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POLY(AZOMETHINE SULFONES) WITH THERMOTROPIC LIQUID CRYSTALLINE BEHAVIOR

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ABSTRACT

New poly(azomethine sulfones) with linear structures containing sulfonyl bis(4-phenoxyphenylene) and oxo bis(benzylideneaniline) or methylene bis(benzylideneaniline) units were prepared in the conventional literature manner by condensing the dialdehyde sulfone monomer (V) with diamines such as 4,4′-oxydianiline (IIIa) and 4,4′-methylenedianiline (IIIb), or by condensing an azomethine biphenol (IX) with 4,4′-sulfonyldichlorobenzene (II). Three model compounds which reproduced the above structures were also synthesized. The resulting polymers were confirmed by IR, ^{1}H-NMR, and elemental analysis, and were characterized by inherent viscosities, thermogravimetric analysis (TGA), and x-ray diffraction. The thermotropic liquid crystalline (TLC) behavior was studied using polarization light microscopy (PLM), thermooptical analysis (TOA), and DSC. A nematic texture was observed only for 4,4′-oxydianiline-units-based polymers. The reaction of polymer VIIIb containing $-CH_2-$ links between the mesogens with the model compound IX led to polymer X which exhibited TLC behavior.

INTRODUCTION

Main-chain liquid-crystalline polymers (LCP) are of interest for the possible mechanical strength that may be imparted to the material.

Polyazomethines (PAM) are an important class of thermotropic polymers that have potential as high performance fibers [1]. PAM are also interesting because of their structural similarity to their carbon analogs, the stilbenes. As such, they present a convenient way of installing extended conjugation into the mesogenic structure [2]. Various polymers containing azomethine (AM) linkages in the polymer backbone, such as polyethers [1, 2], polycarbonates [3], polyamides [4-6], polyesters [7], polyurethanes [8, 9], etc., are described in the literature.

LC aromatic copolyether sulfones were obtained as copolyesters [10], segmented copolymers [11, 12], or block copolymers [13-15].

There are a few studies concerning poly(azomethine sulfones) (PAMS) [16, 17]. Smith et al. showed that the use of polysulfone (PSF) segments along the PAM backbone would result in an isotropic-anisotropic system with property contributions from each segment. Also, the use of azomethine units along the PSF backbone should result in a product which shows improved solvent resistance [16].

The purpose of this paper is to present the synthesis and characterization of some new linear PAMS containing sulfonyl bis(4-phenoxyphenylene) and oxo bis(benzylideneaniline) or methylene bis(4-benzylideneaniline) units in the backbone, and a study of their TLC behavior.

EXPERIMENTAL

Materials

4,4′-Sulfonyldichlorobenzene (Aldrich) was recrystallized from toluene (mp 146–149°C). 4-Hydroxybenzaldehyde, 4,4′-oxydianiline, and 4,4′-methylenedianiline (all from Aldrich) were used as received. NMP was vacuum distilled over phosphorus pentoxide. 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. ^{1}H-NMR spectra were run on a Jeol 60 MHz NMR spectrometer at 45°C in $CDCl_3$ or DMSO-d_6 using TMS as the internal reference. The inherent viscosities of copolymer 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 by a Gallenkamp hot-block melting point apparatus. Differential scanning calorimetry (DSC) measurements were done

TABLE 1. Characterization of the Model Compounds (VIa, VIb, IX) and Polymers (VII-XI)

Sample code	Color	Yield, %	η_{inh},[a] dL/g	LC[b] phase °C	Birefringence[c]	Transition temperatures, °C, DSC and (TOA)			
						T_g		T_m	T_i
VIa	White	66	–	138-230	s	108 (110)		148 (140)	240 (220)
VIb	Yellow	55	–	128-200	w	106 (–)		146 (130)	186 (–)
IX	Yellow	71	–	244-245[d]					
VIIa	White	38	0.03	180-220	vs	85 (–)	164 (160)	198 (185)	228 (220)
VIIIa1	Yellow	38	0.069	150-[f]	vs	112 (–)		150 (138)	– (–)
VIIIa2	Yellow	75	0.109	140-220	vs	128 (–)		145 (135)	200 (–)
VIIb	Yellow	80	0.069	140-195[e]	–	– (–)		153 (158)	– (–)
VIIIb	Yellow	67	0.109	145-200[e]	–	114 (–)		131 (130)	– (–)
X	Yellow	70	0.263	125-160	s	97 (108)		143 (138)	160 (168)
XI	Yellow	87	0.338	140-200	s	– (–)		147 (140)	– (–)

[a] Measured at a concentration of 0.2 g/dL in NMP at 25 ± 0.1 °C.

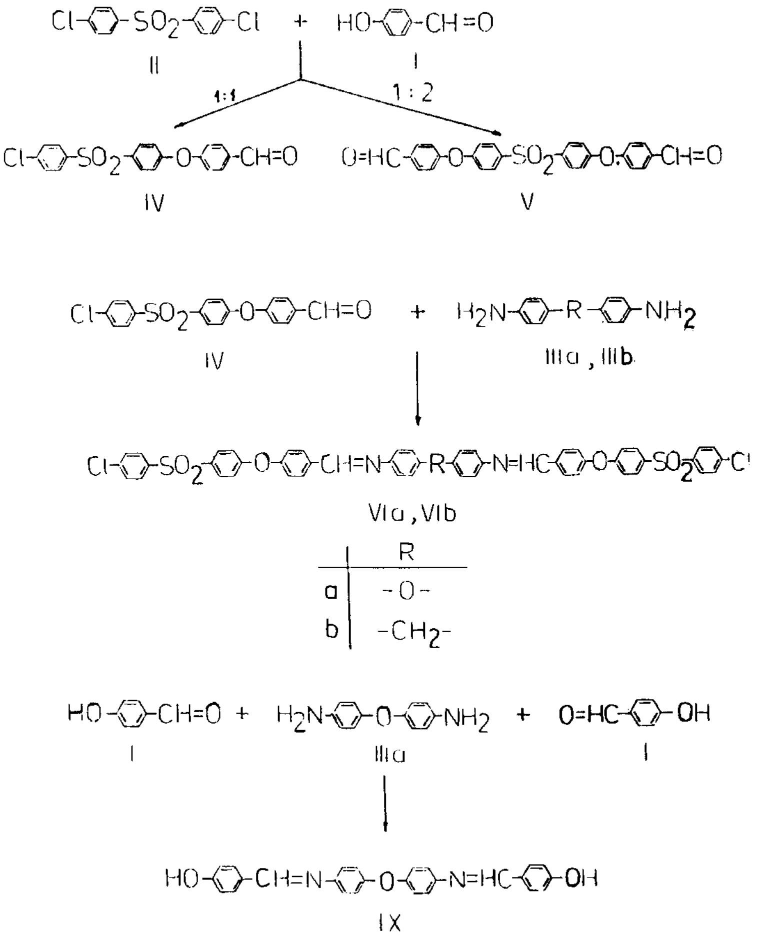
[b] As observed under the polarizing microscope.

[c] Birefringence's intensity as observed under the PLM: vs = very strong; s = strong; w = weak; – = none.

[d] Melting point.

[e] Softening range.

[f] No isotropization temperature was observed.



SCHEME 1.

by using a Mettler TA instrument DSC 12E with a heating rate of 10°C/min in air. TOA was carried out in air with a homemade thermooptical analyzer with a heating rate of 7°C/min as described in the literature [18]. The observation of optical texture was undertaken with a IOR MC1-type polarizing microscope equipped with a heating stage (magnification 150×). TGA was carried out in air with an F. Paulik Derivatograph at a heating rate of 12°C/min. X-ray diffraction patterns were recorded on a Rigaku IIB x-ray diffractometer.

