

## NEW COPOLY(ETHER-IMIDE-SULFONE) OLIGOMERS HAVING PENDANT IONIC GROUPS

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New copoly(ether-imide-sulfone) oligomers have been synthesized by solution polycondensation reaction of bis(*p*-chlorophenyl)sulfone with various imide bisphenols and 2,2-bis(4-hydroxyphenyl)-propane (Bisphenol A). The Williamson polyetherification procedure has been chosen in view to ensure a partial hydrolysis of imide linkages into pendant potassium carboxylate groups. Chemical confirmation of the copolymers was done by using FTIR and <sup>1</sup>H-NMR spectroscopy and elemental analysis. The thermal properties, investigated by DSC and TGA, were discussed in view to outline the influence of the chemical structure on the properties. All the polymers were soluble in aprotic dipolar solvents. A dependence of the reduced viscosity on the concentration has been found and its pattern suggested a possible polyelectrolyte-like behavior for the investigated copolymers.

### INTRODUCTION

Aromatic polysulfones and poly(ether sulfone)s belong to a family of aromatic amorphous thermoplastics with unique high-performance properties as engineering materials. They have high glass transition temperatures ( $T_g$ ), very good thermal stability in the melting state, long-term thermo-oxidative endurance, high distortion-temperature, chemical inertness, good solubility, good electrical insulative properties and flame retardancy.<sup>1,2</sup>

Aromatic polyimides are thermally stable polymers that generally exhibit excellent mechanical strength and outstanding thermal and oxidative stability. Due to the increased performance characteristics demanded for polymers in various practical areas (automobile, aerospace, and electronic industries, etc.) the use of these aromatic polymers is growing steadily and they are of major commercial and industrial importance.<sup>3</sup> However, one drawback for the practical use of these polymers is the difficulty of processing, due to their poor solubility in addition to their high melting or glass transition temperatures. In view to improve the processing of polyimides, many synthetic variations such as copolyimides, poly(amide-imide)s, poly(imide-sulfone)s, poly(ether-imide)s, poly(ester-imide)s have been studied. Insertion of ester, amide, ether, or other

flexible groups, in the polymer chain has been found to have a good effect on the processability.<sup>4</sup>

Aromatic polymers containing aryl ether or aryl sulfone moieties generally have excellent mechanical properties, lower glass transition temperatures, greater chain flexibility and tractability than their corresponding counterparts without these groups in the chain.<sup>5</sup> The decrease of glass transition temperature and the improved solubility are attributed to the flexible linkages that provide lower energy of internal rotation of the polymer chain.<sup>6</sup>

In our continuing effort to develop easily processable high-performance polymers, having both high thermal stability and good solubility, we have prepared a series of new copoly(ether-imide-sulfone) oligomers by using the Williamson polyetherification. This procedure has been chosen in view to ensure a partial hydrolysis of imide linkages into pendant potassium carboxylate groups, which could ensure some new features to these oligomers, such as polyelectrolyte-like behavior.

### RESULTS

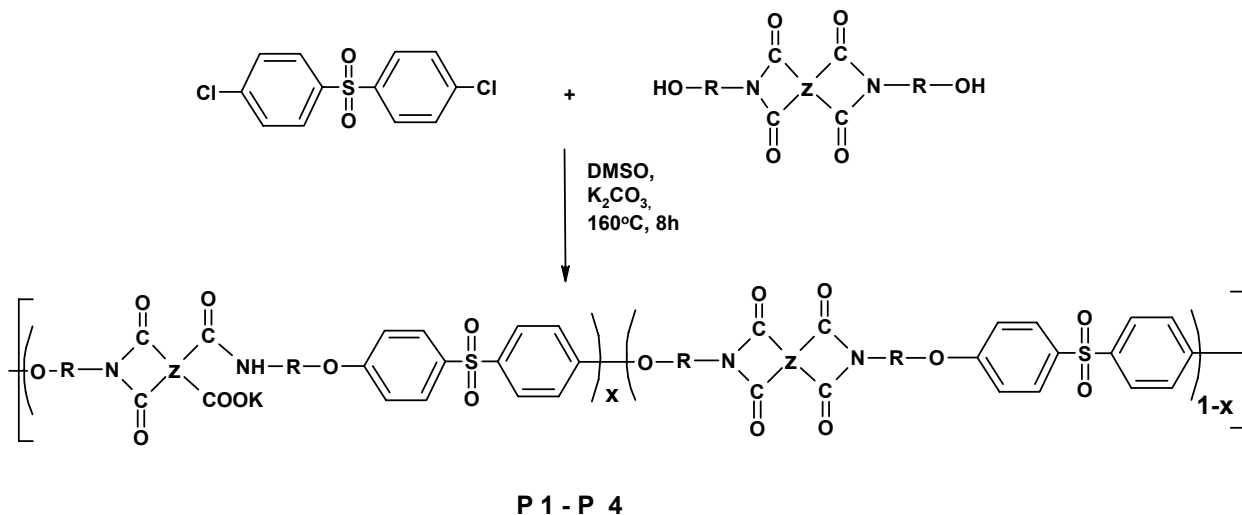
The alternated and random polymers and copolymers have been prepared using the classical Williamson condensation reaction of aromatic

