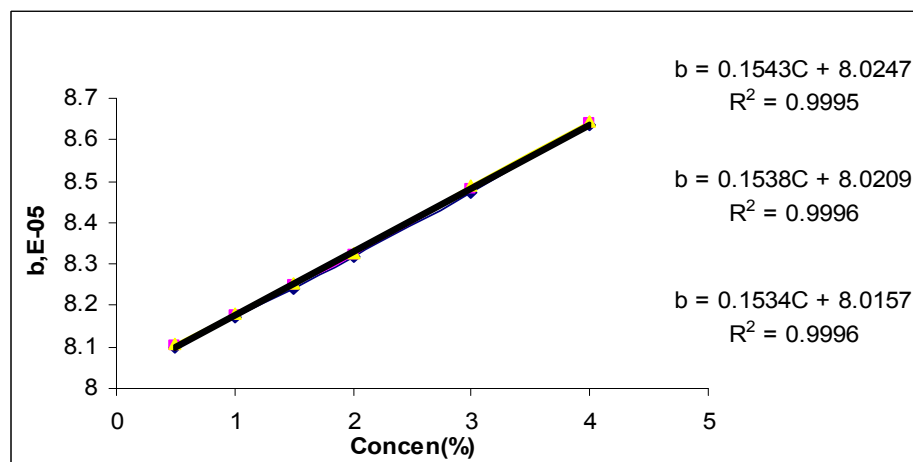


Fig 529: The plots of van der waals constant (b) against concentration (%) at 30°, 35° and 40°C for PES-C in chloroform.

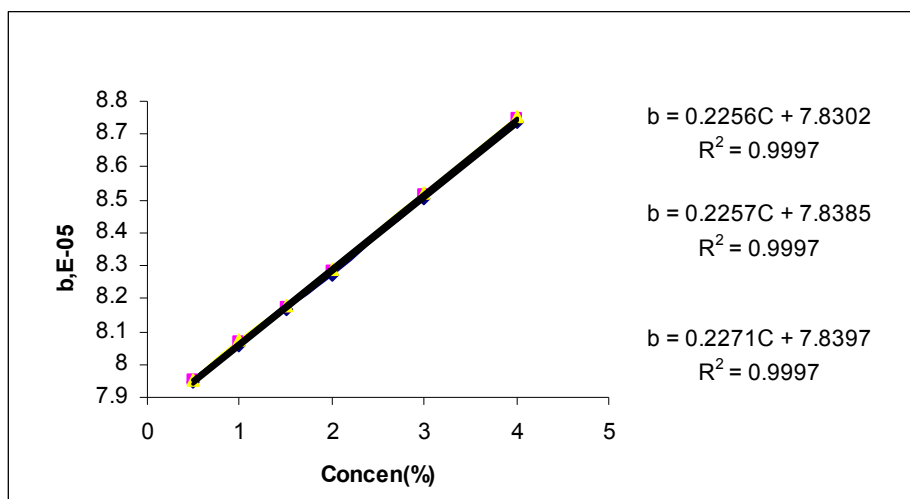


Fig 5.30: The plots of van der waals constant (b) against concentration (%) at 30°, 35° and 40°C for PES-C in1, 2-dichloroethane.

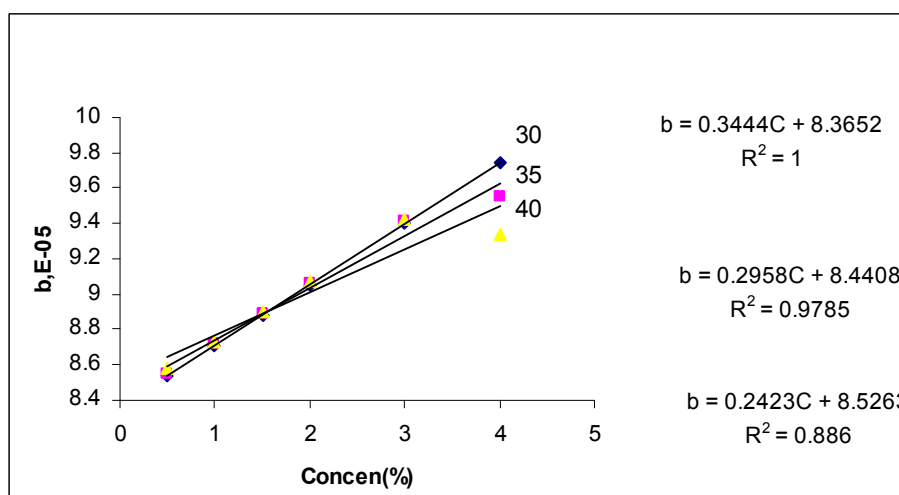


Fig 5.31: The plots of van der waals constant (b) against concentration (%) at 30°, 35° and 40°C for PES-C in 1, 4-dioxane

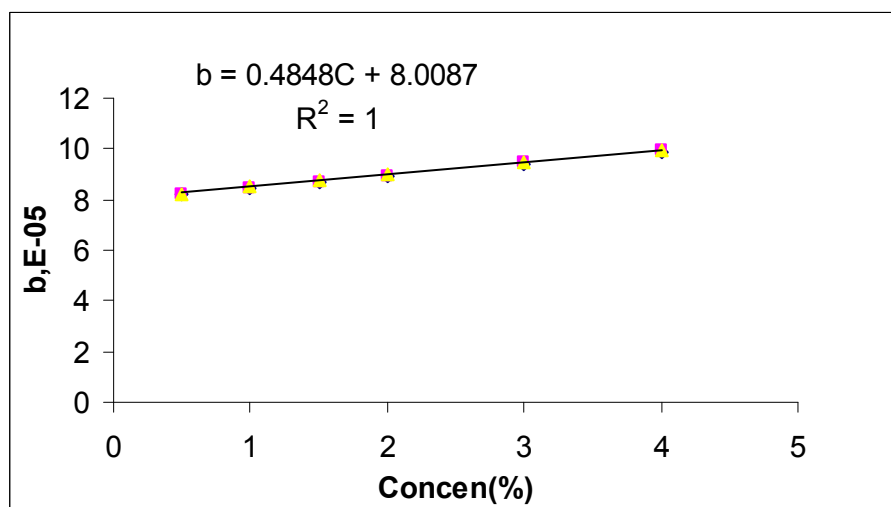


Fig 5.32: The plots of van der waals constant (b) against concentration (%) at 30°, 35° and 40°C for PES-C in THF.

