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Synthesis and thermal behaviour of new poly(azomethine-ether)

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Abstract

A new poly(azomethine-ether) was synthesized by the reaction of bisphenol A with a thermotropic azomethine monomer, namely 4,4′-oxy-bis(4-chlorobenzylideneimino phenylene). In order to understand the influence of the molecular weight on the thermal properties, four fractions were isolated from the initial polymer. They were investigated by elemental analysis and spectroscopic methods (IR, UV, ^{1}H NMR) and their thermal behaviour was studied by differential scanning calorimetry, optical microscopy, thermogravimetrical analysis. An increase of the thermal transition temperatures and mesophase order with increasing molecular weight was noticed.

Keywords: Polyazomethine; Liquid crystal; Thermotropic

1. Introduction

Aromatic polyazomethines (PAMs) are an attractive class of high performance polymers, due to their high thermal stability, excellent mechanical strength, and good optoelectronic properties [1–4]. They are also studied in fundamental researches [5]. Unfortunately, PAMs are in general infusible polymers and have poor solubility, drawbacks which would minimize their practical applications. There are many reported data about thermotropic liquid crystalline polyazomethines, such as: poly(azomethine-ester)s [6], poly(azomethine-ether)s [7], poly(azomethine-carbonate)s [8], poly(amide-azomethine-ester)s [9], poly(acrylate-azomethine)s [10], thermosetting polyazomethines [11], poly(azomethine-sulfone)s [12,13], in which various chemical structures were used with the aim to reduce the melting temperature, to improve the solubility and to promote specific properties such as mesomorphism [14].

As reported in these papers, the transition temperatures decrease with the introduction of flexible spacers, but the solubility is still not satisfactory. An improvement of the solubility was reported for poly(azomethine-ether)s containing methoxy substituents [6]. Some studies on poly(ethersulfone)s showed that the introduction of bisphenol A unit into backbone leads to a very good solubility, while maintaining a high thermal stability [15].

These were the reasons which prompted us to synthesize a new poly(azomethine-ether) by reacting bisphenol A with a thermotropic azomethine monomer **M**, namely 4,4′-oxy-bis(4-chlorobenzylideneiminophenylene). The chemical structure of this

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monomer contains an ether linkage, which is known to be efficient in reducing the melting temperature (T_m), by increasing the conformational entropy in the liquid crystalline (LC) phase, and also by reducing the isotropization temperature ($T_{lc\text{-}i}$), through a decrease of both rigidity and effective axial ratio of the molecule. The choice of bisphenol A as co-monomer was motivated by the fact that its two adjacent phenylene rings are joined through a single tetrahedrally coordinated carbon atom, making thus very effective kinks which have a drastic influence on the stability of the LC phase, although the effect on T_m is not so pronounced as in the case of the flexible spacer [14]. On the other hand the presence of CH_3 units led to a good solubility.

Our study was based on three main objectives: (i) to synthesize a poly(azomethine-ether) with low transition temperature and good solubility in common organic solvents; (ii) to investigate the thermotropic properties of polymers obtained by fractionation; (iii) to study the influence of the molecular weight on the thermal properties in terms of both thermotropic behaviour and thermal stability. In this paper we have chosen to pay less attention to the mesophase characterization, which will be the subject of a future work.

2. Experimental

2.1. Reagents

Oxy-bis(4-aminophenylene) (mp. 190–192 °C, Aldrich), 4-chlorobenzaldehyde (mp. 45–47 °C, Merck), 2,2′-bis(4-hydroxyphenyl)propane (bisphenol A, mp. 158–159 °C, Merck) were used as-received. Dimethylsulfoxide (DMSO) was dried over calcium hydride and distilled under vacuum before use. Anhydrous potassium carbonate was dried at 120 °C in a vacuum oven before use.