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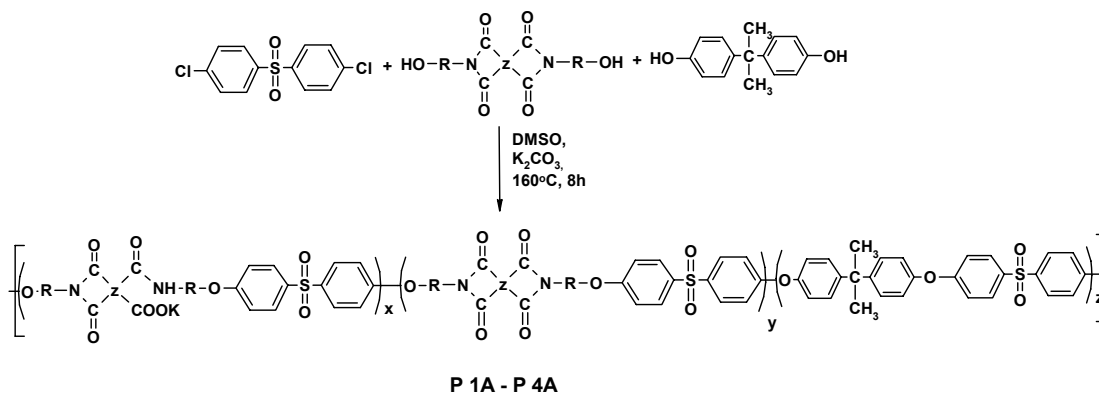
sulfone dichloride with imide bisphenols having various structures, or with a mixture of bisphenol A and imide bisphenols, respectively.

This Williamson polyetherification procedure has been chosen in view to ensure both polyether

chain formation and a partial hydrolysis of imide linkages into pendant potassium carboxylate groups, as described in Scheme 1 and 2.



Scheme 1 – Synthesis of polyether(imide-sulfone)s **P1 – P4**.



Code	Z	R
P 1; P 1A		
P 2; P 2A		
P 3; P 3A		
P 4; P 4A		

Scheme 2 – Synthesis of copoly(ether-imide-sulfone)s **P1A – P4A**.

The structures of the polymers were confirmed by using FTIR and <sup>1</sup>H-NMR spectra and by elemental analysis. For all of the polymers and copolymers the FTIR spectra showed the presence of the absorption band corresponding to the imide group (imide I at about 1778, 1722; imide II at about 1380 cm<sup>-1</sup>). The sharp peaks occurring at 1243-1249 cm<sup>-1</sup> are due to the asymmetrical vibrations of the ether linkage. Also the spectra showed the presence of the absorption band corresponding to the pendant groups COO<sup>-</sup> at 1584 cm<sup>-1</sup>. Characteristic absorption bands and their assignments are presented in Table 1.

The <sup>1</sup>H-NMR spectra of the polymers showed three types of signals, which were assigned correspondingly: the singlet at 9.23-9.85 ppm is due to the NH-CO protons, the multiplet between 6.24 and 8.43 ppm belongs to the aromatic protons, the singlet at 1.23-1.60 ppm is due to the aliphatic segment ((CH<sub>3</sub>)<sub>2</sub>C < ) from the bisphenol A units. Figures 1-3 show representative <sup>1</sup>H-NMR spectra of starting imide bisphenol **4** and corresponding copolyether(imide-sulfone)s **P4** and **P4A**, therefrom.

Table 1

Structure confirmation of the synthesized polymers by FTIR and elemental analysis

