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Poly(Azomethine Sulfones). I. Synthesis and Characterization of New Poly(Azomethine Sulfones) Containing Ortho/Para Aromatic Moieties

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POLY(AZOMETHINE SULFONES). I. SYNTHESIS AND CHARACTERIZATION OF NEW POLY(AZOMETHINE SULFONES) CONTAINING ORTHO/PARA AROMATIC MOIETIES

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ABSTRACT

New poly(azomethine sulfones) with linear structures containing methylene bis(2-oxobenzylidene aniline), methylene bis(4-oxobenzylidene aniline), 1,4-bis(4-oxobenzylidene amino)phenylene and 1,4-bis(2-oxobenzylidene amino)phenylene units were prepared in the conventional literature manner by the reaction of azomethine bisphenols (M 1-4) with 4,4'-sulfonyl bischlorobenzene. The resulting polymers were confirmed by IR, ¹H-NMR and elemental analysis, and were characterized by UV measurements, viscosities, solubilities, DSC and thermo-gravimetric analysis (TGA) in air. A difference in the solubility and thermal behavior between the polymers with ortho- and para- chains was observed. The hydrolytic stability of the polymers in 10% wt aqueous sulfuric acid was reasonable

INTRODUCTION

Polyazomethines (PAM) are an important class of thermotropic polymers having numerous desirable features making them useful materials in technical applications [1-3].

There are a few studies concerning poly(azomethine sulfones) (PAMS) [1, 4-8]. An attractive feature of this class of polymers is the effect of the balance between isotropic sulfone containing segments and rigid anisotropic azomethine segments on the properties of polymers. It is interesting that all the attempts reported in the literature showed small viscosity values, ranging among 0.03 and 0.29 dL/g.

Our previous works reported the functionalization of polysulfones (PSF) with pendant aldehyde groups and further chemical modification into phenolic azomethine groups [9], or thermotropic liquid crystalline (TLC) behavior of PAMS [10].

The purpose of this paper is to present the synthesis and characterization of some new linear PAMS containing ortho- and para-oxobenzylideneaniline units, and a comparison of the properties derived therein.

EXPERIMENTAL

Materials

4,4'-Sulfonyldichlorobenzene (Aldrich) was recrystallized from toluene (mp 147-149°C). 2-Hydroxybenzaldehyde, 4-hydroxybenzaldehyde and 4,4'-methylenedianiline (Aldrich) were used as received. 4-Aminoaniline was resublimed under vacuum (mp 143-145°C). N-Methyl-pyrrolidin-2-one (NMP) was vacuum distilled over phosphorus pentoxide. Dimethylsulfoxide (DMSO) and chlorobenzene (PhCl) were dried over calcium hydride and distilled under vacuum before use. Anhydrous potassium carbonate was dried at 120°C in a vacuum oven before use.

Techniques

The IR spectra were recorded on a Specord M90 Carl Zeiss Jena spectrophotometer by using the KBr pellet technique. ¹H-NMR spectra were run on a Jeol 60 MHz NMR spectrometer at 60°C in DMSO-d₆ using TMS as the internal reference. The reduced viscosities of polymer solutions (0.2% w/v) in NMP were determined at 25 ± 0.1°C by using an Ubbelohde suspended level viscometer. Melting and softening points were determined with an IOR MC1-type polarizing

microscope equipped with a heating stage. Differential scanning calorimetry (DSC) measurements were done by using a Mettler TA instrument DSC 12E with a heating rate of 20°C /min in nitrogen. TGA was carried out in air with a F. Paulik derivatograph using 50 mg sample at a heating rate of 12°C per minute. Electronic spectra were recorded in DMSO in the range 260–450 nm with a Specord M42 Carl Zeiss Jena Spectrophotometer. Optimized geometries and relative total enthalpy of formation values were obtained using Molecular Mechanics Force field, MMX minimization [11].

Monomer (M1–4) Synthesis

All monomers (M1–4) were prepared and purified as described [10].

4,4'-Methylene Bis(2-hydroxybenzylideneaniline) (M1)

Yellow crystals: yield, 81%; mp 204–209°C.

Analysis: Calcd for $C_{27}H_{22}N_2O_2$ (406.46): C, 79.78; H, 5.45; N, 6.89%.