2.2. Measurements

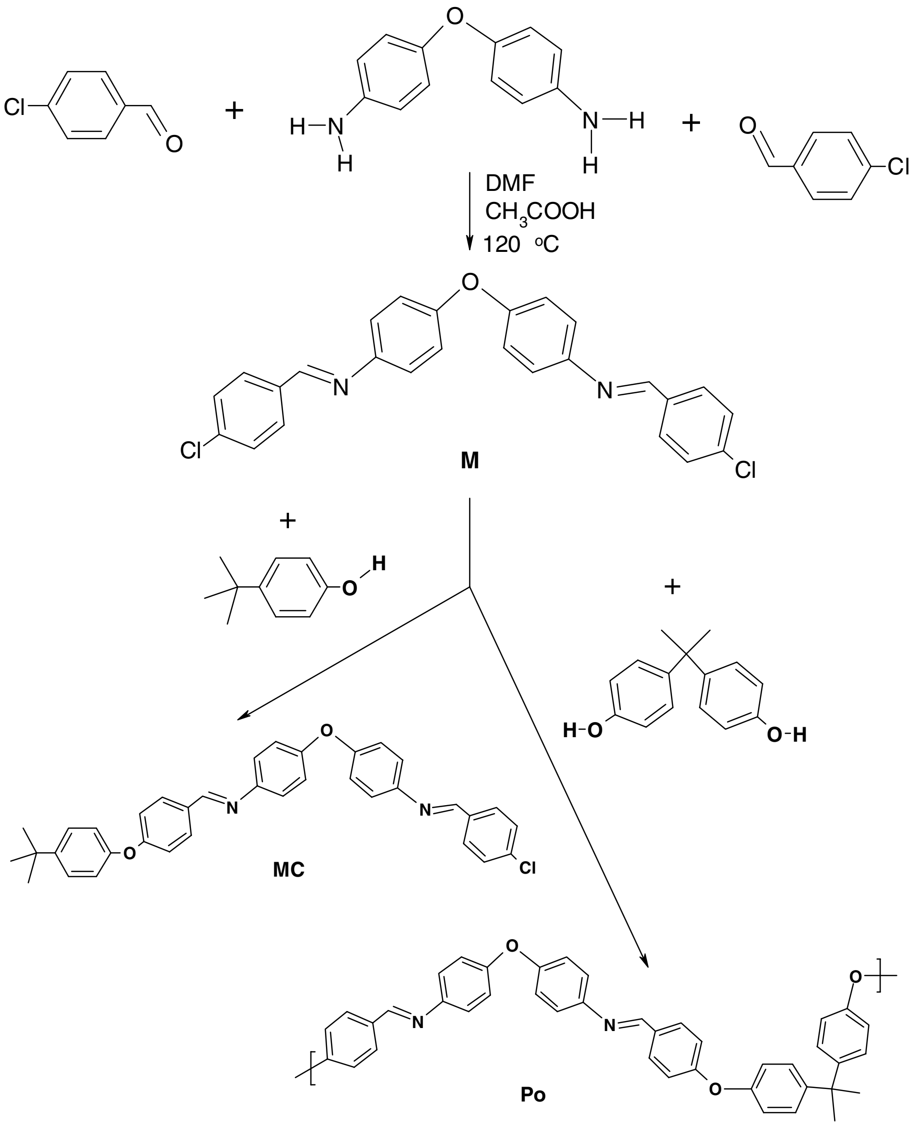
Infrared (IR) spectra were recorded on a Specord M80 Carl Zeiss Jena Spectrophotometer, using KBr pellets. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded by a Jeol 60 MHz spectrometer using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal reference. Chemical shifts are reported in parts per million (ppm). UV–vis spectra were obtained on Carl Zeiss Jena SPECORD M42 spectrophotometer in DMF solutions using 10-mm quartz cells fitted with poly(tetrafluoroethylene) stoppers. Differential scanning calorimetry (DSC) was performed with a Mettler TA Instrument DSC 12E at a heating rate of 5 °C/min or 10 °C/min, under nitrogen atmosphere. The transition temperatures were read at the top of the endothermal and exothermal peaks. Glass transition temperatures (T_g) were read at the middle of the change in the heat capacity. The samples were first heated with 10 °C/min up to the isotropic state (as determined by optical polarizing microscopy), quenched to the room temperature, then reheated with 10 °C/min. Mesophases for pure compound **M** and polymer fractions **P1**–**P4** were studied by observations of the textures with an Olympus BH-2 polarized light microscope under cross-polarizers with a THMS 600/HSF9I hot stage. The temperature at which isotropic phases occurred was taken as the isotropization temperature (T_i). Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature using a TUR-M62 Diffractometer, and nickel-filtered CuKα radiation. Thermogravimetrical analysis (TGA) was carried out by using a MOM Q Derivatograph, Hungary, at a heating rate of 9 °C/min, in air. Solubility tests of the polymers were performed in common solvents such as: acetone, methanol, carbontetrachloride (CCl_4), chloroform ($CHCl_3$), dimethylsulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), *N*-methylpyrrolidine-2-one (NMP). Molecular weight distributions of polymers were measured by gel permeation chromatography (GPC), in $CHCl_3$ solutions. Viscosities were measured with an Ubbelohde suspended level viscometer in DMF (0.2 wt.%), at 20 °C.