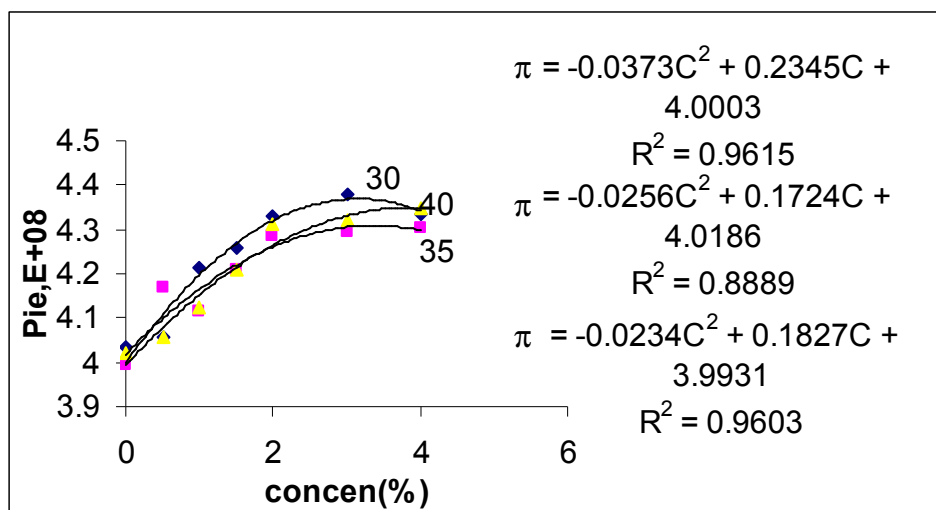


Fig 5.33: The plots of internal pressure (π) against concentration (%) at 30°, 35° and 40°C for PES-C in chloroform

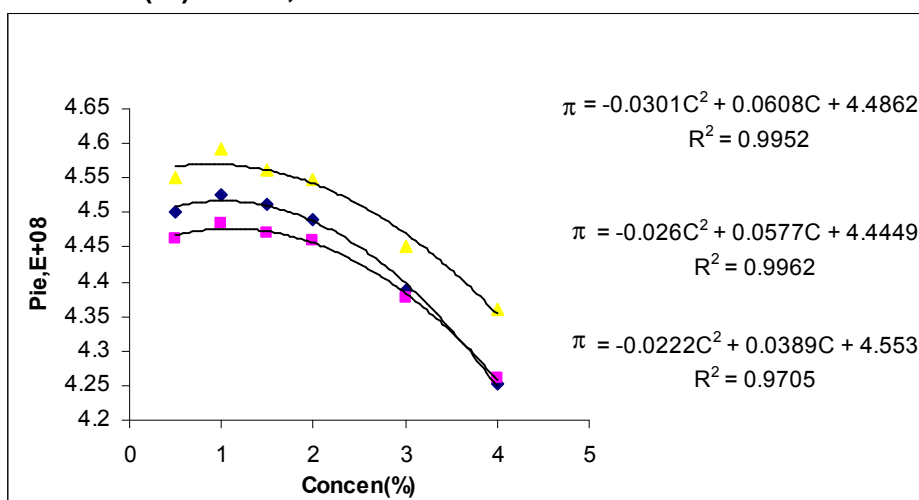


Fig 5.34: The plots of internal pressure (π) against concentration (%) at 30°, 35° and 40°C for PES-C in 1,2-dichloroethane

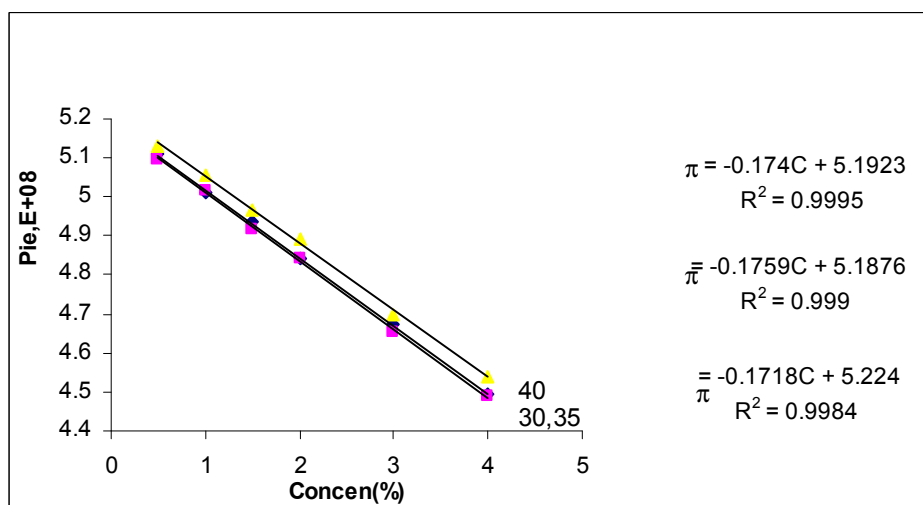


Fig 5.35: The plots of internal pressure (π) against concentration (%) at 30°, 35° and 40°C for PES-C in 1,4-dioxane

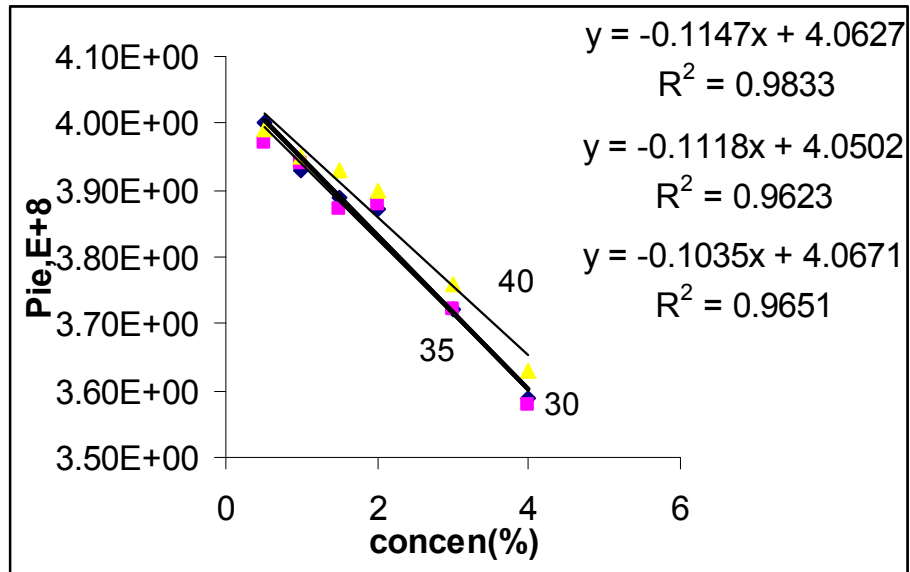


Fig 5.36: The plots of internal pressure (π) against concentration (%) at 30°, 35° and 40°C for PES-C in THF

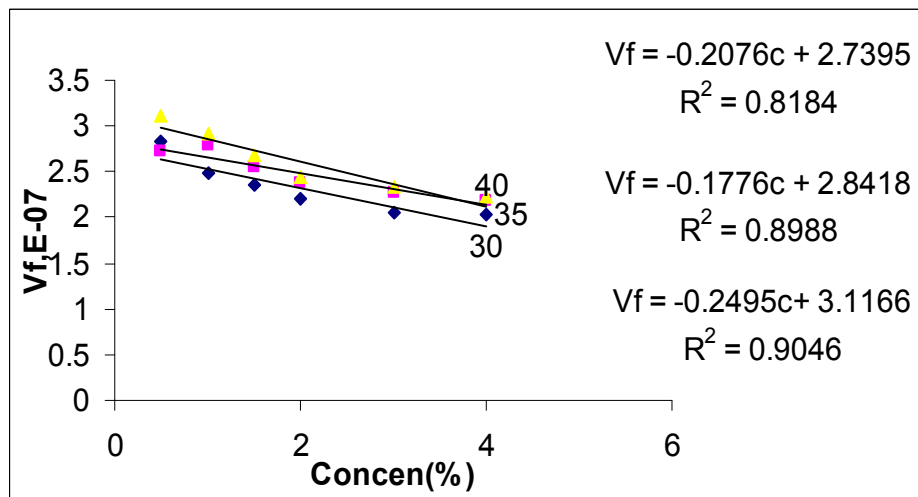


Fig 5.37: The plots of free volume (V_f) against concentration (%) at 30°, 35° and 40°C for PES-C in chloroform