Found: C, 79.86; H, 5.35; N, 7.12%. IR (cm^{-1}) 1625 (CH=N), 1605, 1575, 1500 (aromatic). 1H -NMR (DMSO- d_6 , TMS): 8.775 (s, 2H, CH=N), 7.75, 7.50 (m, 2H, ortho to -CH=), 7.25 (m, 4H, ortho to -N=, 4H, ortho to -CH₂-), 7.025, 6.80 (m, 6H, aromatic), 4.05 (s, 2H, -CH₂-)

1,4-Bis(2-hydroxybenzylideneamino)phenylene (M2)

Orange crystals: yield, 87%; mp 208°C

Analysis: Calculated for $C_{20}H_{16}N_2O_2$ (316.36); C, 75.93; H, 5.15; N, 8.85%.

Found: C, 75.80; H, 5.02; N, 9.12%. 1H -NMR (DMSO- d_6 , TMS): 8.9 (s, 2H, CH=N), 7.6–6.7 (m, 12H, aromatic)

4,4'-Methylene Bis(4-hydroxybenzylideneaniline) (M3)

Yellow crystals: yield, 91%; mp 215–217°C

Analysis: Calculated for $C_{27}H_{22}N_2O_2$ (406.46): C, 79.78; H, 5.45; N, 6.89%.

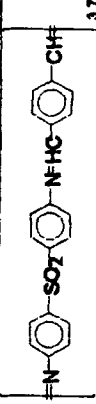
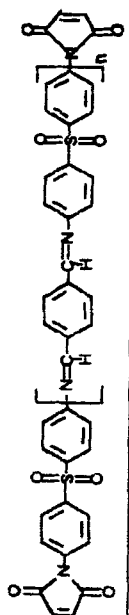
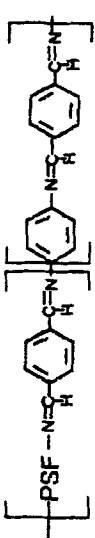

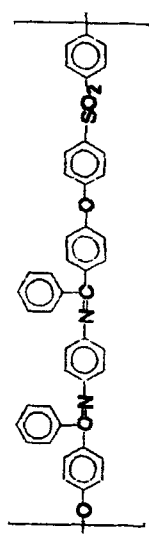
Found: C, 80.06; H, 5.60; N, 7.0%. IR (cm^{-1}) 1615 (CH=N), 1590, 1575 (sh), 1525, 1170, 840 (aromatic). 1H -NMR (DMSO- d_6 , TMS): 8.375 (s, 2H, CH=N), 7.80, 7.65 (d, 4H, ortho to -CH=), 7.10 (s, 8H, ortho to -N=, ortho to -CH₂-), 6.925, 6.775 (d, 4H, ortho to OH), 3.925 (s, 2H, -CH₂-)

1,4-Bis(4-hydroxybenzylideneamino)phenylene (M4)

Yellow-ochre crystals : yield, 75%; mp 225–226°C (lit.: 225–226°C [12])

Analysis: Calcd for $C_{20}H_{16}N_2O_2$ (316.36): C, 75.93; H, 5.15; N, 8.85%.

TABLE I. Viscosity and Molecular Weight Data for Poly(Azomethine-Sulfones) from Literature^a

No	Polymer Structure	Viscosity	Molecular Weight	References
1.			≈ 1300	[1]
2.		n=1 0.032 ^b n=4 0.037 ^a n=7 0.044 ^a	≈ 750 ≈ 1800 ≈ 2800	[6]
3.		0.20 ^b 0.29 ^b		[4]
4.		0.122 ^c	≈ 8900	[7]
5.		0.06 ^d		[8]

^aInherent viscosity, 0.5 g/dL in DMF.

^bIntrinsic viscosity, in methylene chloride at 24°C

^cReduced viscosity, 0.5 dL/g in DMF.

^dIntrinsic viscosity, in chloroform at 25°C.

TABLE 2. The Properties of Polymers P1-4

Polymer	Color	Yield, %	Softening range, °C	Reduced viscosity, ^a dL/g	H _f ^c , kCal/mol
P1	brown-dark	82	>300	0.20 ^b	4.55
P2	brown-ochre	86	>300	0.10	12.96
P3	ochre	92	>300	0.14 ^b	9.35
P4	ochre	95	>300	0.16 ^b	11.50

^aMeasured in NMP at a concentration of 0.2 g/dL at 25°C.

^bPartially soluble in NMP.

^cRelative total enthalpy of formation.