Code	FTIR absorption bands of representative chemical linkages (cm <sup>-1</sup> )									Elemental Analysis	
	=C-H aromatic	C-H (CH <sub>3</sub> )	COO <sup>-</sup>	C-Cl	Imide		SO <sub>2</sub>		C-O-C	N% Calcd. (Found)	S% Calcd. (Found)
					I	II	Asym	Sym			
<b>P1</b>	3089	2966	1582	1088	1778 1722	1374	1318	1153	1243	4.56 (3.81)	5.22 (5.44)
<b>P2</b>	3090	2967	1582	1089	1776 1719	1377		1154	1249	3.96 (3.51)	4.54 (5.66)
<b>P3</b>	3067	-	1583	1090	1778 1719	1380		1152	1244	3.90 (3.43)	4.46 (3.93)
<b>P4</b>	3090	-	1582	1089	1779 1724	1377	1321	1153	1243	3.90 (3.48)	4.46 (5.27)
<b>P1A</b>	3090	2966	1584	1089	1778 1722		1320	1153	1245	1.28 (1.28)	6.07 (5.39)
<b>P2A</b>	3067	2967 2923	1583	1088	1776 1720	1372	1321	1153	1246	1.20 (1.22)	5.58 (5.45)
<b>P3A</b>	3066	2967 2928	1584	1089	1778 1722	1371	1321	1153	1245	1.17 (1.76)	5.52 (5.16)
<b>P4A</b>	3064	2965 2926	1584	1090	1779 1725	1375	1321	1153	1245	1.17 (1.24)	5.52 (5.39)

When using bisphenol A together with bisphenol imide, the resulting copolymer contains three types of chemical units (see scheme 2): partially hydrolyzed imide-sulfone units; intact imide-sulfone units and bisphenol A - polysulfone units. On the basis of <sup>1</sup>H-NMR measurements it was possible to calculate the composition of the copolymers **P1A-P4A**, by using distinct areas of -NH-CO- and (CH<sub>3</sub>)<sub>2</sub>C< protons. Details of calculation are presented in the footnotes of Table 2.

Elemental analysis data and physical characteristics of the copolymers are presented in Table 1. The elemental composition of samples **P1A-P4A** was calculated by using values of x, y, z given in table 2. As can be seen from table 2 there is a good agreement between calculated and found values for both nitrogen and sulfur content.