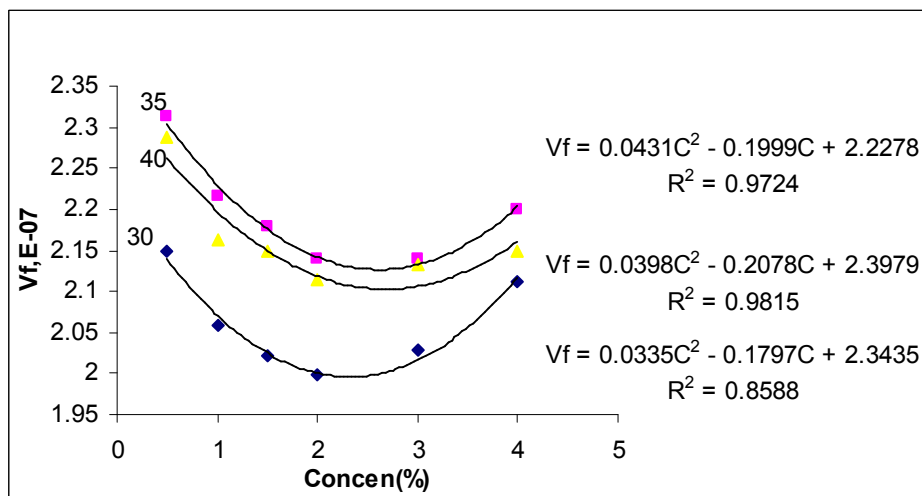


Fig 5.38: The plots of free volume (V_f) against concentration (%) at 30°, 35° and 40°C for PES-C in 1,2-dichloroethane.

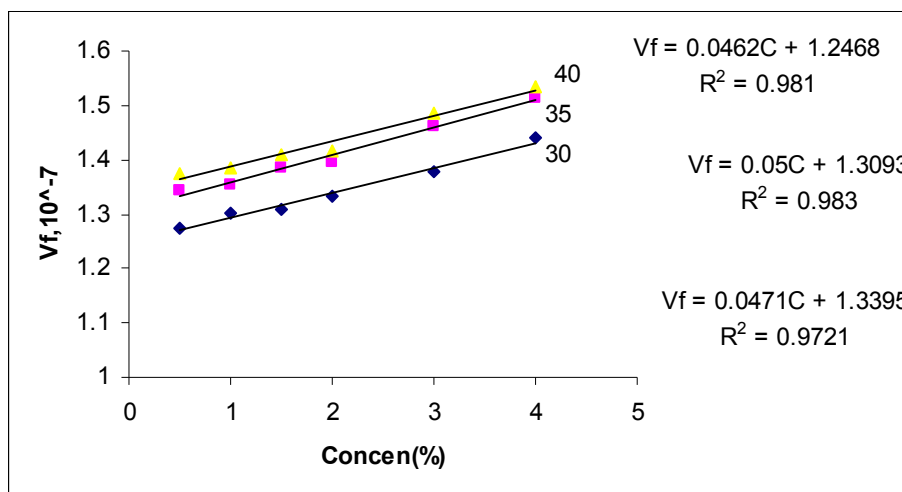


Fig 5.39: The plots of free volume (V_f) against concentration (%) at 30°, 35° and 40°C for PES-C in 1,4-dioxane.

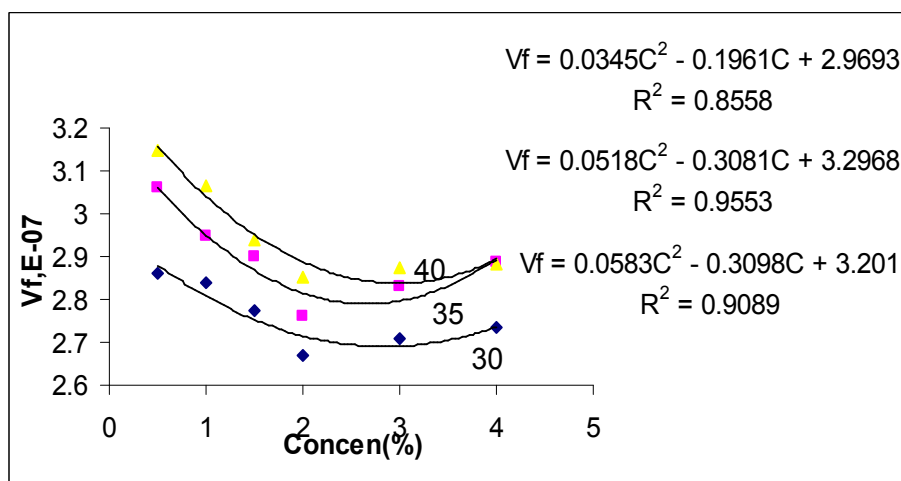


Fig 5.40: The plots of free volume (V_f) against concentration (%) at 30°, 35° and 40°C for PES-C in THF.

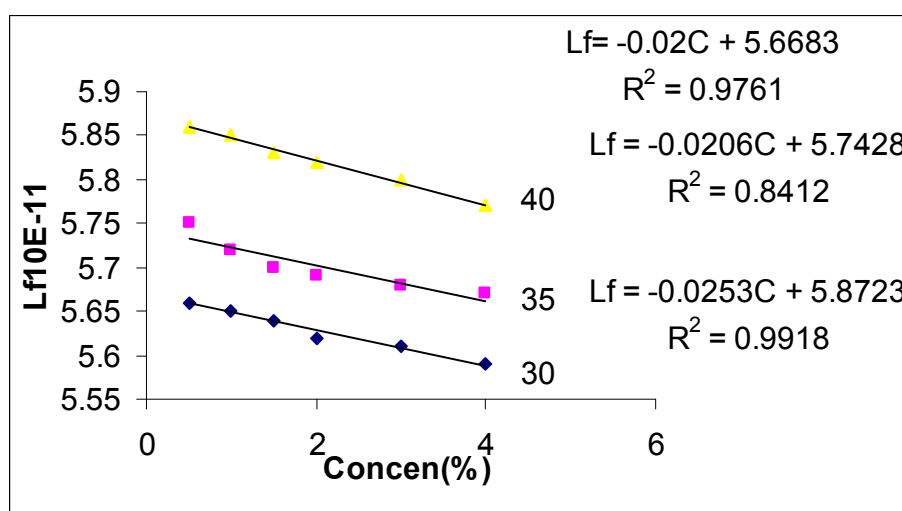


Fig 5.41: The plots of intermolecular free path length (L_f) against concentration (%) at 30°, 35° and 40°C for PES-C in chloroform.

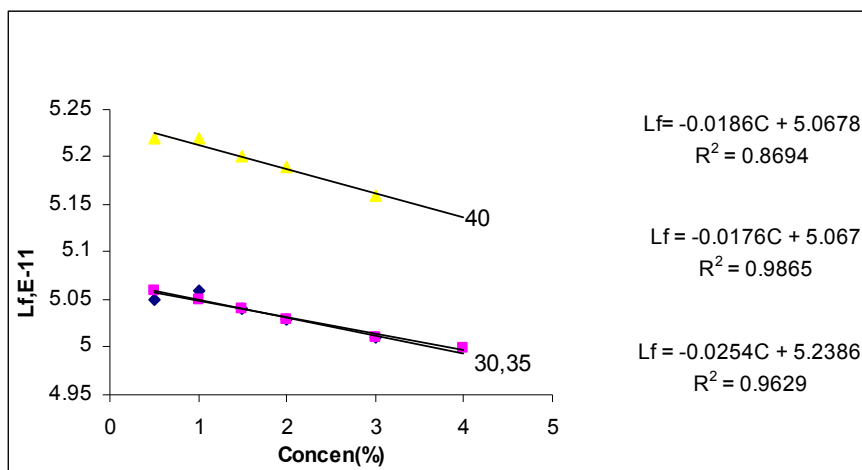


Fig 5.42: The plots of intermolecular free path length (L_f) against concentration (%) at 30°, 35° and 40°C for PES-C in 1, 2- dichloroethane.