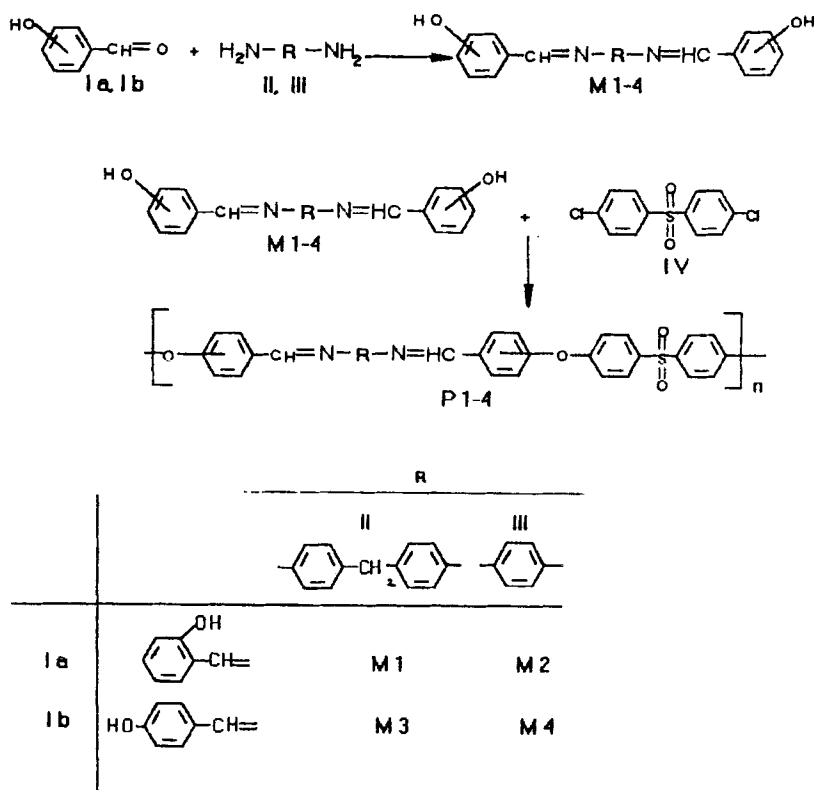
Found: C, 74.98; H, 5.03; N, 8.74%. IR (cm⁻¹) 1630 (CH=N), 1600, 1458 (aromatic). ¹H-NMR (DMSO-d₆, TMS): 8.5 (s, 2H, CH=N), 8.05-7.35(m, 12H, aromatic).

Polymers (P1-4) Synthesis

All the polymers were obtained, isolated and purified as described [10]. The properties of the polymers are listed in Table 2.

RESULTS AND DISCUSSION

Table 1 lists information checked by us regarding poly(azomethine sulfones) reported in the literature [1, 4, 6-8]. As can be seen, only two structures are obtained by polyetherification: Structures (3) and (5). The molecular weight or viscosity values for these structures are either unreported, or small. In our previous paper [10] we used both polyetherification and polycondensation methods and we obtained higher values of (η_{red} ; 0.26 and 0.34 dL/g, respectively). As we have only different links, i.e. -O- semirigid, or -CH₂- flexible links in the above discussed structures, we achieved the present investigation with the aim to see if the introduction of rigid aromatic moieties (p)-C₆H₄- and deviations from the linearity induced by ortho- aromatic links (o)-C₆H₄- will influence in a different manner the package of chains with the corresponding consequences on the properties. All the polymers were obtained with high yields (Table 2), using the classical polyetherification reaction [10] between azomethine AM bisphenols M 1-4 and



SCHEME 1

4,4'-sulfonyl bis chlorobenzene IV (Scheme 1). The polymers are brown to ochre fine powders. Their structures were confirmed by IR spectra, elemental analysis data and $^1\text{H-NMR}$ spectra for polymer P2. The $^1\text{H-NMR}$ spectrum of polymer P2 in DMSO-d_6 at 60°C (Figure 1) showed a large multiplet for CH=N protons at 8.6–9.0 ppm. The founded integral's ratios agree with the calculated one. Generally, because all the obtained polymers possessed reduced degree of polymerization, the difference occurred for the chemical shift in the 8.6–9.0 ppm region, probably could be due to some different resonance of the CH=N protons from the end of chains and those from the structural unit. From the IR spectra of polymers, using the KBr pellet technique (Figure 2), can be seen the appearance of the characteristic absorption bands at $1630\text{--}1640\text{ cm}^{-1}$ ($-\text{CH=N}-$), $1330, 1160\text{ cm}^{-1}$ ($-\text{SO}_2-$), and 1250 cm^{-1} (C-O-C). Carefully observing the C-O-C absorption bands at 1250 cm^{-1} , one can see a significant difference in transmittance values: the P1,2 values (ortho-), are