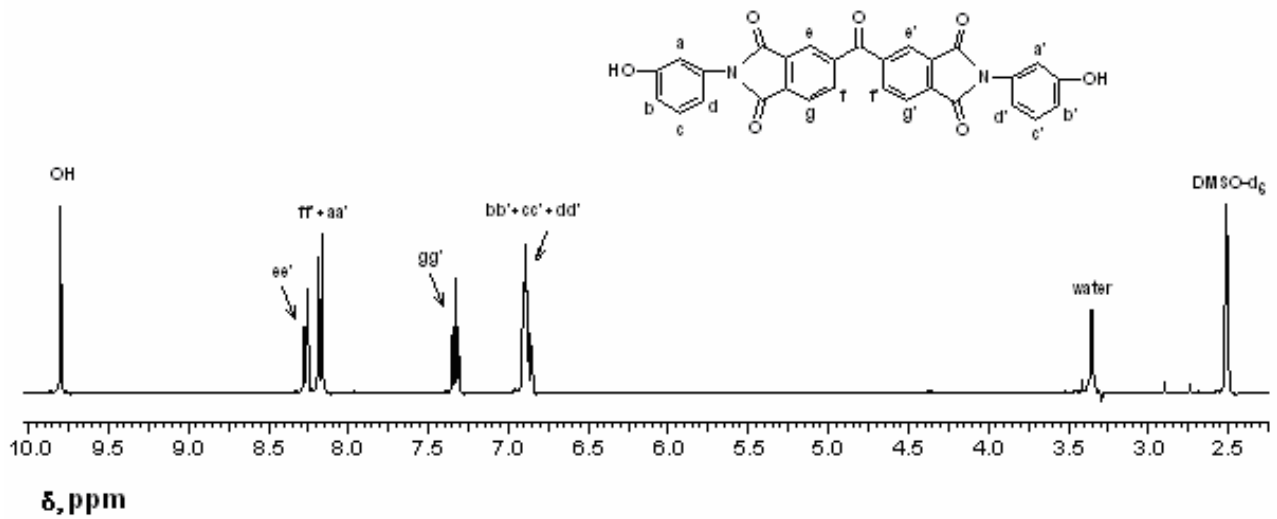
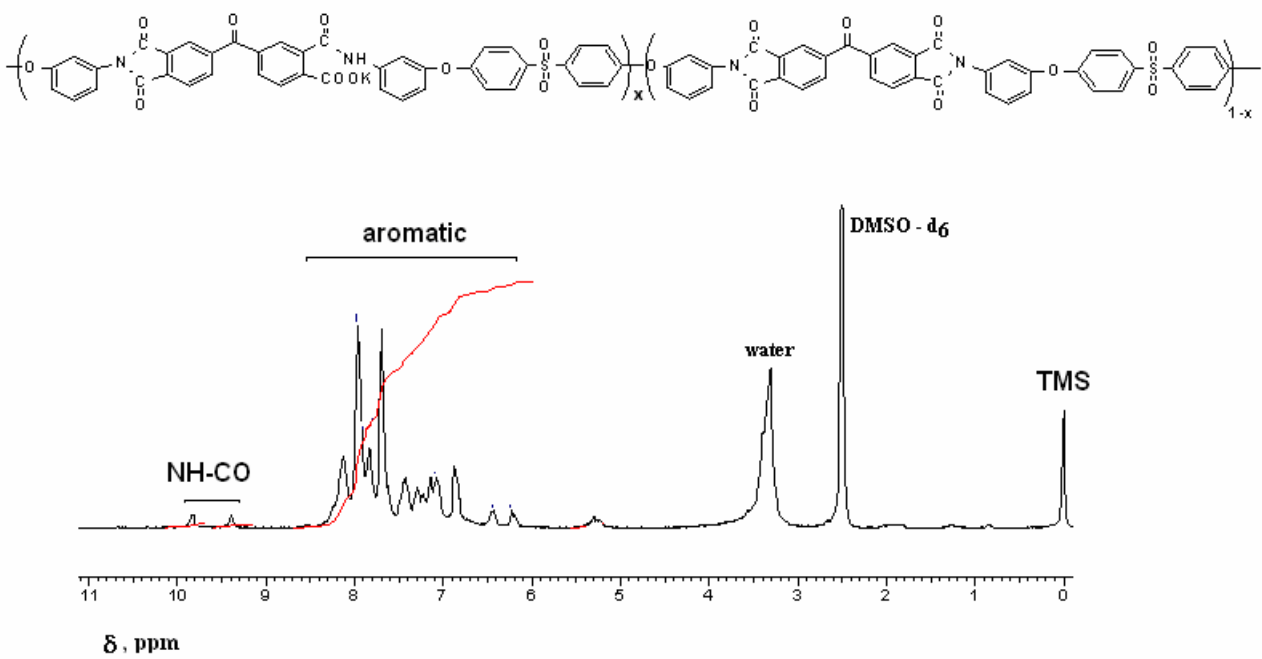
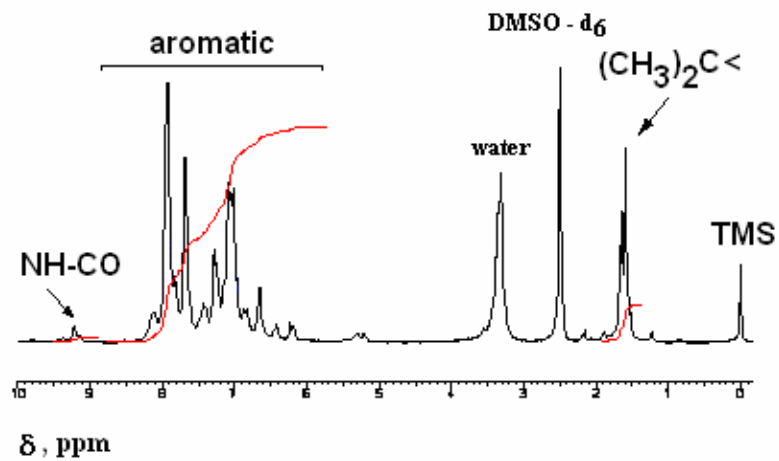
Fig. 1 – <sup>1</sup>H NMR spectrum of sample 4.Fig. 2 – <sup>1</sup>H NMR spectrum of sample P4.Fig. 3 – <sup>1</sup>H NMR spectrum of sample P4A.

Table 2

Copolymer's composition calculated from <sup>1</sup>H-NMR data

Sample	A <sub>NH-CO</sub>	A <sub>&gt;C(CH3)2</sub>	x <sup>a</sup>	y <sup>b</sup>	z <sup>c</sup>
P 1A	0.012	0.111	0.32	0.18	0.50
P 2A	0.006	0.110	0.16	0.34	0.50
P 3A	0.008	0.084	0.29	0.21	0.50
P 4A	0.010	0.107	0.28	0.22	0.50

$$^a x = 6 * \{A_{(NH-CO)} / A_{>C(CH_3)_2}\} * z; \quad ^b x + y + z = 1; \quad y = 0.5 - x; \quad ^c z = 0.5$$

The solubilities of these copolymers were tested in various common solvents, and the results are listed in Table 3. All the copolymers showed good solubility in aprotic dipolar solvents (DMF, DMSO, DMAc, NMP), and in 1,4-dioxane. In other solvents like chloroform, methanol, acetone, the polymers were insoluble, except for the polymers **P1**, **P1A**, **P2A**, which were partially soluble in acetone. The presence of ether and sulfone linkages in the polymeric chain constitutes an effective factor in improving the solubility of the polyimides. This fact makes the present

polymers much more suitable candidates for practical applications by spin-coating and casting processes. PLM data observations revealed that all the copolymers melted in the range of 129-210 °C. The highest  $T_m$  value of 210 °C, in the case of sample **P3**, could be explained by the presence of increased content of *para*-substituted units in the backbone. Interestingly, sample **P3** exhibited an intense birefringence in the melting state, under shearing stress applied, which suggests a possible thermotropic character. This behavior remains to be investigated in a future work.