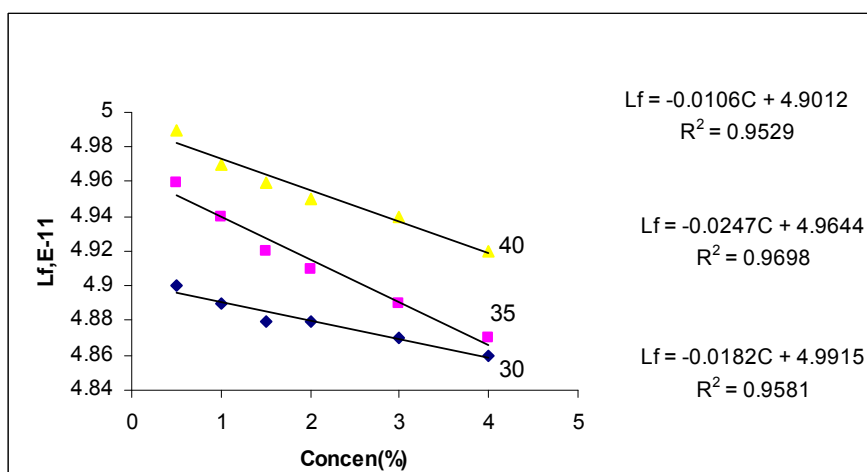


Fig 5.43: The plots of intermolecular free path length (L_f) against concentration (%) at 30°, 35° and 40°C for PES-C in 1, 4- dioxane.

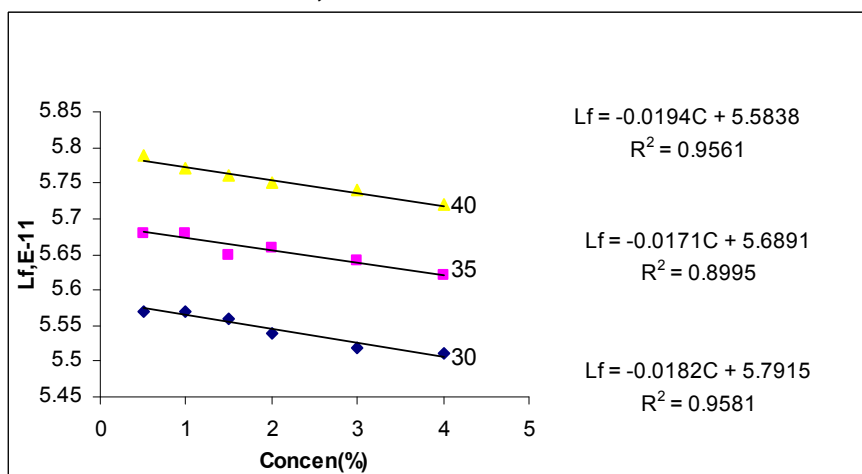


Fig 5.44: The plots of intermolecular free path length (L_f) against concentration (%) at 30°, 35° and 40°C for PES-C in THF.

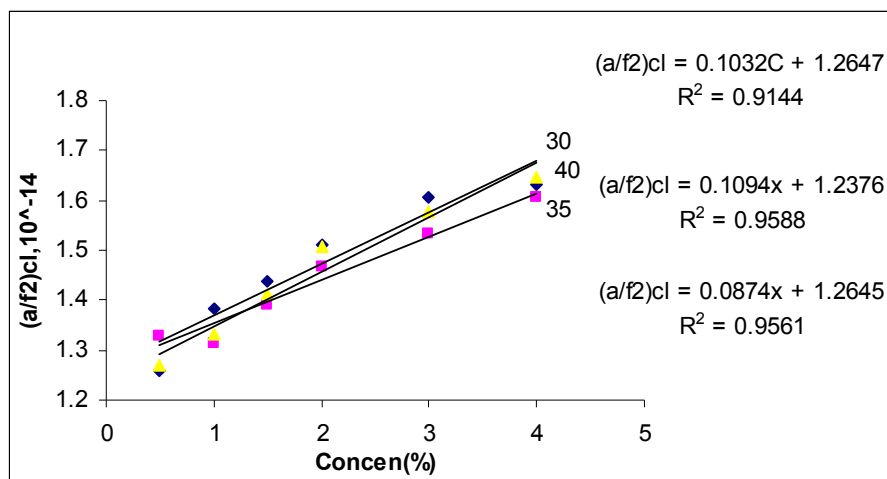


Fig 5.45: The plots of classical absorption coefficient $((\alpha/f^2)_{cl})$ against concentration (%) at 30°, 35° and 40°C for PES-C in chloroform.

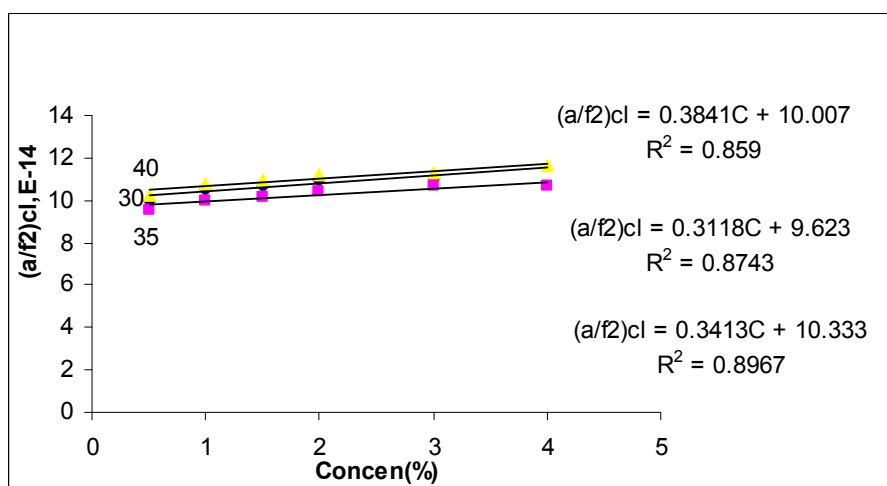


Fig 5.46: The plots of classical absorption coefficient $((\alpha/f^2)_{cl})$ against concentration (%) at 30°, 35° and 40°C for PES-C in 1, 2-dichloethane.