Monomer Synthesis

4-(4-Chlorophenylenesulfonylphenoxy)benzaldehyde (IV)

The synthesis of this monomer is described elsewhere [19]. The monomer was reprecipitated with water:methanol (1:1) from 1,4-dioxane, filtered, then stirred 18 hours with methanol and dried under vacuum for 48 hours. Softening range 55–

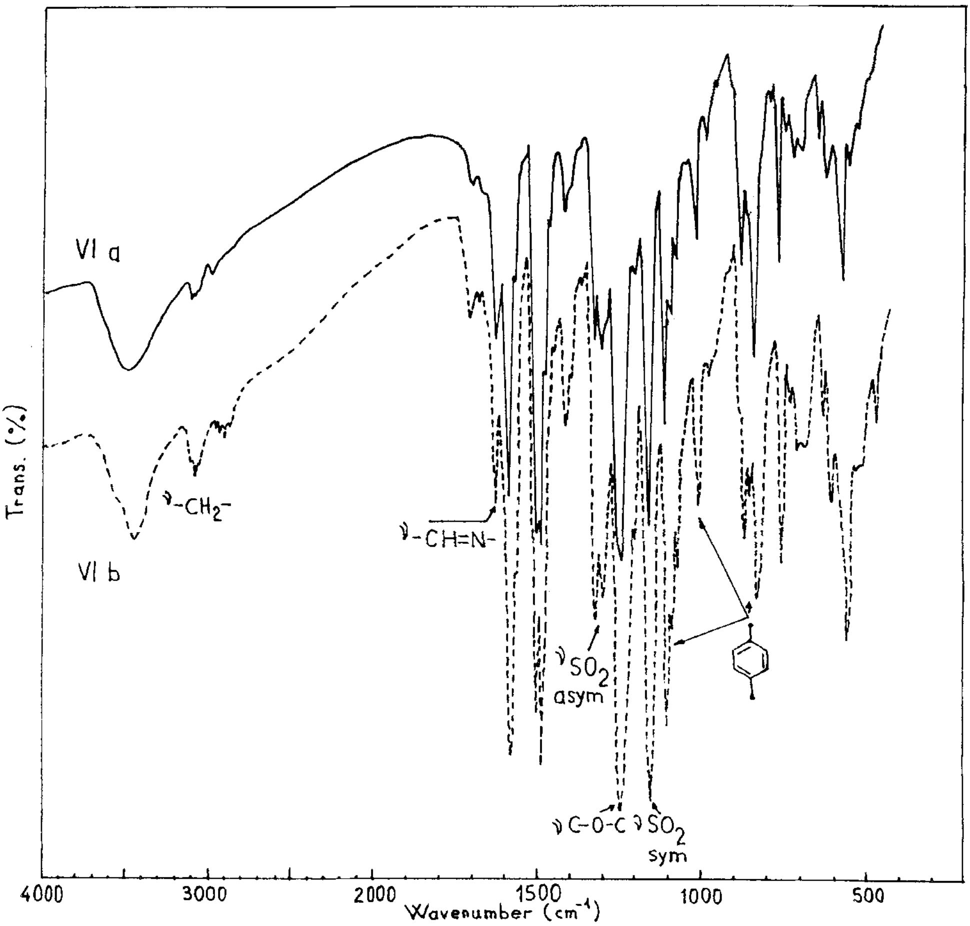


FIG. 1. The IR spectra of model compounds VIa and VIb.

60°C, IR (cm^{-1}) 1705 ($-CH{=}O$), 1325 ($-SO_2-$ asymmetrical vibrations), 1250 ($C-O-C$ aromatic ether), 1160 ($-SO_2-$ symmetrical vibrations), 1015, 840 (aromatic ring). ^{1}H-RMN ($CDCl_3$, TMS): 6.94-7.12 (m, 4H, ortho to $-O-$), 7.30-7.44 (m, 2H, ortho to $-Cl$), 7.74-7.93 (m, 4H, ortho to $-SO_2-$, 2H, ortho to $-CH{=}O$), 10.12 (s, 1H, $-CH{=}O$).

Sulfonyl bis(4-formylphenoxyphenyl) (V)

The synthesis of this monomer is described elsewhere [19]. The same purification procedure described above was also used for this monomer. Softening range 111-115°C, IR (cm^{-1}) 1700 ($-CH{=}O$), 1330 ($-SO_2-$ asymmetrical vibrations), 1250 ($C-O-C$ aromatic ether), 1165 ($-SO_2-$ symmetrical vibrations), 1025, 840 (aromatic ring). ^{1}H-RMN (DMSO-d_6, TMS): 6.87-7.31 (m, 8H, ortho to $-O-$),

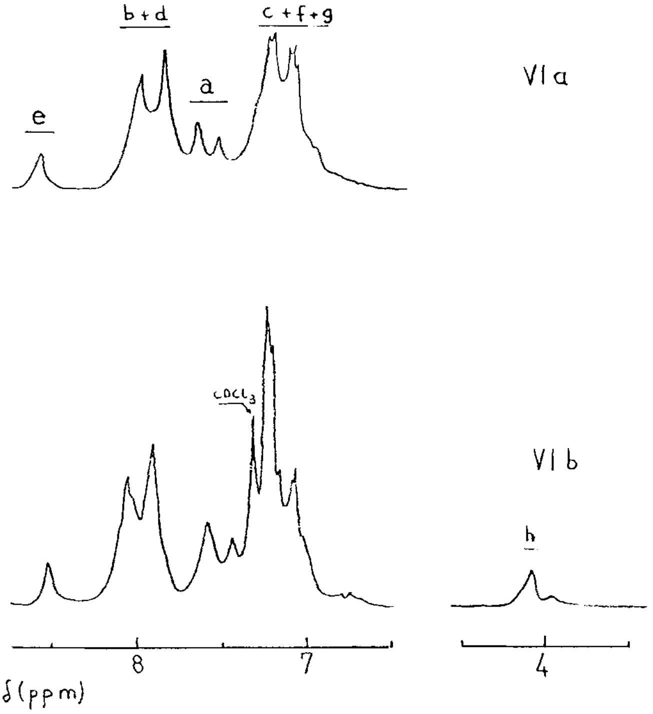
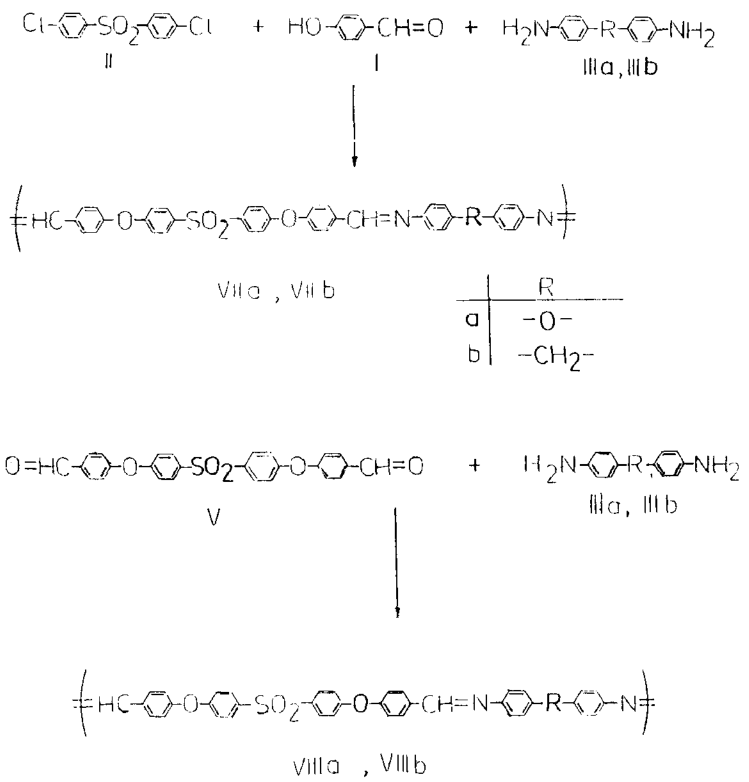


FIG. 2. The ^{1}H-NMR spectra of model compounds VIa and VIb.