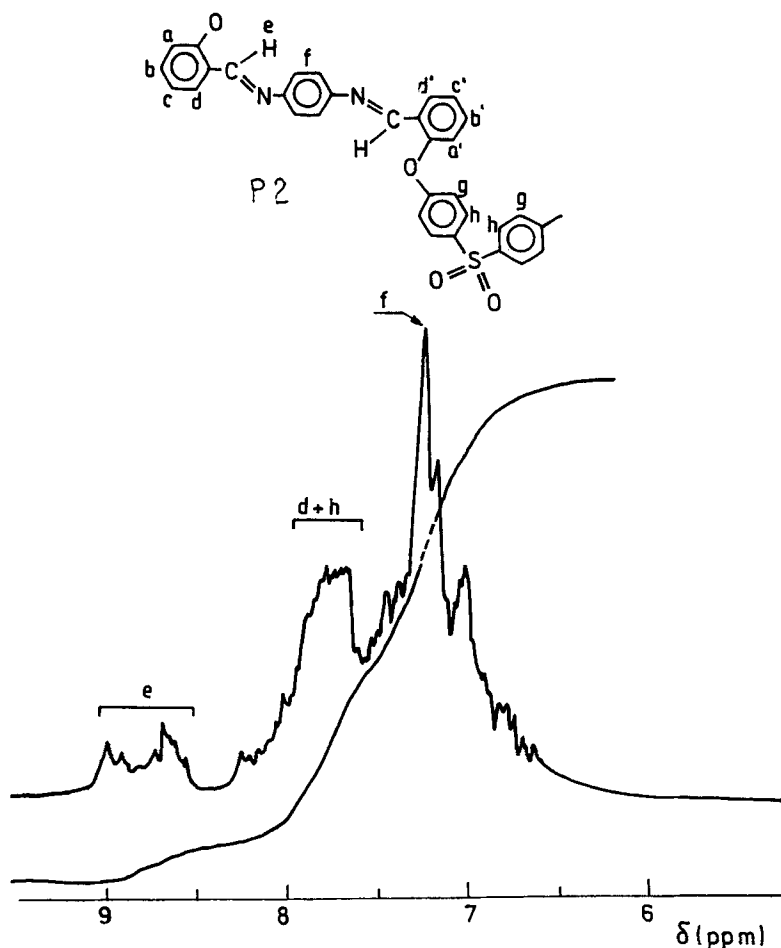


Figure 1. The $^1\text{H-NMR}$ spectra of polymer P2.

smaller than P3,4 (para-). To be more precise, we take a base line through 1800 and 900 cm^{-1} points, free of any absorptions. The SO_2 symmetric absorption band at 1160 cm^{-1} was used as a reference band. Using a calculation method [13], we obtained the values listed in Table 3. As can be seen, while $\text{CH}=\text{N}$ ratios showed very small differences, the para- C-O-C ratios (P3,4) are higher than ortho- (P1,2) ones. This unusual behavior could be due to a different kind of package of chains similar to the IR behavior of amorphous and crystalline polymers [13]. It was reported that poly-Schiff bases undergo degradation in the presence of strong protonic acids due to hydrolysis of $\text{CH}=\text{N}$ - linkages [1, 14, 15]. However, after