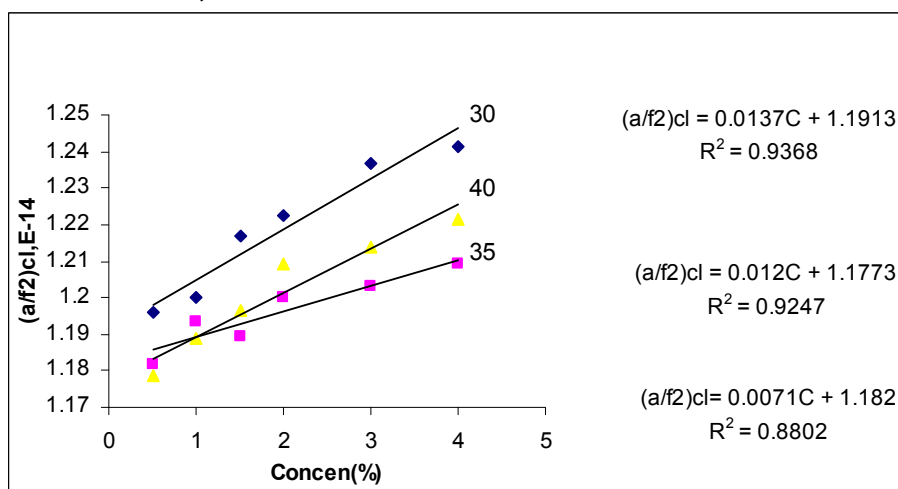


Fig 5.47: The plots of classical absorption coefficient $((\alpha/f^2)_{cl})$ against concentration (%) at 30°, 35° and 40°C for PES-C in 1, 4-dioxane

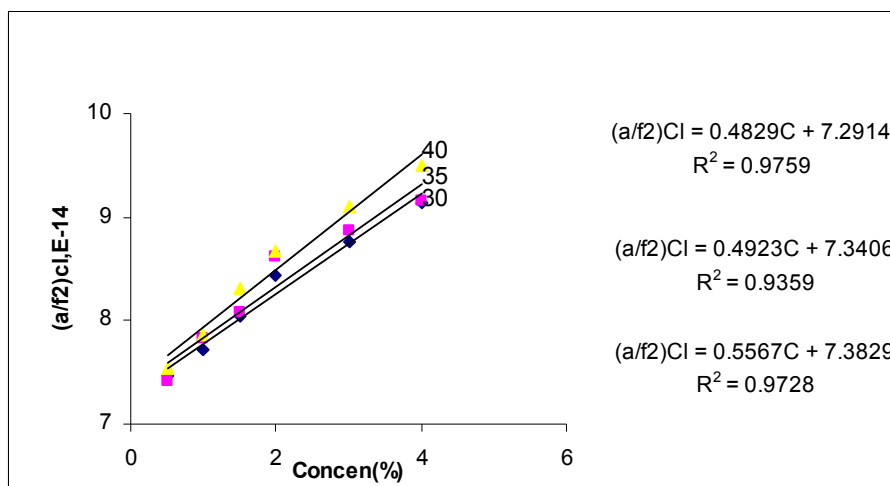


Fig 5.48: The plots of classical absorption coefficient $((\alpha/f^2)_{cl})$ against concentration (%) at 30°, 35° and 40°C for PES-C in THF.

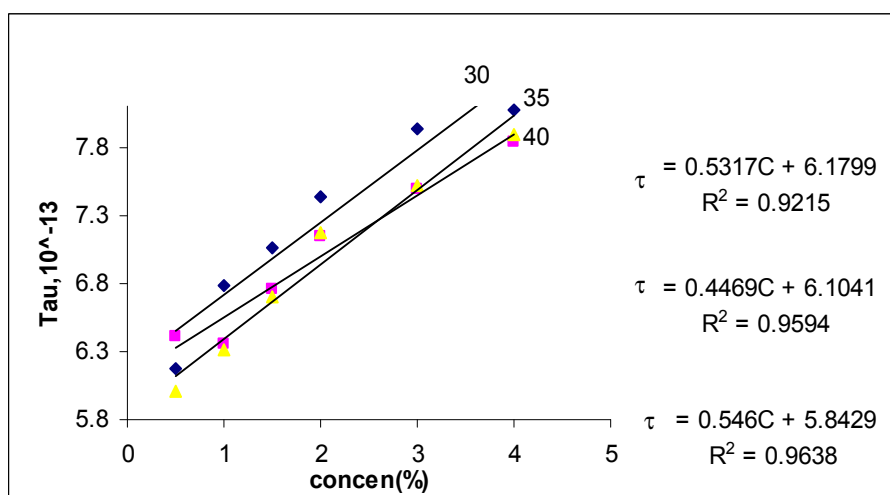


Fig 5.49: The plots of viscous relaxation time (τ) against concentration (%) at 30°, 35° and 40°C for PES-C in chloroform.

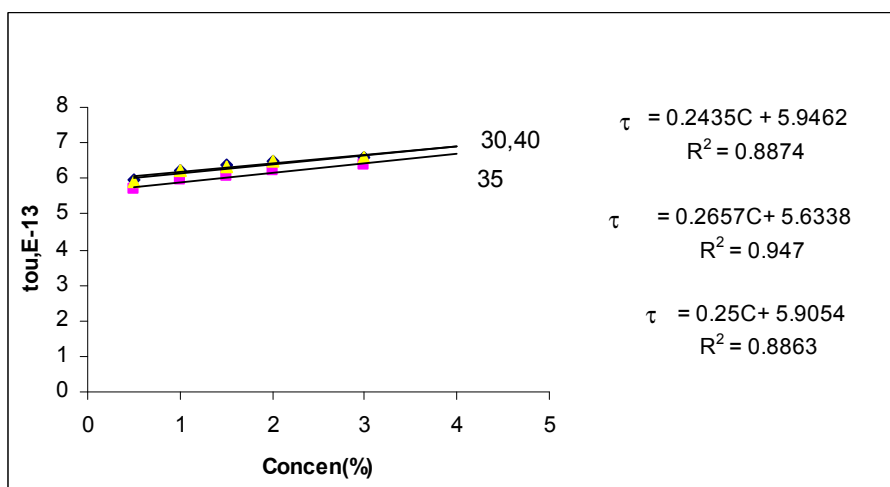


Fig 5.50: The plots of viscous relaxation time (τ) against concentration (%) at 30°, 35° and 40°C for PES-C in 1, 2-dichloroethane

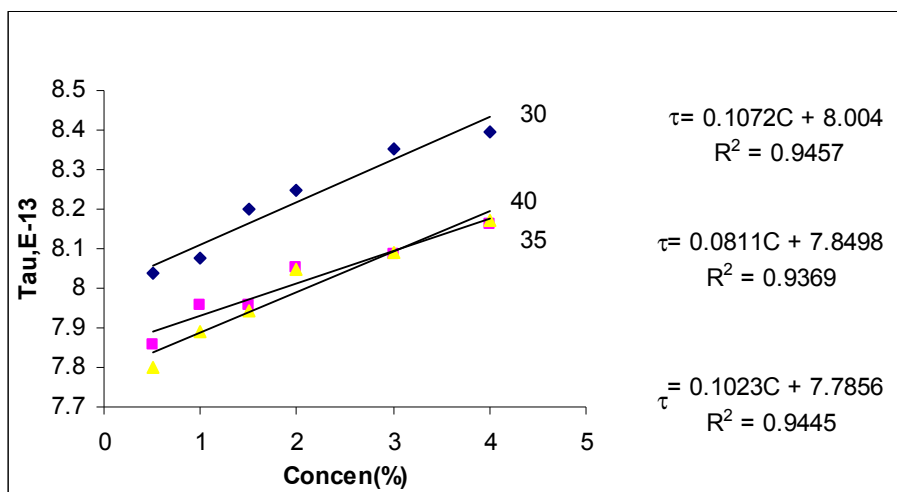


Fig 5.51: The plots of viscous relaxation time (τ) against concentration (%) at 30°, 35° and 40°C for PES-C in 1, 4-dioxane.