Table 3

Solubility of copoly(ether-imide-sulfone)s

Solvent	$\delta^a$	P1	P2	P3	P4	P1A	P2A	P3A	P4A
Water	23.43	- <sup>b</sup>	-	-	-	-	-	-	-
Methanol	14.49	-	-	-	-	-	-	-	-
Dimethylsulfoxide	13.04	+	+	+	+	+	+	+	+
Dimethylformamide	12.15	+	+	+	+	+	+	+	+
N-Methyl-2pyrrolidone	11.17	+	+	+	+	+	+	+	+
Dimethylacetamide	11.12	+	+	+	+	+	+	+	+
1,4-Dioxane	10.01	+	+	+	+	+	+	+	+
Dichloromethane	9.90	-	-	-	-	-	-	-	-
Acetone	9.75	+	-	-	+	+	+-	-	+
Tetrahydrofuran	9.52	+	+-	+-	+-	+	+	+-	+
Chloroform	9.21	-	-	-	-	-	-	-	-
Ethyl acetate	9.07	-	-	-	-	-	-	-	-
Toluene	8.90	-	-	-	-	-	-	-	-

<sup>a</sup> Solvent solubility parameter <sup>7</sup> (cal/cm<sup>3</sup>)<sup>1/2</sup>

<sup>b</sup> + = soluble at room temperature; +- = partially soluble; - = insoluble.

Table 4

Thermal behavior of the copoly(ether-imide-sulfone)s

Code	T <sub>g</sub> <sup>a</sup> (°C)	T <sub>m</sub> <sup>b</sup> (°C)	T <sub>10%</sub> <sup>c</sup> (°C)
P1	97	160	
P2	61	138	345
P3	110	210	
P4	79	176	325
P1A	74	129	370
P2A	82	133	410
P3A	109	178	430
P4A	65	139	375

<sup>a</sup> Glass transition temperature (T<sub>g</sub>) determined under nitrogen by DSC, heating rate of 10°C/min.

<sup>b</sup> Melting temperature determined by optical polarized light microscopy (PLM)

<sup>c</sup> Temperature corresponding to the 10 % weight loss.

As a general remark, one can say that the introduction of kinked bisphenol A units into the copolymers structures led to a significant decrease of their melting temperatures.

Thermogravimetric analysis in air showed that all the polymers are thermally stable, having the temperature of 10 % weight loss in the range of 325 – 430 °C (table 4). It was observed that the pendant COOK groups decrease the thermal stability. Samples **P1A** and **P4A** having higher content of pendant COOK have lower  $T_{10}$  value than sample **P2A** which has the lowest content of COOK groups. The sample **P3A** has the higher  $T_{10}$  value, of 439 °C, which could be explained by the higher thermal stability afforded by its *para*-substituted phenylene units.

The glass transition temperature of polymers ranged between 61 °C and 110 °C, as determined by DSC. Representative DSC thermograms are given in Fig 4. As can be seen from table 2, the incorporation of bisphenol A into the polymer backbone by polycondensation led to a decrease of  $T_g$ , due to the increase in flexibility of the polymer backbone. Samples **P3** and **P3A** have the highest  $T_g$  values, 110 °C and 109 °C, respectively, due to the increased rigidity of the macromolecular chains containing all *p*-substituted phenylene rings in the repeating unit. The lower  $T_g$  values for the rest of polymers could be due to the presence of *m*-substituted phenylene rings in the repeating unit, which increase the free volume.