TABLE 2. ^{1}H-NMR Chemical Shifts of the Model Compounds VIa and VIb and in Polymers VIIa, VIIb, VIIIa2, and VIIIb. Assignments of the Protons Are Presented in Scheme 4

Sample code	Protons type					
	a	b + d	c + f + g	e	h	i
VIa	7.67-7.54	8.00-7.85	7.23-7.13	8.58	–	–
VIb	7.59-7.46	8.06-7.91	7.25-7.08	8.52	4.10	–
VIIa	7.75-7.60	8.08-7.92	7.30-7.02	8.67	–	6.77-6.64
VIIb	7.60-7.40	8.04-7.91	7.21-7.03	8.52	4.08	6.73-6.60
VIIIa2	7.81-7.65	8.12-7.97	7.32-7.06	8.69	–	6.77-6.68
VIIIb	7.65-7.40	8.00-7.75	7.20-7.08	8.50	4.00	6.77-6.60



SCHEME 2.

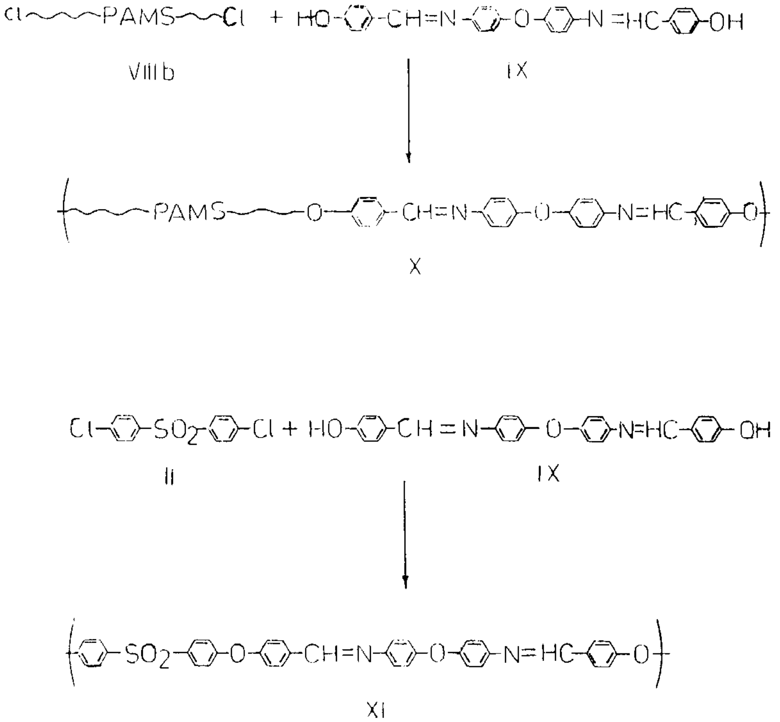
7.62–7.73 [m, 2H, ortho to Cl, monomer (IV) traces], 7.88–8.05 (m, 4H, ortho to $-SO_2-$, 4H, ortho to $-CH=O$), 10.17 (s, 2H, $-CH=O$).

Oxo bis(4-chlorophenylsulfonylphenoxybenzylideneaniline) (VIa); Methylene bis(4-chlorophenylsulfonylphenoxybenzylideneaniline) (VIb); Oxo bis(4-hydroxybenzylideneaniline) (IX)

The same synthesis system described previously [19] was charged with 4 g (10.73 mmol) IV, 1 g (4.994 mmol) IIIa [or 1 g (5.044 mmol) IIIb], 10 mL NMP, and 30 mL chlorobenzene. The solution was stirred 1 hour at RT, then 4 hours at 130–135°C, and 6 hours at 150–155°C to complete the reaction. The reaction mixture was cooled at RT, precipitated with a mixture of water-methanol (1:1), filtered, washed with water, and then refluxed in methanol for 6 hours. The products were dried at 60°C in a vacuum oven for about 18 hours. The model compound (IX) was synthesized using I and IIIa as reagents, as described in the literature [20]. The properties of model compounds are listed in Table 1.

In-Situ Synthesis of Polymers (VIIa, VIIb)

A 250-mL four-necked flask fitted with a condenser, a thermometer, a dry nitrogen inlet, a mechanical stirrer, a Dean-Stark trap, and a Claisen adaptor was charged with a mixture of 5 g (0.04094 mol) I, 5.8 g (0.0202 mol) II, 7 g anhydrous



SCHEME 3.

potassium carbonate, 50 mL DMSO, and 100 mL chlorobenzene. The entire system was continuously purged with dry nitrogen. The mixture was heated at 130–137°C for 6 hours. During this time the PhCl–water azeotrope was collected in the Dean-Stark trap. Then 4 g (0.01998 mol) IIIa [or 3.96 g (0.01998 mol) IIIb] was added and the reaction was continued for 6 hours at 150–155°C. The reaction mixture was allowed to cool at RT and then coagulated in water-methanol (1:1). The polymer was filtered, washed with water, heated in methanol under reflux for 6 hours, and dried at 60°C for 48 hours in a vacuum oven.

The properties of the polymers are listed in Table 1.

Two-Step Synthesis of Polymers (VIIIa, VIIIb)

The same synthesis system used to obtain the model compounds was charged with 6 g (0.01309 mol) V, 2.6 g (0.01298 mol) IIIa [or 2.57 g (0.01298 mol) IIIb], 30 mL DMSO, and 50 mL PhCl. The reaction mixture was heated at 130–135°C for 4 hours, at 150–155°C for 10 hours, cooled at RT, precipitated with a mixture of water–methanol (1:1), filtered, and washed with water and then with methanol at RT. The polymer was then refluxed in methanol for 2 hours. After filtration the product was dried at 60°C in a vacuum oven about 24 hours.

The properties of polymers VIIIa and VIIIb are listed in Table 1.