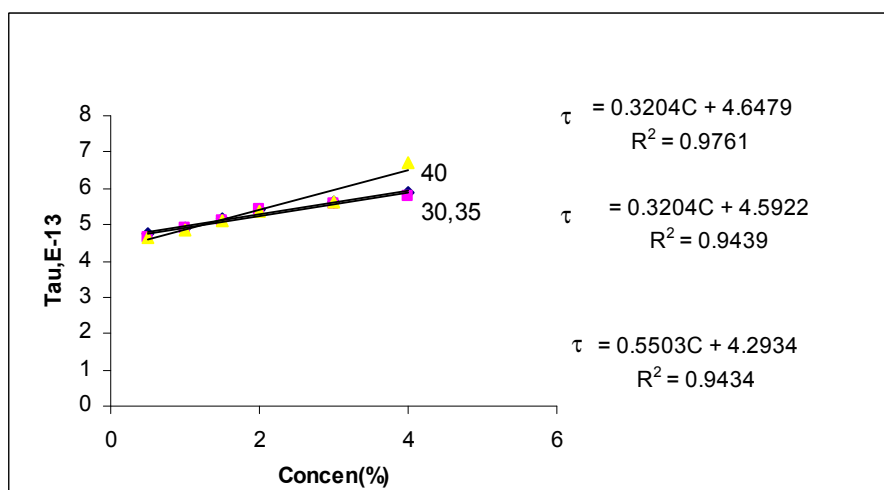


Fig 5.52: The plots of viscous relaxation time (τ) against concentration (%) at 30°, 35° and 40°C for PES-C in THF.

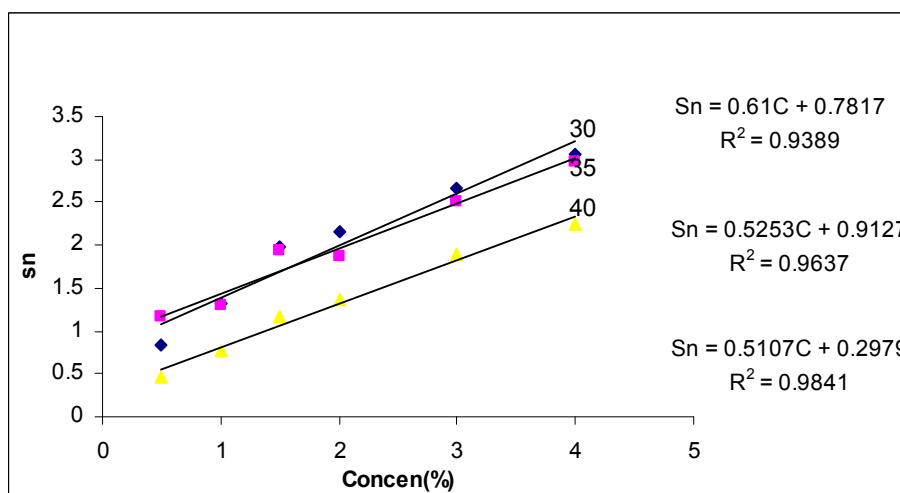


Fig 5.53: The plots of solvation number (Sn) against concentration (%) at 30°, 35° and 40°C for PES-C in chloroform.

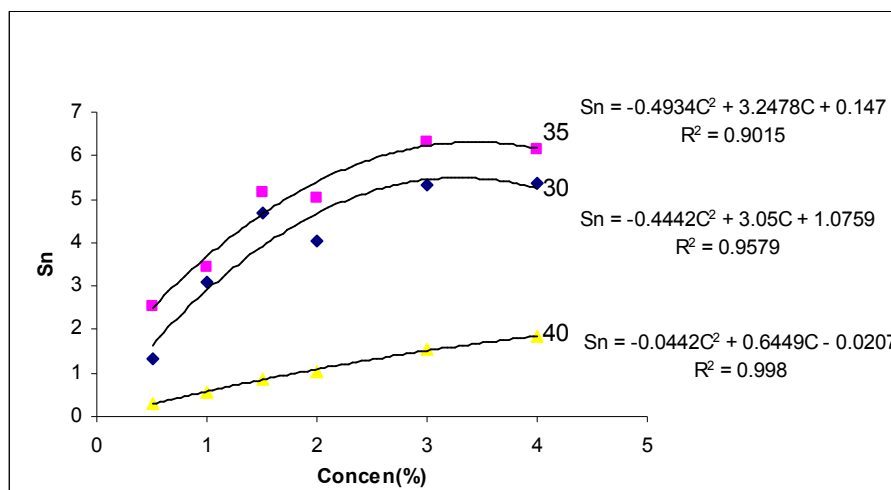


Fig 5.54: The plots of solvation number (Sn) against concentration (%) at 30°, 35° and 40°C for PES-C in 1, 2-dichloroethane.

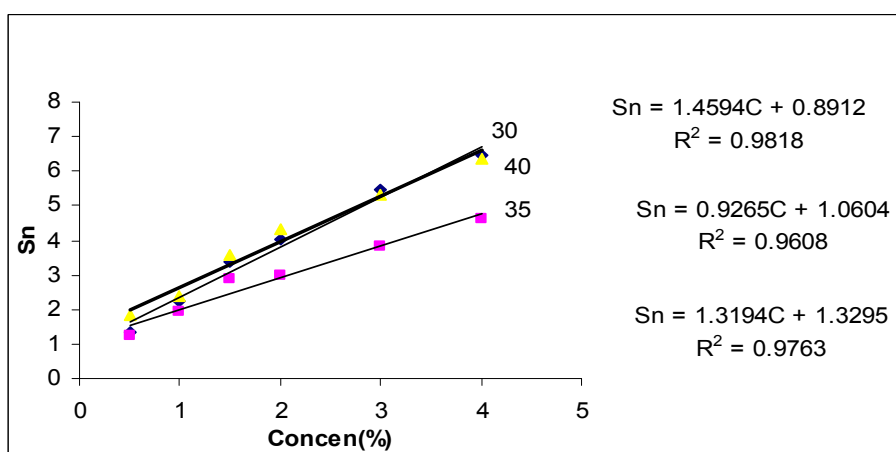


Fig 5.55: The plots of solvation number (Sn) against concentration (%) at 30°, 35° and 40°C for PES-C in 1, 4-dioxane.

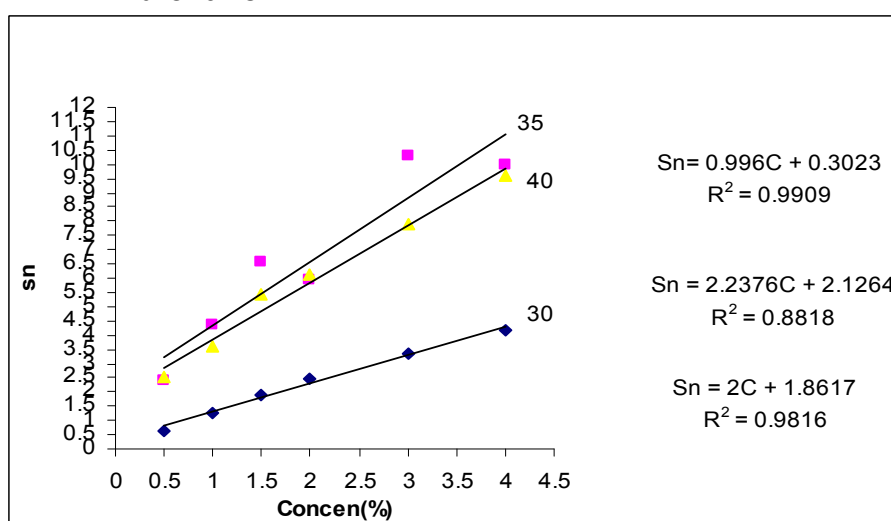


Fig 5.56: The plots of solvation number (Sn) against concentration (%) at 30°, 35° and 40°C for PES-C in THF