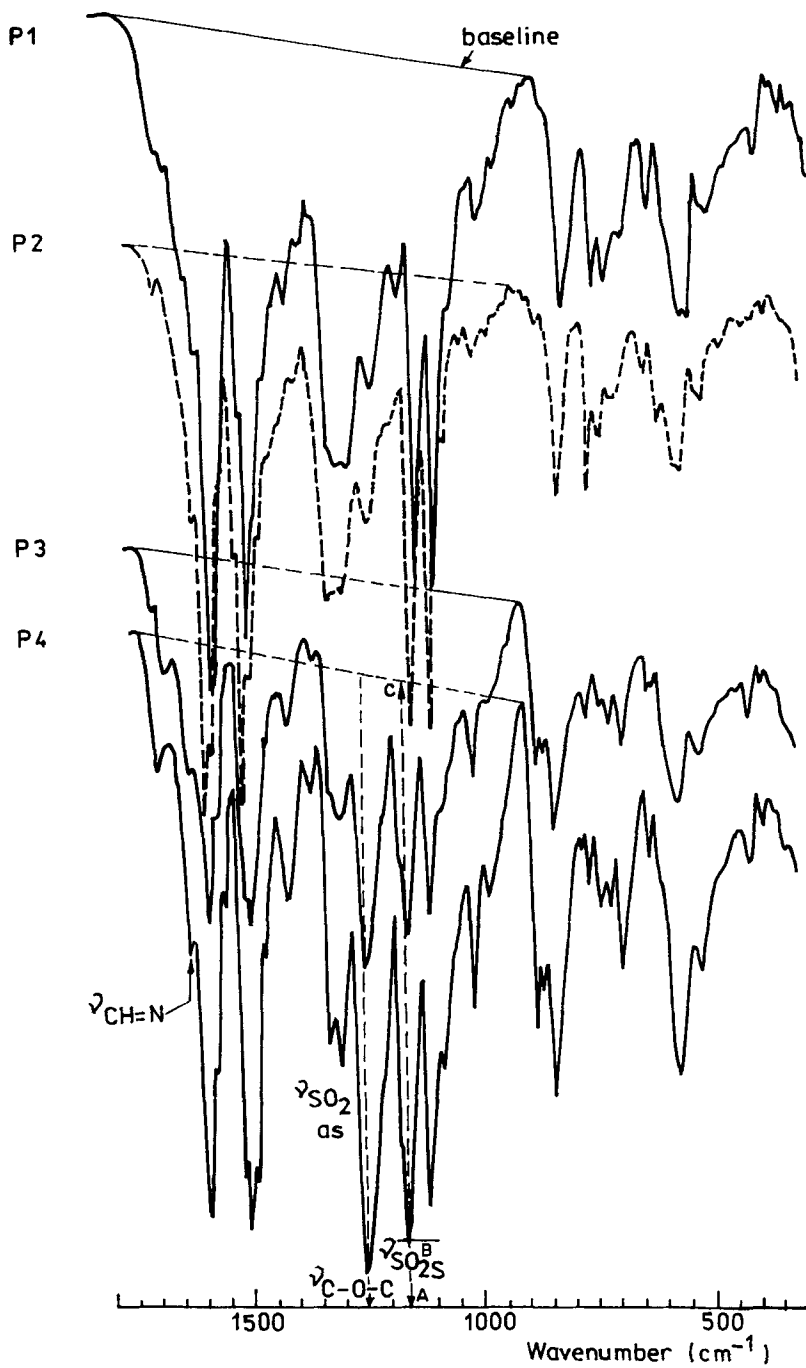


Figure 2. The IR spectra of polymers P1-4.

TABLE 3. IR Absorption Ratios for Polymers P1-4^a

Polymer	Reference SO ₂ sim 1160 cm ⁻¹	A _{CH=N} 1635-1640 cm ⁻¹	A _{C-O-C 1250} cm ⁻¹	A _{CH=N/A_{ref}}	A _{C-O-C/A_{ref}}
P 1	0.43	0.21	0.22	0.49	0.51
P 2	0.35	0.16	0.16	0.46	0.46
P 3	0.23	0.12	0.27	0.52	1.17
P 4	0.52	0.19	0.57	0.36	1.10

^aCalculated with the formula $A = \log (AC/AB)$ [13]

refluxing 36 hours of 0.1g polymer in 10% wt aqueous sulfuric acid, no change was observed for all polymers P1-4 in the N% content, or in IR spectra. This fact could be concluded as a reasonable hydrolytic stability, in the tested conditions.

A computer modeling of the structural unit of the polymers (Figure 3) revealed that ortho- structures (P1, P2) were more coiled than para- ones (P3, P4). As can be seen the imine linkage (CH=N) is not coplanar with one of the neighboring phenylene ring, as already reported [16]. The relative total enthalpy of formation values (Table 2) ranged between 4.55 and 12.96 kCal/mol. The elemental analysis of polymers P1-4 (Table 4) showed good agreement between the calculated and found values. The higher value of S/N ratio for P4 could be due to an incomplete removal of DMSO in the purification step. On the basis of chlorine end group analysis data [9] we calculated the corresponding molecular weights and, even those values are not real, they showed a significant difference between the ortho-polymers (P1,2) and para- ones (P3,4); P3,4 being at least twice higher than P1,2. Also, higher yields (92, 95%) were obtained for P3,4 than lower values (82, 86%) for P1,2. This situation could be explained by a higher reactivity of para-bisphenols M3,4 in comparison with the ortho- ones M1,2, which are sterically hindered during the nucleophilic attack.