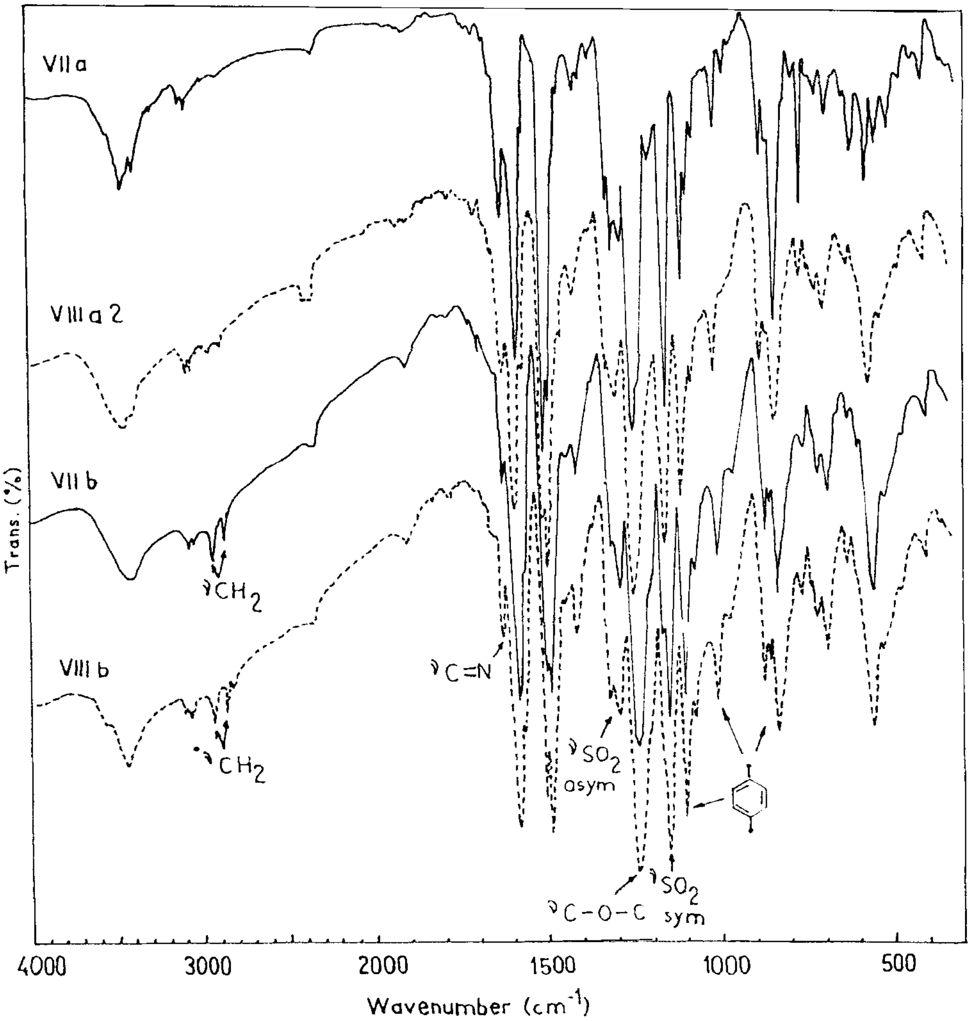


FIG. 3. The IR spectra of polymers VIIa, VIIIa2, VIIb, and VIIIb.

Polymer (X, XI) Synthesis

Polymers X and XI were prepared by the classical polycondensation reaction [21].

Their characteristics are listed in Table 1.

RESULTS AND DISCUSSION

Model Compounds Synthesis

In order to facilitate the assignments of the IR and ^{1}H-NMR spectra, three model compounds (VIa, VIb, IX) were synthesized (Scheme 1). The IR spectra of model compounds (Fig. 1) showed the complete disappearance of the aldehyde

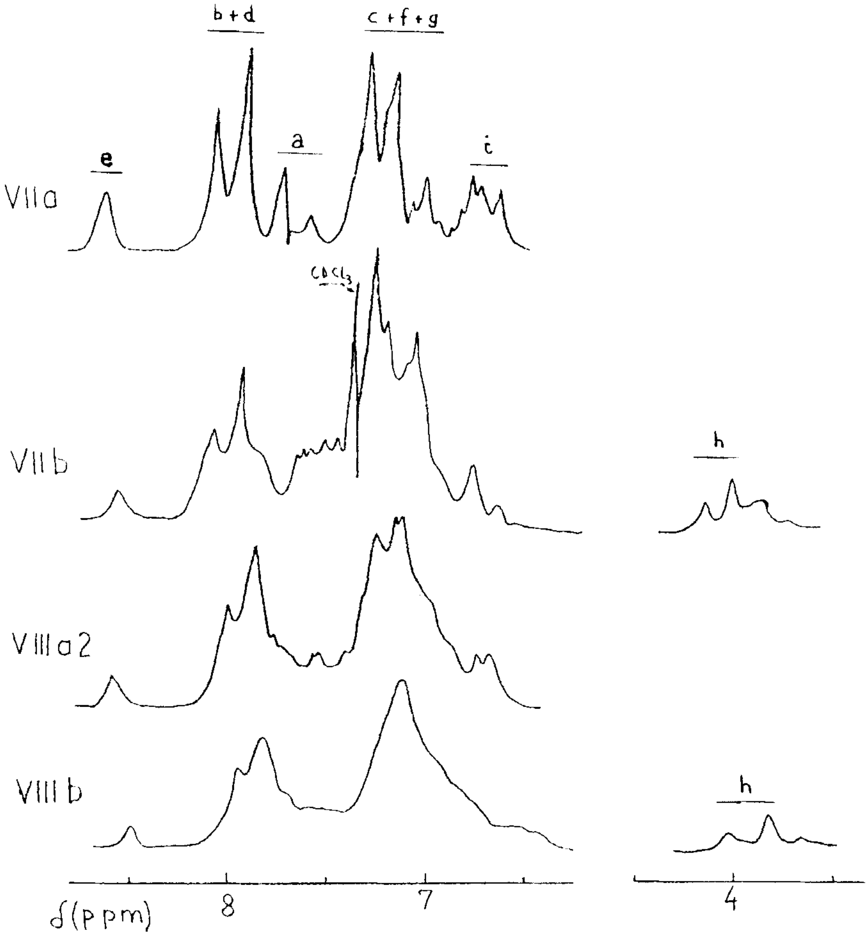


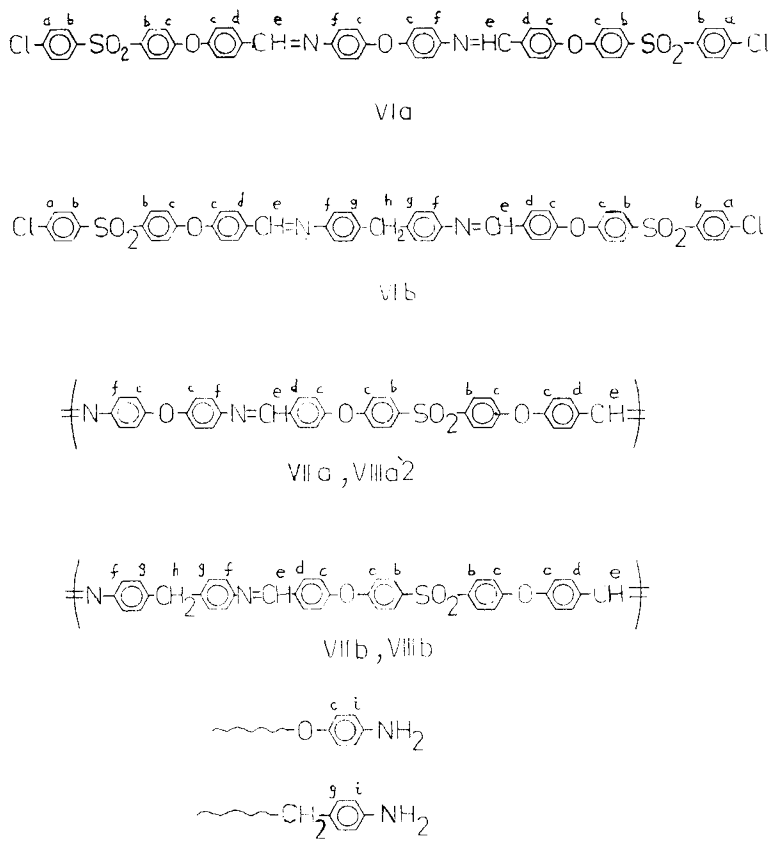
FIG. 4. The ^{1}H-NMR spectra of polymers VIIa, VIIb, VIIIa2, and VIIIb.

absorption band at 1680 cm^{-1} and the appearance of the characteristic absorption band of the azomethine group (1625 cm^{-1}). Other representative bands for these structures are indicated in Fig. 1. The ^{1}H-NMR spectra of model compounds VIa and VIb are presented in Fig. 2. The corresponding assignments of the peaks are listed in Scheme 4 and Table 2.