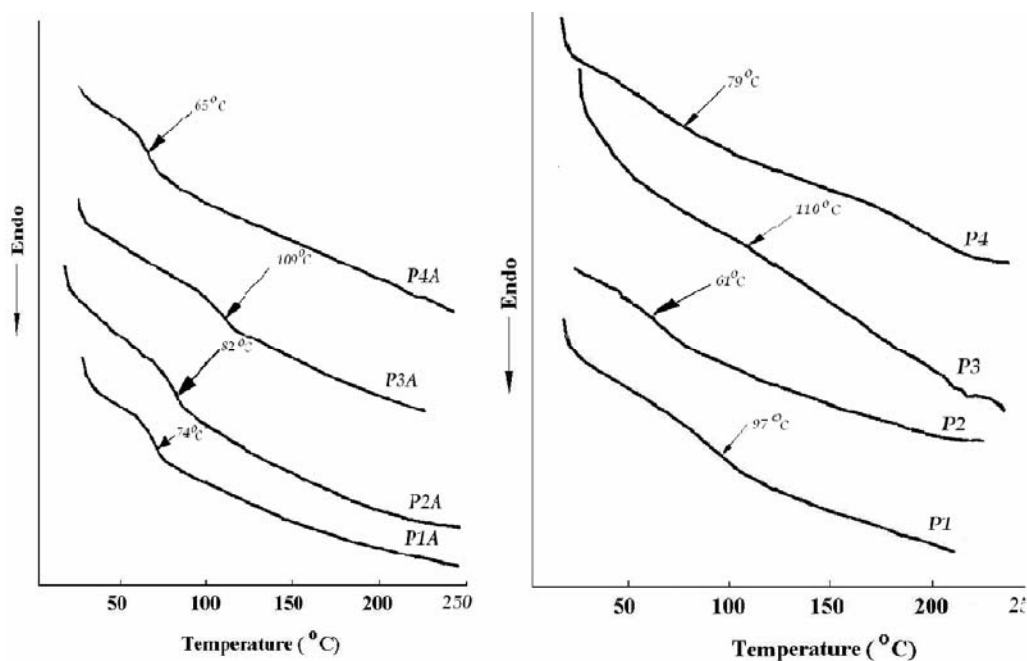


Fig. 4 – Differential scanning calorimetry traces of poly(ether-imide-sulfone)s (10 °C/min second heating run).

As expected, the presence of pendant  $\text{COOK}^+$  groups influences the concentration dependences of the reduced viscosity values (Figures 5). According to these data, the most rigid structures **P3** and **P3A** present the highest values of the viscosity, whereas the more flexible chains **P1** and **P1A** give the lowest values of the viscosity. The reduced viscosity strongly increases with increasing concentration for **P3** sample for which a possible thermotropic behavior was observed by PLM. For all samples, the experimental curves obtained for low concentration deviate upward from their linear dependences. This can be due to intermolecular electrostatic repulsive interactions

between the pendant charged groups of the macromolecules which increases at high dilution.<sup>8</sup> The change of the homopolymer structure through copolymerization with bisphenol A determines a difference in the viscometric behavior at concentrations higher than 0.5 g/dL. Thus, the four types of structures display a different viscometric behavior by copolymerization, as depicted in Figure 5. Qualitatively, the copolymerization induces different effects: small increase (sample **P1A**) or a decrease (sample **P2A**, **P3A**, **P4A**) of the viscosity; the difference in the viscometric behavior is more clearly observed for samples **P3A** and **P4A** which have more flexible chains.

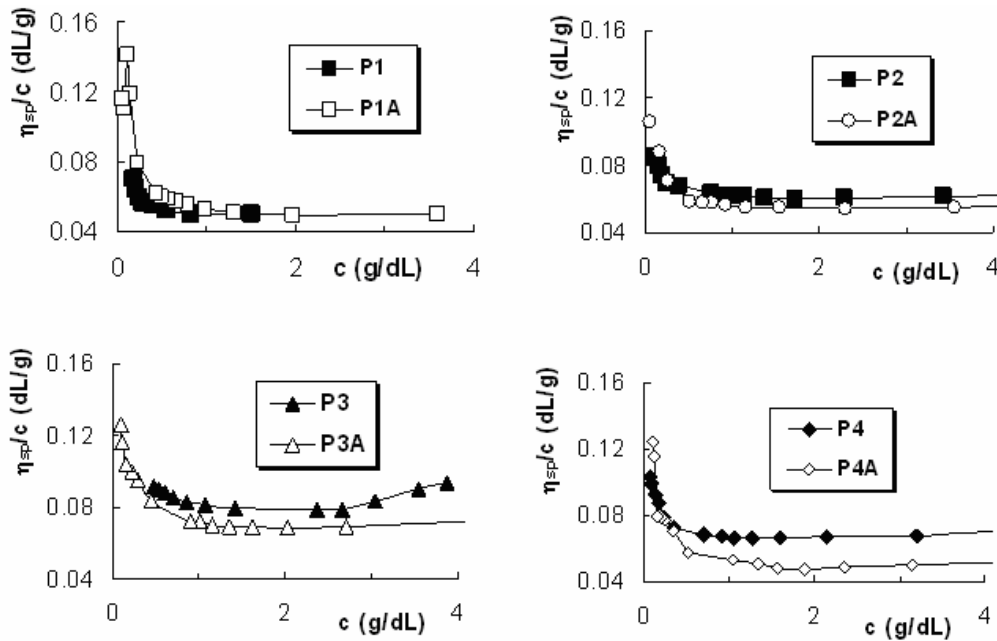


Fig. 5 – Comparative plots of the reduced viscosity vs. concentration for copoly(ether-imide-sulfone)s.