The reduced viscosities values ranged between 0.10 and 0.20 dL/g; the soluble part of the polymer being measured for the polymers P1, P3 and P4.

The polymers did not soften below 300°C and attempts to found a glass transition by DSC (Figure 4) failed, proving that all polymers are rigid enough, having T_g higher than the decomposition temperature.

The solubilities (Table 5) showed that P1,2 are more soluble than P3,4, as expected. The solubility parameters of polymers are probably at least higher than 10.67.

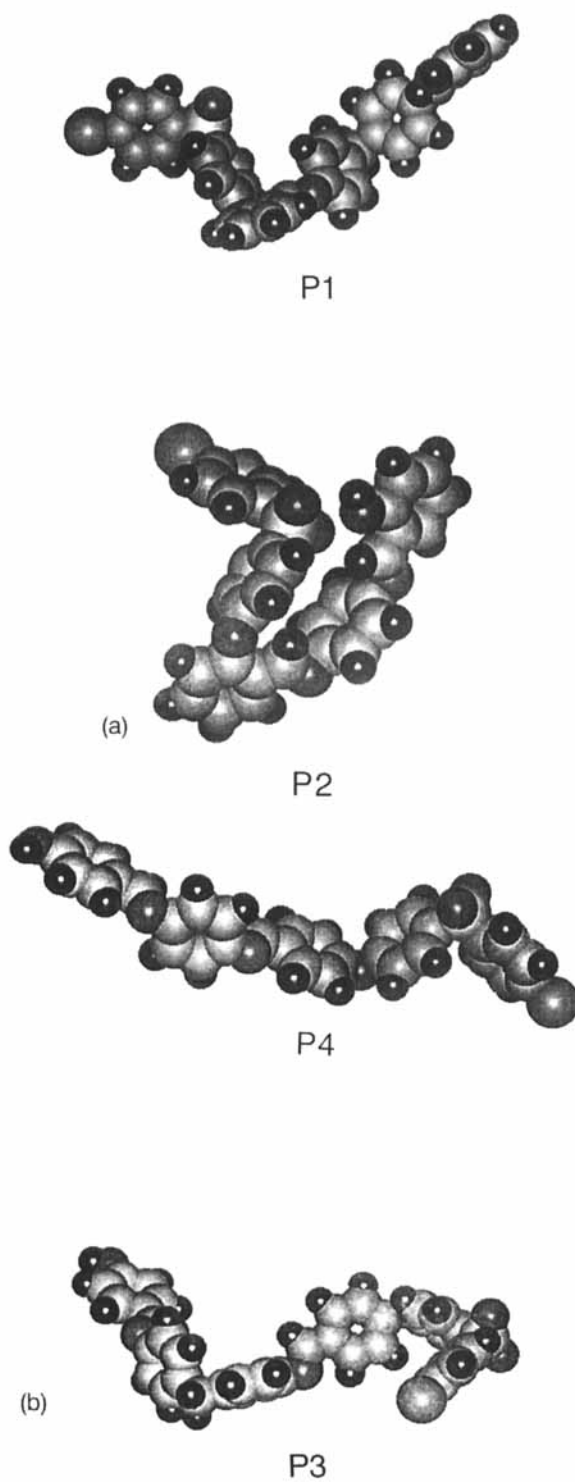


Figure 3. The difference between the package of structural units of polymers: (a) P1,2 (ortho-); (b) P3,4 (para-).

TABLE 4. Elemental Analysis of Polymers P1-4^a

Polymer	MW ^b	S/N		Cl, %	
		Calcd	Found	Calcd	Found
P 1	~2500	1.14	1.33	1.41	1.49
P 2	~2200	1.14	1.26	1.64	1.86
P 3	~5000	1.14	1.34	0.71	0.76
P 4	~4800	1.14	1.85	0.74	0.75

^aThe calculated values were obtained taking into account the chlorine end groups [9].

^bQualitative molecular weight values calculated from the chlorine end group content.