Polymer Synthesis

Three reaction paths were chosen to obtain the desired structures.

1. In-situ reactions of I, II, and IIIa (or IIIb) monomers according to the literature cited procedures [20, 21] resulted in polymers VII.
2. Two-step reactions:
   a. Synthesis and separation of dialdehyde sulfone monomer (V)
   b. The reaction of monomer V with IIIa (or IIIb) resulted in polymers VIII (Scheme 2).



SCHEME 4.

3. The classical polycondensation reaction between monomer II and the model compound azomethine (IX) led to polymer XI (Scheme 3).

Representative IR and ^{1}H-NMR spectra of polymers are presented in Figs. 3 and 4. The assignment of protons is listed in Scheme 4 and Table 2. ^{1}H-NMR spectra showed that some polymers are in fact oligomers and contain amino and chlorine end groups. The chlorine end groups are due to the traces of monoaldehyde (IV) contained in the dialdehyde (V) as discussed before [19]. The elemental analysis of model compounds VIa, VIb, and IX and of polymers VII–VIII (Table 3) showed good agreement between the calculated and found values. The inherent viscosity values listed in Table 1 ranged between 0.03 and 0.338 dL/g and confirmed that the polymers obtained are most likely oligomers.

The small yield (38%) for polymer VIIIa1 led us to synthesize a new polymer with the same structure (VIIIa2); a much higher yield (75%) was obtained.

Thermotropic Liquid Crystalline Properties of Polymers

As is well known, PSFs are in the class of engineering thermoplastics, generally amorphous, and have an isotropic behavior in polarized light when in the melt [16], so there are some difficulties in obtaining TLC properties for the PSF struc-

TABLE 3. Elemental Analysis of Model Compounds VIa, VIb, and IX and Polymers VII and VIII[a]

Sample code	C, %		H, %		S/N		Cl, %	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
VIa	66.0	66.6	3.77	4.30	2.29	2.29	7.79	7.20
VIb	67.47	67.10	4.0	4.73	2.29	2.42	7.81	7.25
IX	76.45	75.95	4.93	5.31	6.86	6.96[b]		
VIIa	70.37	69.82	4.19	3.80	1.14	1.10	3.01	3.56
VIIIa1	70.37	69.83	4.19	4.57	1.14	1.15	3.01	3.16
VIIIa2	71.87	71.29	4.20	4.59	1.14	1.85	1.46	1.63
VIIb	73.62	73.05	4.55	4.44	1.14	1.55	1.97	1.06
VIIIb	72.65	72.07	4.55	4.64	1.14	1.76	3.02	2.70
X	70.40	70.44	4.42	4.56	1.14	1.38	1.54	1.17
XI	70.40	69.87	4.42	4.48	1.14	1.65	1.54	1.24

[a] The calculated values were obtained taking into account the chlorine and amine end groups [19].

[b] Nitrogen (%) content.

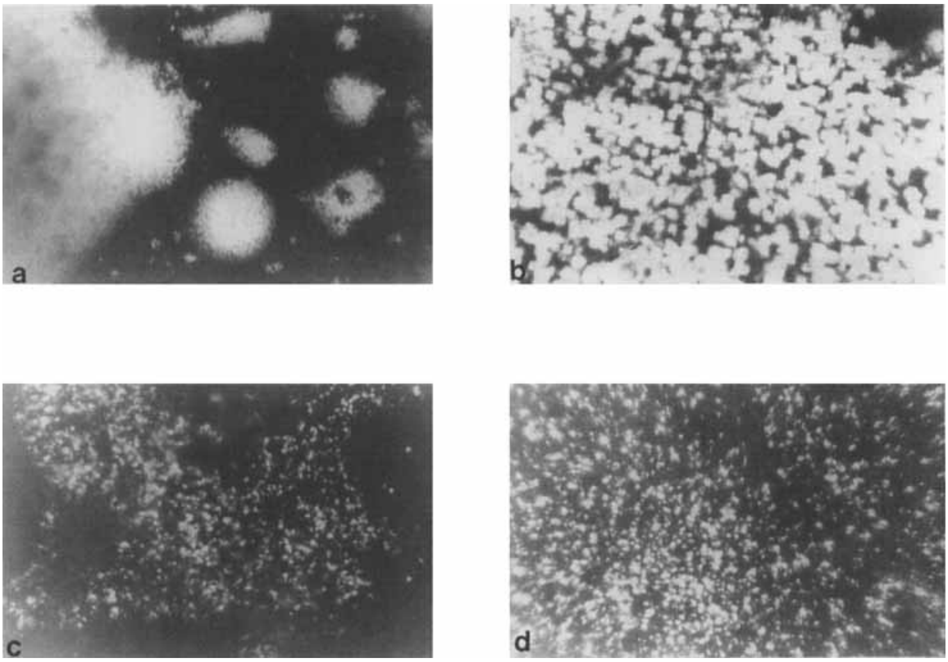


FIG. 5. Optical polarization micrographs of the model compounds (a) VIa at 200°C (150×) and (b) VIb at 145°C (300×); and polymers (c) X at 150°C and (d) XI at 160°C (heating cycle, 150×).

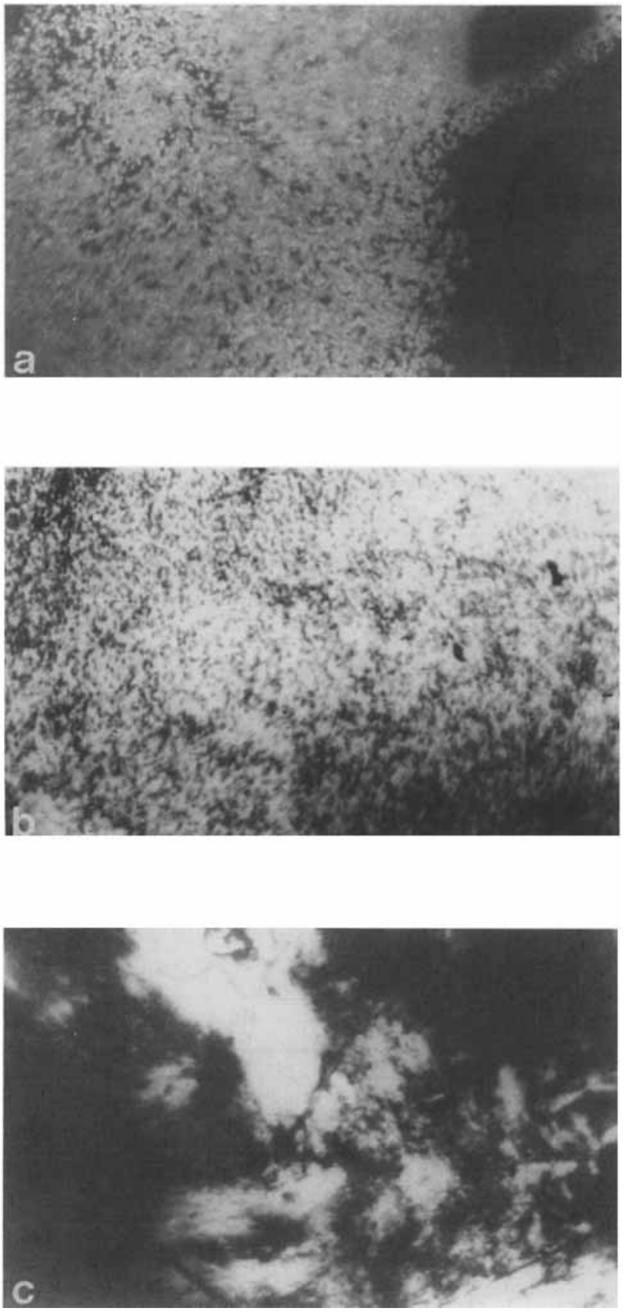


FIG. 6. Optical polarization micrographs of the polymers (a) VIIa, (b) VIIIa1, and (c) VIIIa2 at 205°C (heating cycle, 150×).