The WAXD measurements on powder samples at room temperature showed an amorphous

morphology for all the investigated samples (Figure 6).

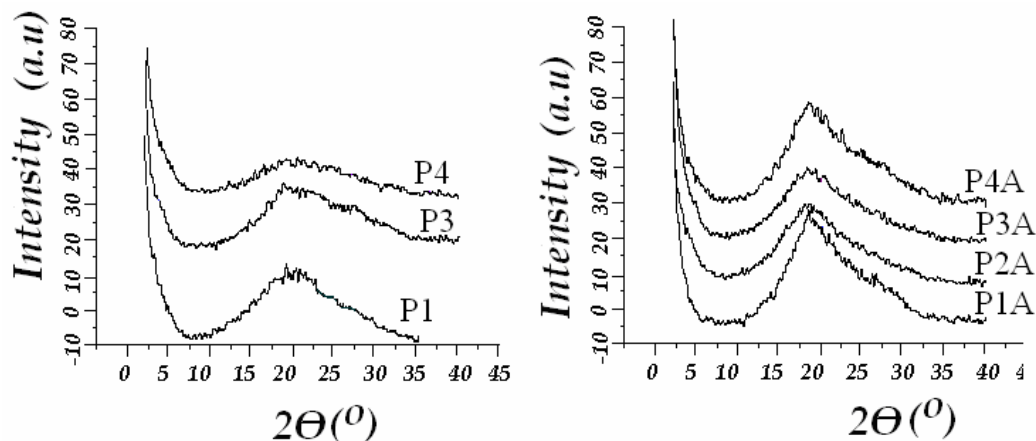


Fig. 6 – WAXD diffractograms of copoly(ether-imide-sulfone)s at room temperature.

## EXPERIMENTAL

### Materials

Sulfonyl bis(4-chlorophenyl) (Aldrich) was recrystallized from toluene (melting point 147 - 149 °C). 2,2'-Bis(4-hydroxyphenyl)-propane (Bisphenol A, Fluka), dimethyl sulfoxide (Aldrich) were used as received. Anhydrous potassium carbonate was dried at 120 °C in vacuum oven before use.

All the solvents used for solubility tests (Aldrich) were used as received.

### Measurements

Fourier Transform-Infrared (FTIR) spectra were recorded on a FT-IR Bruker Vertex 70 Spectrophotometer in transmission mode, by using KBr pellets.

Proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectra were recorded by a BRUKER Advance DRX 400 MHz spectrometer using DMSO-d<sub>6</sub> as solvent and tetramethylsilane (TMS) as internal reference. Chemical shifts are reported in parts per million (ppm).

Thermogravimetric analysis (TGA) was carried out in air, by using a MOM Q Derivatograph (Hungary), at a heating rate of 10 °C / min. The decomposition temperature T<sub>10</sub> was considered the temperature at 10% weight loss of the sample.

Differential scanning calorimetry (DSC) measurements were performed with a Mettler TA DSC 12E Instrument, at a heating rate of 10 °C/ min, under nitrogen atmosphere. The second heating cycle was used to determine the glass transition temperatures (T<sub>g</sub>) of the samples. The melting behavior of copolymers was measured with an Olympus BH-2 polarized light microscope equipped with a THMS 600/HSF91 hot stage under crossed polarizers.

Wide Angle X ray Diffraction (WAXD) measurements were performed on powder samples, by using a Bruker D8 ADVANCE Diffractometer, using the Ni-filtered Cu-K $\alpha$  radiation ( $\lambda = 0.1541$  nm). A MRI-WRTC – temperature chamber (with nitrogen atmosphere) and MRI-TCPU1 - Temperature Control and Power Unit were used. The working conditions were 36 kV and 30 mA. All the diffractograms were investigated in the range of  $1.5 \div 40$  (2 theta degrees), at room temperature. All the diffractograms were reported as observed.

The solubility of the copolymers was determined in a series of common solvents like: acetone, methanol, chloroform (CHCl $_3$ ), dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF), N-methyl-pyrrolidine-2-one (NMP).

The viscometric measurements were carried out in DMF at 25 °C, by using Ubbelohde suspended-level viscometer. The kinetic energy corrections were found to be negligible. The flow time for the solvent was 166.8 s. The flow volume of the viscometer was greater than 5 ml, making drainage errors unimportant. Flow times were obtained with an accuracy of  $\pm 0.02$  %.