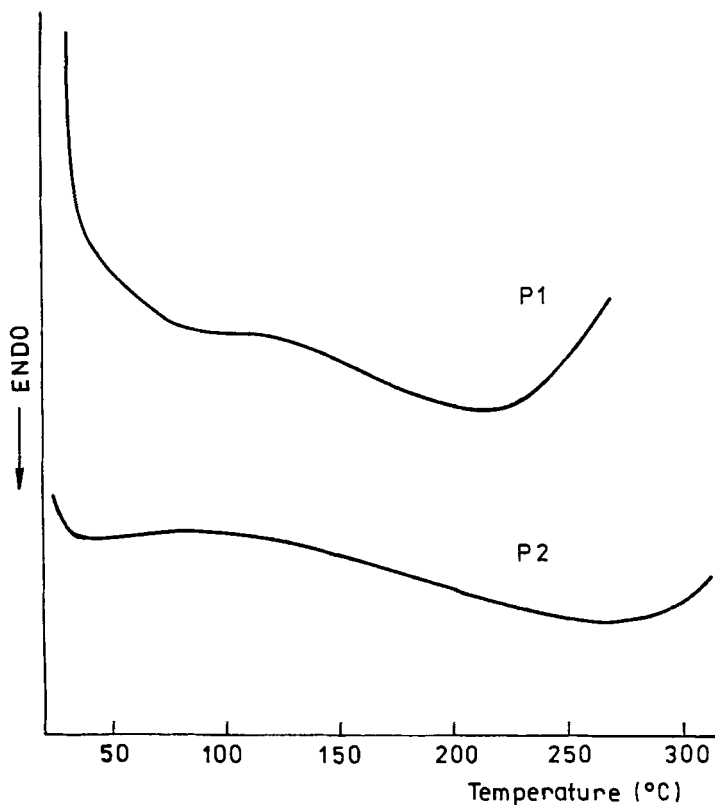


Figure 4. The DSC curves of polymers P1 and P2, second heating cycle at a heating rate of 20 °C/min (P1) and 10°C/min (P2) in nitrogen.

TABLE 5. The Solubility of Polymers P1-4

Solvent series ^a					
Polymer	DMSO 13.04	DMF 12.15	NMP 11.17	Nitrobenzene 10.67	Chloroform 9.21
P 1	PS	PS	PS	I	I
P 2	S	S	S	PS	I
P 3	I	I	I	I	I
P 4	PS	PS	PS	PS	PS

^aArranged in the decreasing order of their (solubility parameter) values, after Hansen [17].

S = soluble, I = insoluble, PS = partially soluble.

TABLE 6. The Thermal Behavior of Polymers P1-4

TGA Temperature (°C) for Various % Decompositions							
Polymer code	Ti ^a	5	10	20	30	40	50
P 1	295	380	410	460	503	543	580
P 2	322	365	408	455	498	533	568
P 3	315	410	448	500	545	580	>60 0
P 4	325	412	450	505	550	-	-

^aTi = Initial decomposition temperature

In the UV spectra of the polymers P1, P2, and P4 in DMSO was observed a large bathochromic shift of the π - π^* absorption band due to C=N bands from the absorption maximum (342 nm) of P1 to a longer wavelength (358 nm) for P2, due to an increase in the conjugation. We observed the same shift for P4, but in this case beyond a hypsochromic effect, a new absorption band occurred at 285 nm, like a hypsochromic shift. However, literature UV data for PAM [12] reported hypsochromic shifts only when metha- chains quantitatively exceed the para- ones. At the moment, we have no explanation for this phenomenon. Further investigations are underway, and the results will be reported. The thermal behavior of polymers (Table 6, Figure 5) showed similar decomposition patterns. As expected, the decomposition began around 300°C and the polymers P3,4 with para- chains proved to be more thermally stable than P1,2 with ortho- chains.