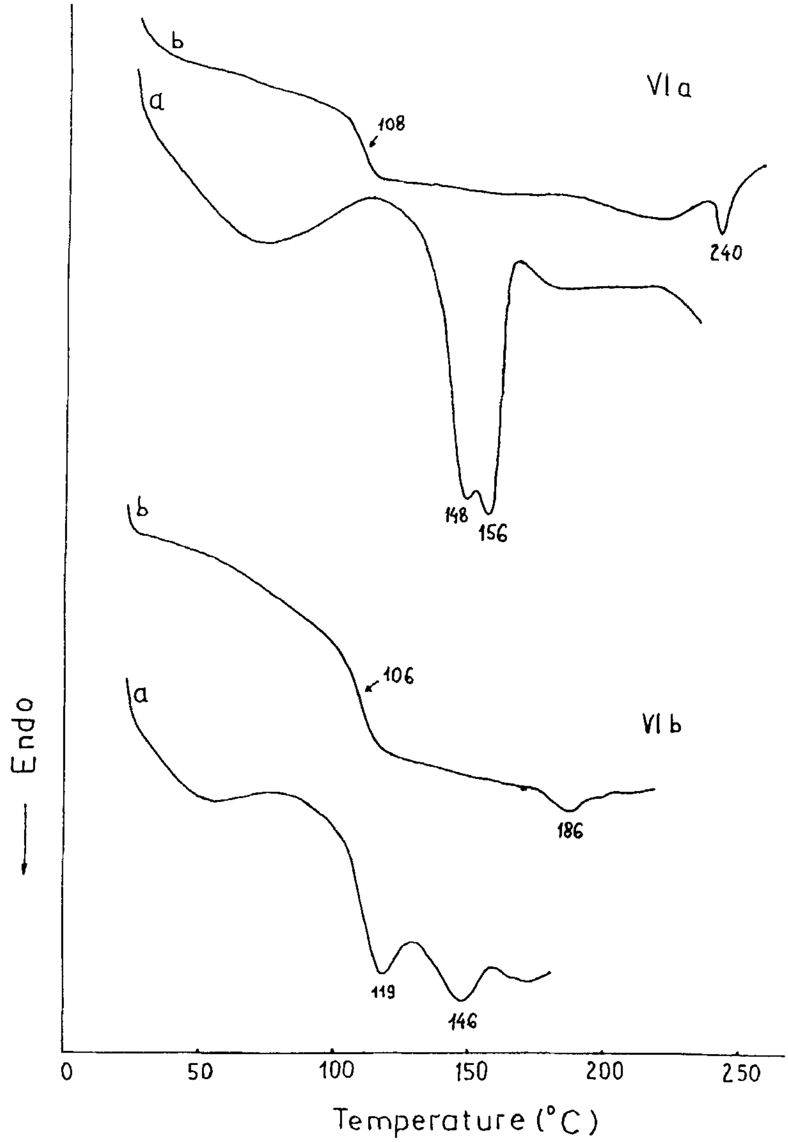


FIG. 7. The DSC curves of model compounds VIa and VIb: (a) first heating cycle and (b) second heating cycle at a heating rate of 10°C/min.

ture mainly due to the bulkiness of the $-SO_2-$ group but also due to the deviation from a linear structure of the macromolecular chains caused by the existence of etheric and methylenic links on the backbone [22–24].

In this work we studied whether the "anisotropic" rigid AM mesogens placed on the "isotropic" main chain of the PSF type can induce TLC properties and so overcome the unfavorable factors mentioned above.

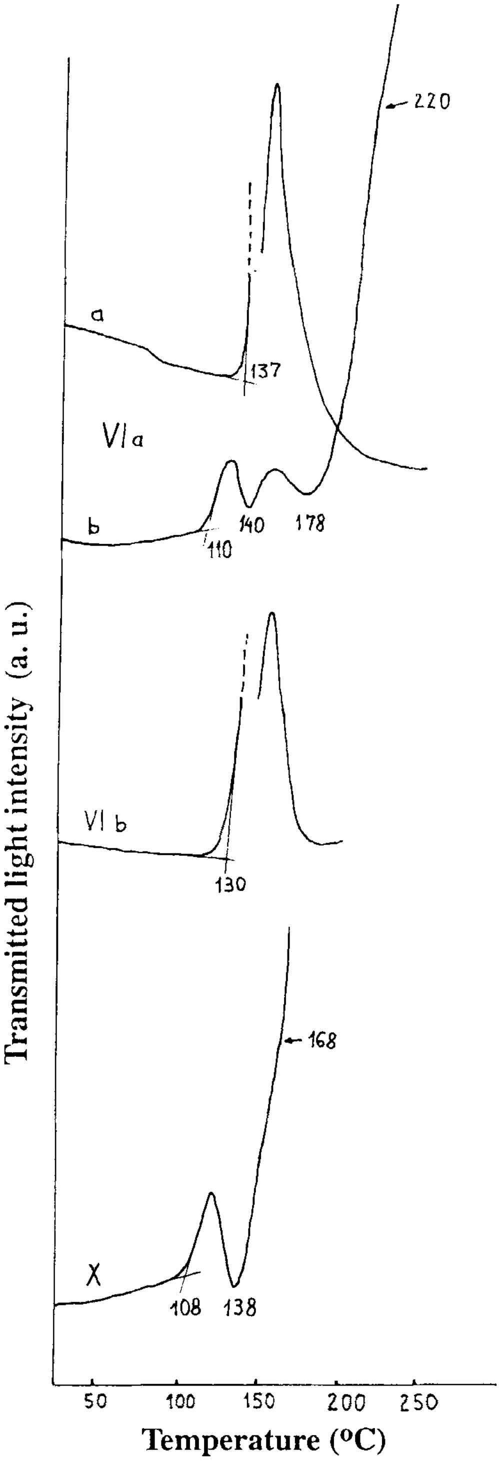


FIG. 8. The TOA curves of model compounds VIa and VIb and polymer X.