#### Synthesis of the imide bisphenols

The imide bisphenols: N,N'-bis(*m*-hydroxyphenyl)-pyromellit-diimide (**1**), N,N'-bis(*m*-hydroxyphenyl)-oxydiphthalic-diimide (**2**), N,N'-bis(*p*-hydroxyphenyl)-benzophenontetracarboxylic-diimide (**3**) and N,N'-bis(*m*-hydroxyphenyl)-benzophenontetracarboxylic-diimide (**4**) have been prepared by the reaction of pyromellitic dianhydride, oxydiphthalic dianhydride or benzophenontetracarboxylic dianhydride with *m*-aminophenol or *p*-aminophenol in a 1 / 2 molar ratio, using DMF as solvent, at reflux, according to previously reported methods.<sup>9</sup> The resulting imide bisphenols were purified by recrystallization from DMF or DMF/ethanol mixture.

#### Synthesis of the polymers and copolymers

The synthetic pathway to alternated or random copolymers was the classical Williamson etherification method, in which an aromatic dichloride reacted with a nucleophilic bisphenol. These poly(ether-imide-sulfone)s **P1-P4** were synthesized by the reaction of bis(*p*-chlorophenyl)sulfone with the corresponding monomers **1-4** (Scheme 1).

The copoly(ether-imide-sulfone)s **P1A-P4A** have been synthesized by reacting bis(*p*-chlorophenyl)sulfone with a mixture of bisphenol A and imide bisphenols (**1-4**) in a 1 / 0.5 / 0.5 molar ratio, respectively (Scheme 2). A typical condensation procedure for sample **P1A** follows: 0.8 g (1.998 mmol) of N,N'-bis(*m*-hydroxyphenyl)-pyromellit-diimide, 0.46 g (1.998 mmol) of 2,2-bis(*p*-hydroxyphenyl) propane (bisphenol A), 1.15 g (3.997 mmol) of bis(*p*-chlorophenyl)sulfone, 0.64 g anhydrous potassium carbonate (15 % molar excess) and 10 ml DMSO were charged into a round bottom flask fitted with thermometer, condenser, nitrogen inlet and outlet and magnetic stirrer. The temperature was increased gradually to 100 °C during 1 h. Then, it was increased quickly to 160 °C and maintained under stirring for 8 h. After cooling, the redish - brown reaction mixture was poured into cold water to precipitate the polymer. The polymer was washed three times with cold water and methanol. Finally, the polymers were filtered and dried under vacuum at 50 °C, for 20 h.

## CONCLUSIONS

New copoly(ether-imide-sulfone) oligomers have been synthesized by solution polycondensation reaction of bis(*p*-chlorophenyl)sulfone with various imide bisphenols or with a mixture of imide bisphenols and bisphenol A.

A partial hydrolysis of the imide linkages was realized by performing the synthesis in the presence of potassium carbonate. The proposed structures have been verified by FTIR and <sup>1</sup>H-NMR spectra.

An upward deviation in the plots of the reduced viscosity on the concentration has been found at low concentrations. Its pattern suggested a possible polyelectrolyte-like character for the obtained copolymers due to the intermolecular interaction between the chains with ionic pendant groups.

WAXD showed that these copolymers were amorphous in nature. A strong birefringence in the melting state was observed in the case of copolymer **P3**, suggesting a possible thermotropic behavior for this sample.

The incorporation of bisphenol A by ether linkages into the main chain of the polymers was a useful way to improve solubility and to lower both their glass transition and melting temperatures.

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## REFERENCES

1. M. J. El-Hibri, J. Nazabaj, J.I. Equiazabal and A. Arzak, "Poly(arylethersulfone)s", in "Handbook of Thermoplastics", O. Olabisi (Ed.), Marcel Dekker, New York, 1997, Chapter 36, p. 893.
2. L. Marin, V. Cozan and M. Brumă, *Polym. Adv. Technol.*, **2006**, *17*, 664 – 672.
3. M. A. Shahram, *Eur. Polym. J.*, **2005**, *41*, 91 – 96.
4. M. Bruma, I. Sava, F. Mercer, I. Negulescu, W. Dalys, J. Fitch and P. Cassidy, *High Perform. Polym.*, **1995**, *7*, 411 – 420.
5. R. N. Johnson, A. Farnham and R. A. Clendinning, *J. Polym. Sci. Part A: Polym. Chem.*, **1967**, *5*, 2375– 2399.
6. H. J. Jeong, M. Kakimoto and Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.*, **1991**, *29*, 767 – 772.
7. C. M. Hansen, *Ind. Eng. Chem. Prod. Res. Dev.*, **1969**, *8*, 2-11.
8. L. Ghimici and E. S. Drăgan, „Transport properties of soluble polyelectrolytes”, in: „Focus on Ionic Polymers”, Research Signpost, India, 2005, p. 49 – 92.
9. M. Brumă, B. Schulz, T. Kopnick and J. Robison, *High Perform. Polym.*, **2000**, *12*, 429 – 443.