2.3. Monomer synthesis

2.3.1. 4,4′-Oxy-bis(4-chlorobenzylideneimino-phenylene) (*M*)

The preparation of the azomethine monomer was performed by the acid-catalyzed condensation of the oxy-bis(4-aminophenylene) and 4-chlorobenzaldehyde in a 1:2 molar ratio (Scheme 1).

In a round bottom flask 1 g (5 mmol) oxy-bis(4-aminophenylene), 1.4 g (10 mmol) 4-chlorobenzaldehyde, 14 mL *N*,*N*-dimethylformamide were placed and a few drops of glacial acetic acid as catalyst were added under magnetical stirring. The reaction mixture was heated at 120 °C for 1 h. After cooling, the solid product was filtered, washed with acetone and twice recrystallized from DMF, then dried under vacuum at 50 °C for 24 h. Crystalline yellow-nacreous plates were obtained in 92.3% yield, mp. 243 °C.



Scheme 1. Synthesis of the monomer **M**, model compound **MC** and poly(azomethine-ether) **P0**.

Analysis: (**M**) calculated for $C_{26}H_{18}Cl_2N_2O$ (445.33): C 70.12 %, H 4.07 %, N 6.29 %, Cl 15.92 %; found: C 69.88 %, H 4.54 %, N 6.63 %, Cl 16.13%. IR (KBr, cm^{-1}): 1620 (HC=N), 1230 (C–O–C), 1090 (p-C_6H_4–Cl).

2.4. Model compound synthesis

*2.4.1. 4-[4-(4-(4-Chlorobenzylideneiminophenoxy)-phenyliminomethylidene)-phenoxy]-t-butylphenyl (**MC**)*

In a three necked round bottomed flask fitted with thermometer, condenser, nitrogen inlet and magnetical stirrer were placed 1 g (2.24 mmol) **M** and 6 mL DMSO. The mixture was heated at 140 °C under stirring, until a clear solution was obtained. Then a mixture of 0.38 g (2.53 mmol) 4-*t*-butyl phenol dissolved in 4 mL DMSO and 0.36 g 2.60 mmol) anhydrous potassium carbonate was added slowly. The reaction mixture changes its color into brown and the temperature was increased at 160 °C and maintained for 6 h. After cooling to room temperature, the content of the flask was poured into distilled water. The solid formed was filtered and washed several times with water to remove the inorganic salts, then with methanol to remove the eventually unreacted traces of 4-*t*-butyl phenol. To remove the traces of unreacted monomer **M**, the product was heated into acetone at the reflux for 1 h, then hot filtered. After cooling, the filtrate was precipitated with water, washed with water then with methanol and finally dried at 70 °C, under vacuum, for 24 h. Yield 74%, mp. 135 °C.

Analysis (**MC**) calculated for $C_{36}H_{31}ClN_2O_2$ (559.11): Cl 6.34%, N 5.01%; found Cl 6.87%, N 5.26%. IR (KBr, cm^{-1}): 3080 (═C–H), 2970, 2870 (C–H stretch. CH_3), 1625 (–CH═N–), 1590, 1500 (arom.), 1246 (C–O–C), 1090 (p-C_6H_4–Cl), 875, 840, 825 sh. (1,4-disubstituted ring). ^{1}H NMR ($CDCl_3$, TMS, δ ppm): 8.70 (m, 2H, ═CH–), 8.25–7.00 (m, 20H, arom.; $CDCl_3$), 1.40 (m, 9H, –$CH_3)_3$).

2.5. Synthesis of polyazomethine P0

One gram (2.25 mmol) **M**, 0.51 g (2.25 mmol) bisphenol A, 0.36 g anhydrous potassium carbonate and 6 mL DMSO were placed in a reaction vessel fitted with mechanical stirrer, thermometer, reflux condenser and nitrogen inlet. The reaction mixture was stirred vigorously, while the temperature increased at 160 °C and maintained for 8 h. After cooling at room temperature, the reaction mixture was precipitated in cold water. The solid polymer (**P0**) was washed three times with water and once with methanol. Four polymer fractions were obtained by fractionation with methanol, in the following way:

Step 1. Polymer **P0** was stirred with methanol at room temperature for 2 h, then filtered. From the filtrate the polymer fraction **P1** was extracted.

Step 2. The solid from step 1 was stirred with methanol at 40 °C for 2 h, then filtered. From the filtrate the polymer fraction **P2** was extracted.