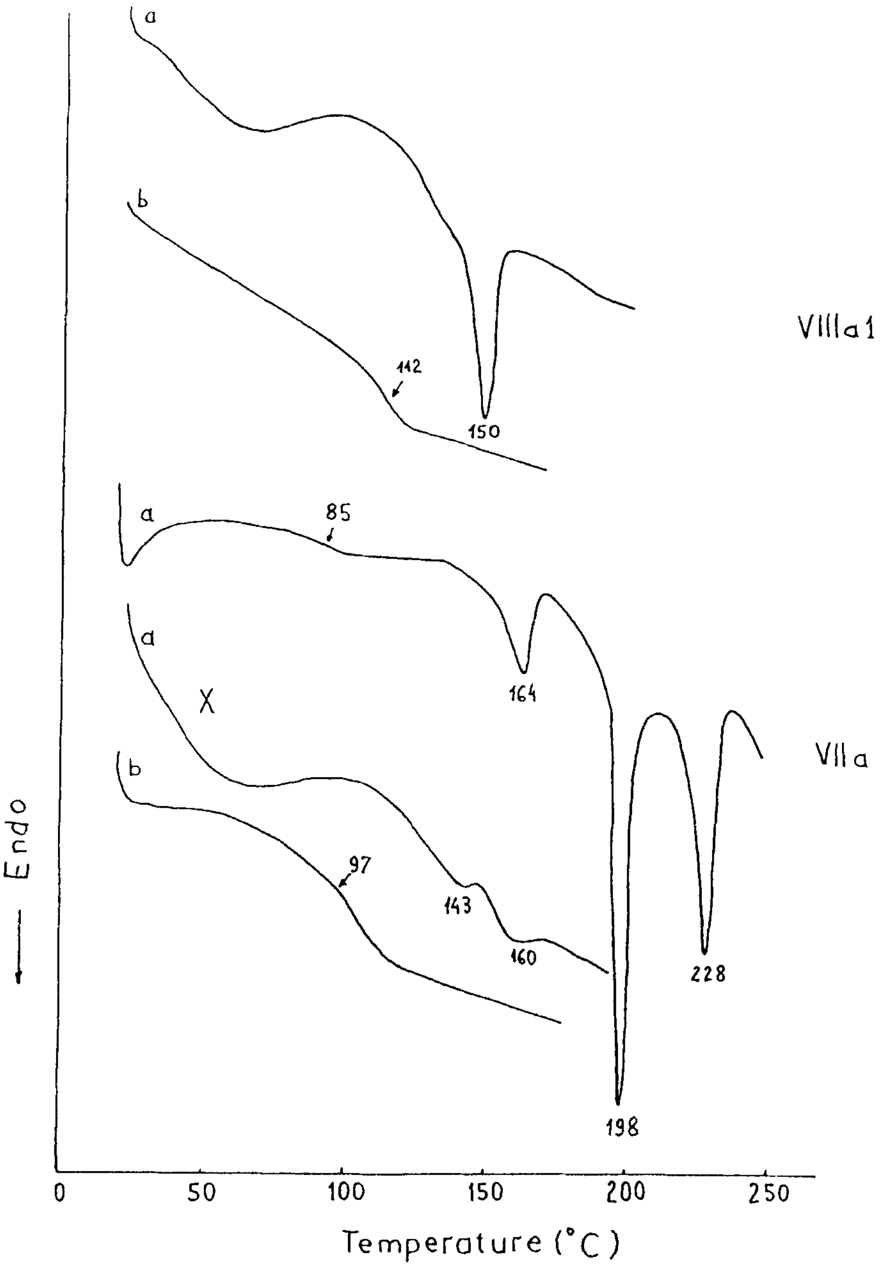


FIG. 9. The DSC curves of polymers VIIa and VIIIa1: (a) first heating cycle and (b) second heating cycle. DSC curves of polymer X: (a) first heating cycle and (b) third heating cycle.

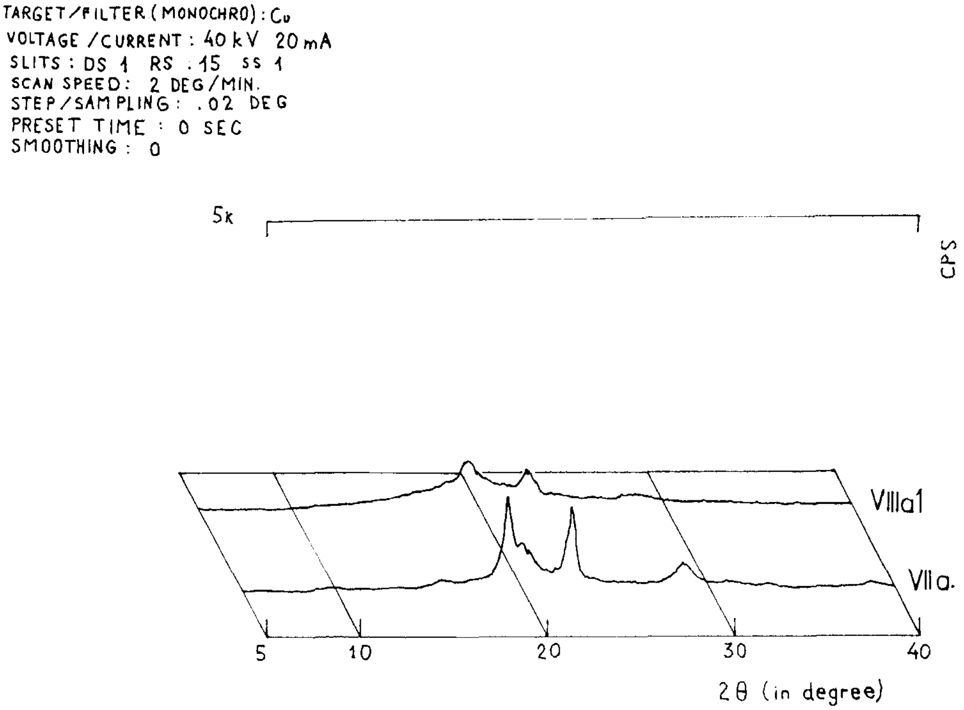


FIG. 10. X-ray diffraction curves of polymers VIIa and VIIIa1.

The TLC properties of polymers were studied by using PLM, TOA, and DSC measurements (listed in Table 1).

The PLM observations showed a nematic texture for both model compounds (VIa, VIb) and polymers (VIIa, VIIIa) obtained with the diamine (IIIa) (Figs. 5 and 6), but no birefringence was observed for those polymers obtained with the diamine (IIIb), (VIIb, VIIIb). These observations agree well with DSC and TOA data (Table 1, Figs. 7–9).

TABLE 4. The Thermal Behavior of Polymers VII–X

Polymer code	TGA temperature (°C) for various % decompositions					
	T_i[a]	5	10	20	30	40
VIIa	255	350	395	455	525	585
VIIIa1	225	310	410	515	570	600
VIIIa2	250	400	460	535	585	600
VIIb	230	350	430	510	570	600
VIIIb	245	385	445	522	580	600
X	165	265	365	500	565	600

[a] T_i = initial decomposition temperature.

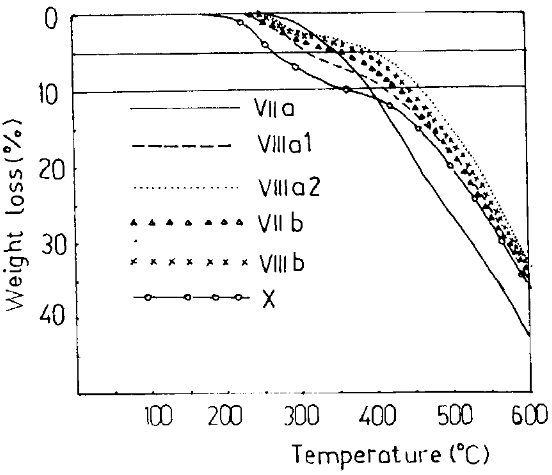


FIG. 11. TGA curves for polymers VII-X.

TOA reflects the variability of LC polymer's birefringence in the course of heating and cooling processes, including the phase transitions regions. Thus, it is very helpful in its recognition of the transition temperatures of the polymers as a complementary method [25-27].