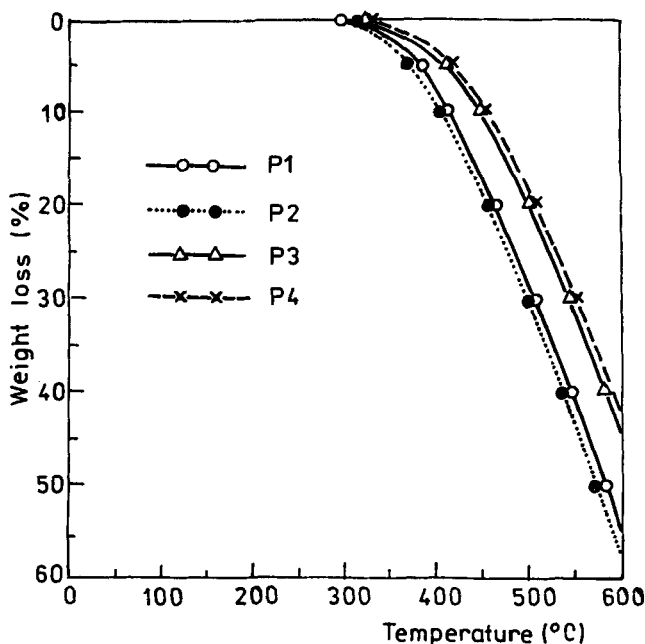


Figure 5. TGA curves of polymers P1-4.

CONCLUSIONS

New linear PAMS were obtained using the classical polyetherification reaction between AM bisphenols (M1-4) and 4,4'-sulfonyl bis(4-chlorophenyl). The polymers having η_{red} values at least equal with those reported in the literature, are thermally stable up to 300°C and dissolved only in aprotic dipolar solvents. A significant difference was observed in the solubility and thermal behavior of the ortho-linked polymers (P1,2) with respect to para-linked ones (P3,4). The polymers seem to be reasonable hydrolytically stable in 10% wt aqueous sulfuric acid while refluxing for 36 hours.

REFERENCES

- [1] G. F. D'Alelio, J. V. Crivello, R. K. Schoenig, and T. F. Huemmer, *J. Macromol. Sci.-Chem.*, *A1(7)*, 1161-1249 (1967).
- [2] F. W. Harris and K. Sridhar, *Am. Chem. Soc., Div. Polym. Chem, Polym. Prepr.*, *29(2)*, 304-305 (1988).

- [3] T. D. Shaffer and M. L. Shaffer, *Ibid.*, 29(2), 352-353 (1988).
- [4] C. D. Smith, R. L. Holzberlein, and J. E. McGrath, "Synthesis and Characterization of Random and Segmented Poly(Azomethine Sulfones)," in *Polymeric Materials: Science and Engineering*, Proceedings of the American Chemical Society Division of Polymeric Materials, Vol. 60, Dallas, Texas, p. 316.
- [5] G. Rabilloud and B. Sillion, *Eur. Polym. J.*, 26(9), 967-976 (1990).
- [6] J. A. Mikroyannidis, *J. Polym. Sci., Polym. Chem. Ed.*, 27, 3465-3479 (1989).
- [7] El-Sayed M. E. Mansour, A. A. Kassem, H. N. El-Din, and A. A. El-Toukhy, *Macromolecular Reports, A28* (Suppl.2), 103-109 (1991).
- [8] C. Yeakel, K. Gower, R. S. Mani, *Makromol. Chem.*, 194(10), 2779-2787 (1993).
- [9] V. Cozan, E. Butuc, A. Stoleriu, A. Cascaval, Y. Ni, and M. Ding, *J. Macromol. Sci.-Pure Appl. Chem.*, A32(5), 1067-1080 (1995).
- [10] V. Cozan, E. Butuc, A. Stoleriu, M. Rusa, M. Rusu, Y. Ni, and M. Ding, *J. Macromol. Sci.-Pure Appl. Chem.*, A32(7), 1243-1262 (1995).
- [11] N. L. Allinger, *QCPE Bull.*, 7, 141 (1987).
- [12] K. Tamareselvy, K. Venkatarao, H. Kothandaraman, *Makromol. Chem.*, 191(6), 1231-1242 (1990).
- [13] Jan F. Rabek, "Experimental Methods in Polymer Chemistry", John Wiley and Sons, 1980, p. 241.
- [14] M. S. Patel and S. R. Patel, *J. Polym. Sci., Polym. Chem. Ed.*, 20(8), 1985-1992 (1982).
- [15] S. Banerjee and C. Saxena, *J. Polym. Sci., Polym. Chem. Ed.*, 34 (17), 3565-3572 (1996).
- [16] C. J. Young and S. A. Jenekhe, *Macromolecules*, 28, 1180-1196 (1995).
- [17] C. M. Hansen, *Ind. Eng. Chem., Prod. Res. Dev.*, 8, 2 (1969).

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