Step 3. The solid from step 2 was stirred with methanol at reflux for 2 h, then filtered. From the filtrate the polymer fraction **P3** was extracted. The solid from step 3 represents the polymer fraction **P4**. The polymer fraction **P4** was reprecipitated from DMF.

3. Results and discussion

A new poly(azomethine-ether) **P0** was synthesized by the reaction of bisphenol A with a thermotropic azomethine monomer **M**, namely oxy-bis(4-chlorobenzylideneimino phenylene). The synthetic route for the monomer (**M**) and poly(azomethine-ether) **P0** are shown in Scheme 1. After extraction with methanol, the structures of the polymer fractions obtained **P1–P4** were confirmed by IR and ^{1}H NMR spectroscopy. An example containing representative IR absorption bands and their corresponding assignments is illustrated in Fig. 1 for polymer fractions **P1–P4**.

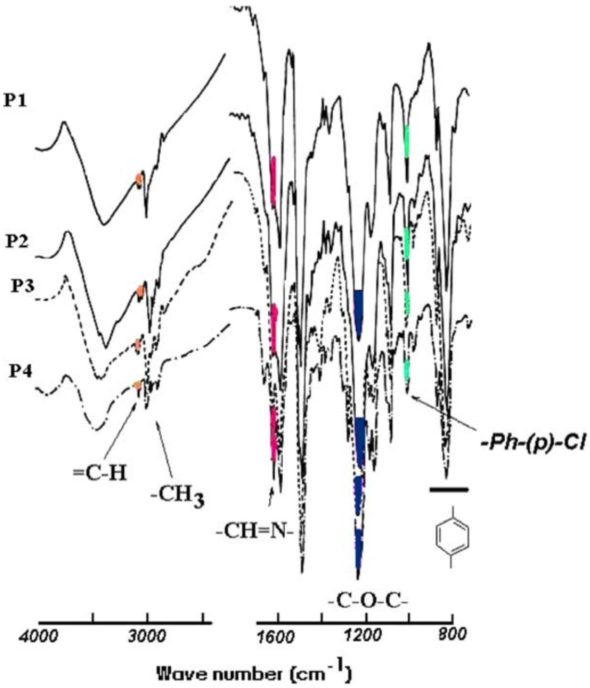


Fig. 1. Infrared spectra of polymer fractions **P1–P4**.

The IR spectra showed the presence of the absorption band corresponding to the azomethine (–CH═N–) linkage (1625 cm^{-1}) belonging to the polymer repeating unit. The sharp peaks occurring at 1230–1240 cm^{-1} and 1160 cm^{-1} in the spectra of the polymers are due to the asymmetrical and symmetrical vibrations of the ether linkage. Other characteristic absorption bands were present also.

^{1}H NMR spectra of the polymers showed three types of signals which were assigned correspondingly: the singlet at 8.4–8.5 ppm –C*H*═N–; the multiplet at 6.63–7.72 ppm aromatic protons; the singlet at 1.43–2 ppm aliphatic protons. The ratio values of the integrals corresponding to aliphatic versus aromatic protons agree with the proposed structure.

In view to confirm the reaction path chosen for the synthesis of polymer **P0** and to understand better the properties of polymer fractions **P1–P4** a model compound (**MC**) was synthesized by reacting the monomer **M** with 4-*t*-butylphenol in a 1/1 molar ratio (Scheme 1).

The IR spectra of MC showed no absorption band in the region 3500 cm^{-1} (consumption of OH groups) and an intense absorption band at 1246 cm^{-1} (formation of the new C–O–C linkage). The presence of some other characteristic absorption bands confirmed the proposed structure: 2970, 2870 cm^{-1} ($-C(CH_3)_3$), 1090 cm^{-1} (Cl–*p*-C_6H_4–).

The ^{1}H NMR spectrum has three types of signals belonging to the different characteristic fragments of the molecule: 8.7 ppm (–C*H*=N–), 8.25–7.00 ppm (aromatic) and 1.40 ppm (aliphatic $-C(CH_3)_3$).

UV–vis electronic spectra were recorded for **M**, **MC** and **P1**–**P4** samples in DMF solutions. The data are collected in Table 1. All the samples exhibited an intense absorption band ranging between 334 nm and 340 nm, due to the π–π* electronic transition of the Ph-CH=N-Ph systems. Similar absorption maxima were reported for polyazomethines containing benzylidene ketone moieties [16].