The variation of various acoustical parameters with concentration and temperature for a given polymer- solvent system provide valuable informations on molecular interactions occurring in the solutions and hence structural changes. The linear increase in Z (Figs. 5.13 to 5.16; $R^2 = 0.8545 - 0.9846$), R (Figs. 5.25 to 5.28; $R^2 = 0.985-1.000$), b (Figs. 5.29 to 5.32; $R^2 = 0.936-0.9998$), α/f^2 (Figs. 5.45 to 5.48; $R^2 = 0.859 - 0.9759$) and τ (Figs. 5.49 to 5.52; $R^2 = 0.8874 - 0.9761$) with C and linear decrease with T ; and linear decrease in κ_s (Figs. 5.17 to 5.20, $R^2 = 0.8361 - 0.9853$), r (Figs 5.21 to 5.24, $R^2 = 0.7988-0.9888$) and L_f (Figs. 5.41 to 5.44; $R^2 = 0.8412 - 0.9865$) with C and linear increase with T indicated the presence of strong molecular interactions. The increase in temperature leads to less ordered structure and volume expansion and hence increases intermolecular free length [66]. A little temperature effect is observed in cases of R and b . The internal pressure and free volume are measure of cohesion forces. In present case π increased nonlinearly up to about 2% in CF system (Fig. 5.33, $R^2 = 0, 0.8888-0.9615$) and has decreased in DCE system (Fig 5.34, $R^2 = 0.9705 - 0.9952$), while in DO and THF systems (Figs. 5.35 and 5.36; $R^2 - 0.9877-0.9995$), it decreased linearly with C and increased with T . V_f decreased linearly with C in CF and DO systems (Figs. 5.37 and 5.39; $R^2 = 0.8184-0.981$) and increased with T , while in DCE and THF systems (Figs. 5.38 and 5.40; $R^2 = 0.8588-0.9724$), it is decreased nonlinearly up to about 2% and then increased non linearly with C . V_f increased nonlinearly with T . The linear or nonlinear increase or decrease in acoustical parameters with C and T support the existence of strong molecular interactions. π , V_f and τ are three basic thermodynamic parameters for liquid systems [64].

The internal pressure of a solution is a single factor, which appears to vary due to internal molecular interactions namely solvation, ion-solvent interactions, solute-solvent interactions and quantum mechanical forces of dispersion, and dielectric forces. The internal pressure plays an important role in transport properties.

The interaction between polymer segments and solvent molecules is of prime importance in polymer solution since extension of high polymer

in solution is markedly influenced by the existence of molecular interactions. The increase in π and decrease in V_f with C indicated increase in cohesive forces, while decrease in π and increase in V_f with C indicated decrease in cohesive forces.

The decrease in κ_s with C supported that the solvated molecules are fully compressed due to electrical forces exist in the solute molecules. Thus, the structural arrangement suggested by the acoustical parameters reveal solvophilicity of PES-C and it is supported by positive values of solvation number S_n (Figs. 5.53 to 5.56). S_n increased linearly with C and decreased with T in CF ($R^2 = 0.9389 - 0.9841$). DO ($R^2 = 0.9783-0.9818$) and THF ($R^2 = 0.8818- 0.9909$) and it increased nonlinearly with C up to about 2% and then decreased with C in DCE system ($R^2 = 0.9015-0.998$). S_n increased up to 35°C and decreased at 40° C in CF, DCE and DO systems, while it increased with T in THF system. The decrease in S_n with C and T is due to decrease in cohesive forces and hence it is indicative of polymer-polymer interaction. When T increases, the tendency of molecules to move away increases and thereby the probability of molecular interactions decreases, which may result in decrease in cohesive forces and ultimately V_f and L_f increase and vice versa [66].

The increase of $(\alpha/f^2)_{cl}$ and τ with C can be explained in terms of the motion of the macromolecular inter chain forces [67], which are influenced by ρ , η and U . The contribution of acoustic relaxation is considered as a result of entropy fluctuation associated in solution of dynamically formed physical entity [68].

The presence of polar groups enhances the molecular interactions. The observed solvophilicity of PES-C is responsible for the change in apparent molar volume ϕ_{v2} and apparent molar compressibility $\phi_{\kappa s}$. The solvation causes change in molecular weight of polymer repeat unit as well as molar volume.

66. R. A. Pethrick, B. T. Poh, British Polymer J., **15**, 149, 1983

67. S. Kalyansundaram, A. Manuel Stephan and A. Gopalan, J. Polym. Mater. **12**, 323, 1995

68. W. Bell and R. A. Pethrick, Polymer. **23**, 369, 1982

The lone pairs of electrons of THF, DO, sulfone and ether linkages of PES-C and chlorine atoms of CF and DCE are electro negative groups, while phenyl rings and H-atoms of CF and DCE are electro positive groups, which form H- bonding with electro negative part of PES-C chains. The observed solvolysis is due to dipole-dipole interactions of opposite type and it is disfavored due to interactions of the same type, resulting in disruption of the structure formed previously. In DCE system structure breaking tendency is observed at high concentration indicating onset of polymer-polymer interaction.

On the basis of experimental observations it is concluded that strong molecular interactions exists in solvent systems studied at three different temperatures. The structural modification is observed at about 2 %. PES-C has structure forming tendency in all the four solvent systems investigated.

CHAPTER -6
A COMPREHENSIVE SUMMARY
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OF
THE WORK

CHAPTER -6

A COMPREHENSIVE SUMMARY OF THE WORK

This chapter of the thesis deals with the brief summary of the work.

CHAPTER-1

This chapter describes up to date literature survey on bisphenols, poly (ether-sulfones) and co poly (ether-sulfone-sulfonates) as well as on the characterization of homo and copolymers.

CHAPTER-2

This chapter deals with the synthesis of bisphenol-C, diphenyl ether disulfonyl chloride, poly (ether -sulfone) (PES-C) and co poly (ether-sulfone-sulfonates) (PSS-1 to PSS-3) and their purification.

CHAPTER-3

This chapter describes the characterization of PES-C and PSS-1 to PSS-3 by solubility, IR, NMR, viscosity, density, chemical resistance, antibacterial and antifungal activities, molecular weight determination by gel permeation chromatography and end group analysis by conductance method. PES-C and PSS-1 to PSS-3 are soluble in common organic solvents. Tough and transparent films of PSS-1, PSS-2 and PSS-3 were prepared from 3% chloroform solutions. The structure of above mentioned homo and copolymers are supported by IR and NMR spectral data. Dilute solution viscosity measurements of PSS-1 to PSS-3, PES-C(6h), PES-C(10h) and PES-C(20h) were made in chloroform(CF), 1-2 dichloroethane(DCE), tetrahydrofuran(THF) and 1,4-dioxane(DO) at 30°C. The intrinsic viscosity $[\eta]$ and Huggin's constant (k') were determined from Huggin's relationship. A little solvent effect is found on intrinsic viscosity. Moreover no systematic trend in k' values are observed indicating polydisperse nature of the homo and copolymers as well as specific interactions occurring in the solutions. Low values of intrinsic viscosities indicated low to moderate molecular weights.