With the exception of the VIIIa1, VIIb, VIIIb, and XI samples, all other TLC polymers showed isotropization, as observed using PLM and DSC.

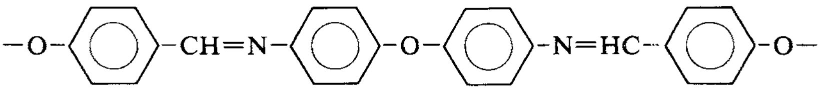
The DSC curve for the model compound VIa in the first heating cycle (Fig. 7) showed closed endothermic peaks at 148 and 156°C. From a comparison with the TOA curve (Fig. 8) and PLM observations, we assigned the peak at 148°C to a crystal-nematic transition. An explanation for the peak at 156°C is not available at the moment because no change in the nematic texture was observed under PLM until isotropization occurred.

The DSC curve for polymer VIIa (Fig. 9) in the first heating cycle showed a glass transition at 85°C and endothermic peaks at 164, 198, and 228°C. The second heating cycle is similar to the first one. The peak at 164°C (160°C by TOA) could be a crystal-to-crystal transition. A similar phenomenon was not found for polymers with higher molecular weights.

The x-ray diffraction curve for polymer VIIa showed a higher crystallinity than did polymer VIIIa1 (Fig. 10).

The intensity of birefringence within the mesophase, as observed by PLM, varied from very strong for VIIa and VIIIa to weak for VIb.

Surprisingly, the "b" series of polymers (VIIb, VIIIb) doesn't exhibit TLC properties. There is no explanation for this behavior. However, the only difference in the chemical structure is that two mesogenic units are bridged by a $-CH_2-$ link in the "b" series while in the "a" series they are bridged by a $-O-$ link. We therefore suppose that the last sequence of chain (1) is more favorable for inducing TLC properties.



(1)

To verify this assumption, a new polymer (X) was synthesized by using a polycondensation reaction between a non-TLC polymer (VIIIb) with chlorine end groups and model compound IX which contains two mesogenic units coupled by a —O— link. (**1**, Scheme 3). Using PLM observations for polymer X, a strong birefringence was found in the melting state between 125 and 160°C. Also, by DSC measurements (Table 1, Fig. 9), a glass transition temperature (T_g) at 97°C (third heating cycle), a crystal–nematic transition temperature (T_m) at 143°C, and a nematic–isotropic transition temperature (T_i) at 160°C (both in the first heating cycle) can be seen. The TOA measurements for this sample gave values in good agreement with the DSC ones (Table 1, Fig. 8). We conclude that the above-discussed assumption is correct.

Thermal Stability of Polymers

The thermal behavior of polymers (Table 4, Fig. 11) showed similar decomposition patterns. The initial decomposition temperature (T_i) ranged between 165 and 255°C and didn't affect the mesophase range, with the exception of sample VIIIa1 for which the isotropization temperature of 240°C (observed by PLM) exceeded by 15°C the T_i value of 225°C.

It's interesting to note that the thermal stability for sample VIIa decreased more rapidly than that of the others, probably due to its smaller molecular weight and its greater chlorine end groups content.

CONCLUSIONS

New TLC poly(azomethine sulfones) were prepared by using in-situ or two-step polycondensation reactions between aldehyde and amine functional-groups-based monomers and the classical polycondensation reaction between monomers with chlorine and hydroxyl functional groups. ^{1}H-NMR spectra and inherent viscosity data showed that some polymers are in fact oligomers and contain amino and chlorine end groups. The polymers with —O— links between mesogens displayed TLC properties while those with —CH_2— links didn't. By introducing —O— linked mesogens on the backbone of a non-TLC polymer (VIIIb), the polymer clearly became LC in the melt. The TLC properties of a new polymer (XI) confirmed our assumption.

REFERENCES

[1] F. W. Harris and K. Sridhar, *Am. Chem. Soc., Div. Polym. Chem., Polym. Prepr.*, *29*(2), 304–305 (1988).

[2] T. D. Shaffer and M. L. Shaffer, *Ibid.*, *29*(2), 352–353 (1988).

[3] S. J. Sun, T.-C. Chang, and C.-H. Li, *Eur. Polym. J., 29*(7), 951-955 (1993).

[4] C.-H. Li and T.-C. Chang, *J. Polym. Sci., Polym. Chem. Ed., 28*(13), 3625-3638 (1990).

[5] C.-H. Li and T.-C. Chang, *Ibid., 29*(3), 361-367 (1991).

[6] C.-H. Li, K.-Y. Hsu, and T.-C. Chang, *Ibid., 29*(10), 1447-1454 (1991).

[7] A. H. Al-Dujaili, R. J. A. Shalash, and T. S. Yasagh, *Eur. Polym. J., 26*(9), 947-950 (1990).

[8] K. Tamareselvy, K. Venkatarao, and H. Kothandaraman, *Makromol. Chem., 191*, 1231-1242 (1990).

[9] S. B. Idage, B. B. Idage, and S. P. Vernekar, *J. Polym. Sci., Polym. Chem. Ed., 30*(3), 513-517 (1992).

[10] Y. Ni, J. Guan, and X. Jin, in *Liquid Crystalline Polymers*, Pergamon Press, 1994, p. 25.

[11] B. C. Auman and V. Percec, *Polymer, 29*, 938-949 (1988).

[12] K. L. Cooper, W. Waehamad, H. Huang, D. H. Chen, G. L. Wilkes, and J. E. McGrath, *Am. Chem. Soc., Div. Polym. Chem., Polym. Prepr., 30*(2), 464 (1989).

[13] S. Brenda and W. Heitz, *Macromol. Chem. Phys., 195*(4), 1327-1339 (1994).

[14] H. C. Shu and C. L. Bar, *Mater. Chem. Phys., 34*(1), 28-34 (1993); *Chem. Abstr., 119*(5), 96314e (1993).

[15] W. Heitz, M. Brenda, G. Heyde, T. Wallach, and A. Karbach, *Am. Chem. Soc., Div. Polym. Chem., Polym. Prepr., 33*(2), 201 (1992).

[16] 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, 1989, Dallas, Texas, p. 316.

[17] G. Rabilloud and B. Sillion, *Eur. Polym. J., 26*(9), 967-976 (1990).

[18] C. Vasile and A. Stoleriu, *Mater. Plast., 27*, 117 (1990).

[19] E. Butuc, V. Cozan, A. Stoleriu, M. Rusu, Y. Ni, and M. Ding, *J. Macromol. Sci.—Pure Appl. Chem., A32*(1), 115-128 (1995).

[20] G. F. D'Alelio, J. V. Crivello, R. F. Schoenig, and T. F. Huemmer, *J. Macromol. Sci.—Chem., A1*(7), 1161-1249 (1967).

[21] R. Wiswanathan, B. C. Johnson, and J. E. McGrath, *Polymer, 25*(12), 1827 (1984).

[22] R. W. Lenz, *Faraday Disc., 79*, 29 (1985).

[23] R. W. Lenz and J.-I. Jin, *Macromolecules, 14*(5), 1405-1411 (1981).

[24] H.-Kh. Mahabadi and L. Alexandru, *J. Polym. Sci., Polym. Chem. Ed., 28*(2), 231-243 (1990).

[25] P. Driscoll, T. Masuda, A. Furukawa, R. W. Lenz, and S. Bhattacharya, *Polym. J., 22*(7), 609-613 (1990).

[26] M. Mucha and M. Kryszewski, *J. Therm. Anal., 33*, 1177-1184 (1988).

[27] M. Mucha, *Colloid Polym. Sci., 267*(10), 876-880 (1989).

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