The densities of PSS-1 to PSS-3 were determined by floatation method. The densities of PES-C (6h), PES-C (10h) and PES-C (20h) were determined by specific volume method. The calculated and experimental densities differ due to solvation effect. The increase in density over calculated value suggested predominant change in M as compared to $\Sigma\Delta V_i$ and vice versa. The chemical resistances of PSS-1 to PSS-3 films were determined by change in weight method at room temperature in pure water and 10% each of aqueous solutions of HCl, H₂SO₄, HNO₃, NaOH, KOH, NaCl after 24h, one week and one month. It is found that polysulfonates possess excellent hydrolytic stability towards water, acids, alkalis and salts.

The biological activities of PSS-1 to PSS-3 were screened against different microorganisms: E. coli, B.mega, B. sub P.Vulgaris and A. niger by cup- plate method. It is found that polysulfonates possess mild antimicrobial and antifungal activities.

The average molecular weight were determine by the gel permeation chromatography and were compared with average molecular weight determined by end group analysis by conductance method from the data it is observed that the average molecular weight and dispersity increased with reaction time.

CHAPTER-4

This chapter deals with the thermo- mechanical and electrical properties of polysulfonates. PSS-1 and PSS-2 possess 19.7 and 18.1 N/mm² tensile strength; 37.8 and 29.5kV/mm electric strength; 8.8×10^{16} and 1.5×10^{14} ohmcm volume resistivity and 1.34 and 1.29 dielectric constant, respectively. The co polysulfonates possess moderate tensile strength and excellent electrical properties. Electric strength and dielectric constant have decreased with change in composition. Electric strength has improved 4 to 5 times upon copolymerization. Electric strength and dielectric constant decreased with change in copolymer composition. Electric strength has improved 4 to 5 times due to copolymerization.

DTA-TG thermograms of PSS-1 to PSS-3 and PES-C were scanned at a heating rate of 150°C /min in an N₂ atmosphere. PSS-1 to PSS-3 followed two step degradation and DTA thermograms showed T_g at about 235°C,

234⁰C and 233⁰C. The observed T_g of PSS-1 to PSS-3 is remarkably higher than polysulfonates based on bisphenol-C (120⁰-142⁰C) but comparable with polysulfonates with rigid moieties (150⁰-280⁰C). The exotherms over temperature range 559⁰-571⁰C are due to further decomposition of copolymer chains and confirmed by rapid weight loss in corresponding TG thermograms. DTA thermogram of PES-C showed T_g at 234⁰C and exothermic decomposition transitions at 485⁰C and 591.4⁰C. PES-C is thermally stable up to about 350⁰C and involved apparently single step decomposition reaction with 93.6% weight loss up to 640⁰C. The temperature of maximum weight loss is 596⁰C. PSS-1 to PSS-3 are thermally stable up to about 350⁰C. The first step involved weight loss of about 27 to 30%, while second step involved 47 to 56%. The kinetic parameters: E_a , A and n for PSS-1 to PSS-3 are determined according to Freeman-Anderson method. The entropy changes (ΔS^*) for both steps is calculated at T_{max} . The large and positive magnitudes of ΔS^* for PSS-1 has confirmed less ordered transition state than individual polymer molecules, while large and negative magnitudes of PSS-2 and PSS-3 confirmed highly ordered transition state. The ether, sulfone and sulfonates linkages are weak points, which degrade selectively and free radicals may form. These radicals may further recombine to form new compound (s), which degrade at higher temperatures.

CHAPTER-5

This chapter describes the acoustical parameters of PES-C in different solvents at three different temperatures: 30⁰, 35⁰, and 40⁰C.

Various acoustical parameters such as isentropic compressibility (κ_s), specific acoustical impedance (Z), Rao's molar sound function (R), Van der wals constant (b), relaxation strength (r), internal pressure (π), classical absorption coefficient ($(\alpha/f^2)_{cl}$), viscous relaxation time (τ), solvation number (S_n), free volume (V_f) and intermolecular free length (L_f) were evaluated according to standard equations and correlated with concentration. A good to excellent correlation coefficients are observed. The data are interpreted in light of solvent and temperature effects on molecular interactions occurring in the solutions.

The linear increase of Z , R , b , $(\alpha/f^2)_{cl}$ and τ with C and decrease with T and linear decrease in κ_s , r and L_f with C and linear increase with T indicated the presence of strong molecular interactions. The increasing temperature caused less ordered structure and more intermolecular distance. The decrease in κ_s with C is due to compressibility of free solvent molecules and chain like structure. Strong polymer-solvent interaction is supported by positive and increase of S_n with C . The S_n increased linearly with C and decreased with T in CF, DO and THF and it increased non linearly with CF up to about 2% and then decreased with C in DCE system. S_n increased up to 35⁰C and decreased at 40⁰C in CF, DCE and DO systems, while it increased with T in THF system. The decrease in S_n with C and T is due to decrease in cohesive forces indicating presence of polymer-polymer interaction. When T increases the tendency of molecules to move away increases and thereby the probability of molecular interactions decreases, which may result in decrease in cohesive forces and ultimately V_f and L_f increase and vice-versa. The internal pressure and free volume are measure of cohesion forces. The solvophilic nature of PES-C is responsible for the change in apparent molar volume ϕ_{V2} and apparent molar compressibility ϕ_{κ_s} .

The increase of $(\alpha/f^2)_{cl}$ and τ with C can be exploited in terms of motion of the macromolecular interchain forces which are influenced by ρ, η and U . The contribution of acoustic relaxation is considered as a result of entropy fluctuation associated in solution of dynamically formed physical entity.

The lone pairs of electrons of THF, DO, sulfone and ether linkages of PES-C and chlorine atoms of CF and DCE are electronegative groups, while phenyl rings and H- atoms of CF and DCE are electropositive groups, which form H-bonding with electronegative parts of PES-C chains. The observed solvolysis is due to dipole-dipole interactions of opposite type and it is disfavored due to interactions of the same type and resulting in disruption of the structure formed previously. In DCE system structure breaking tendency is observed at high concentration indicating onset of polymer-polymer interaction. Thus, strong molecular interactions exist in solvent systems studied at three different temperatures.

ACHIEVEMENTS

List of papers communicated and presented at conferences/seminars/symposia:

(A) List of papers communicated

1. Synthesis and characterization of high performance poly (4, 4'-cyclohexylidene diphenoxy-4, 4'-diphenylene sulfone)
R. R. Amrutia and P. H. Parsania, Journal of Polymer Science
2. Synthesis and Physico-Chemical study of Novel Cardo Copoly (ether-sulfone-sulfonates)
R. R. Amrutia and P. H. Parsania, J. Polym. Mater
3. Effect of temperature on various acoustical parameters of poly (4-cyclohexylidene diphenoxy-4, 4'-diphenylene sulfone) solutions
R. R. Amrutia and P. H. Parsania, Journal of Chem. Eng. data"

(B) Papers presented at conferences / seminars / symposia / workshop

1. Synthesis and characterization of novel high performance poly (4, 4'-cyclohexylidenediphenyloxy-4, 4'-diphenylene sulfone), R. R. Amrutia and P. H. Parsania, "National Seminar Polymer Research in India – Opportunities and Challenges"- September 25, 2004 at Allahabad
2. Synthesis and characterization of novel high performance poly (4, 4'-cyclohexylidenediphenyloxy-4, 4'-diphenylene sulfone), R. R. Amrutia and P. H. Parsania, "4th International Conference on Polymers for advanced technologies-MACRO-2004"-December 14-17, 2004 at Thiruvananthapuram
3. Synthesis and Physico-Chemical study of Novel Cardo Copoly (ether-sulfone-sulfonates), R. R. Amrutia and P. H. Parsania, "National Seminar on Polymers, Surfactants and Gels" March 11-13, 2005 at Vadodara