Inherent viscosity measurements on DMF solutions of samples **P1–P4**, gave values ranging between 0.13 dL/g and 0.95 dL/g, respectively. Glass transition temperatures obtained by DSC scans revealed values increasing from 35 °C (**P1**) up to 100 °C (**P4**). These measurements, corroborated with the solubilities of samples into methanol, suggested the following series of polymer fractions, ordered by the increasing of their molecular weight: **P1 < P2 < P3 < P4**. GPC measurements on chloroform solutions of samples, provided numerical average molecular weight (M_n) values comprised between 1900 (**P1**) and 3700 (**P4**, Table 1), which confirmed the series proposed above. The values of polydispersity index were comprised between 1.44 and 1.85 (Table 1).

The solubility of monomer (**M**), model compound (**MC**) and poly(azomethine-ether) fractions (**P1–P4**) was tested in various common solvents. As can be seen from Table 2, all the polymers showed excellent solubility in dipolar aprotic solvents, such as DMF, DMSO, or NMP. In other solvents (methanol, acetone, carbon tetrachloride) the polymers showed poor solubility, except for the polymer **P1**. The monomer **M** was only soluble in DMSO, DMF, NMP at heating. The model compound **MC** was soluble in all solvents, except for methanol. The enhanced solubilities of polymers and model compound compared with that of the monomer could be explained by the presence of the bisphenol A units in the macromolecular chains and, in the case of sample **MC**, by the presence of bulky *t*-butyl group.

TGA indicates that aromatic poly(azomethine-ether) fractions have good thermal stability in air due to higher stability of aromatic azomethine moiety (Table 1). The polymer fractions **P1**–**P4** undergo 0.1% up to 0.2% weight loss at their isotropization temperatures, which means their mesophases are almost unaffected.

Table 1
Physical characteristics of model compound **MC** and polymer fractions **P1–P4**

Sample code	λ_{max}[a] (nm)	η_{inh}[a] (dL/g)	M_n[b]	PI[c]	T_0[d] (°C)	T_{10}[d] (°C)
MC	334	–	–	–	190	350
P1	340	0.13	1900	1.65	123	231
P2	338	0.42	2500	1.85	131	273
P3	337	0.59	2900	1.68	169	312
P4	334	0.95	3700	1.44	193	351

[a] Measured for polymer solutions in DMF, at a concentration of 0.2 wt.% at 20 °C.

[b] From GPC measurements on chloroform solutions.

[c] PI: polydispersity index ($PI = M_w/M_n$).

[d] From TGA measurements in air: T_0 = initial decomposition temperature; T_{10} = temperature at which 10 weight loss % occurred.

Table 2
Solubility characteristics of monomer **M**, model compound **MC** and polymer fractions **P1–P4**

Sample code	Methanol	DMSO	DMF	NMP	Acetone	Chloroform	Carbon tetrachloride
M	–[a]	+(h)	+(h)	+(h)	–	–	–
MC	–	+	+	+	+	+	+
P1	+	+	+	+	+	+	–
P2	+(h)	+	+	+	±	+	–
P3	+(h)	+	+	+	±	+	–
P4	–	+	+	+	–	+	–

[a] +: Soluble at room temperature; ±: partially soluble at room temperature; −: insoluble at room temperature; +(h): soluble at heating.

The transition temperatures of the poly(azomethine-ether) fractions measured by DSC were compared with those obtained from the optical polarized microscopy measurements. These two methods gave similar results, which are shown in Table 3. The observed differences could be explained by the variations of the heating/cooling rate, amounts of sample used, and presence of an inert gas (nitrogen) in case of DSC measurement, versus air in case of optical microscopy.

A birefringent fluid is the signature of liquid crystallinity [7] and optical polarizing microscopy (OPM) data revealed that our polymer fractions exhibited thermotropic LC behaviour on both heating and cooling, except for sample **P2**. DSC measurements agree well with the transition temperatures observed by OPM measurements (Figs. 2 and 3). In the case of sample **P2**, no transition could be detected in the DSC cooling cycle, which could be due to the partial decomposition of the polymer near the clearing temperature. For this reason the isotropization temperature in DSC thermogram of **P2** was read at onset of the broad peak.

Despite the fact that the recorded DSC thermogram for monomer **M** reveals only a single peak on both heating and cooling, the optical pattern observed by OPM clearly revealed a strong birefringence in the melt at cooling as illustrated in Fig. 4a.

The sample **M** was subjected to successively heating and cooling DSC scans with different rates (°C/min): 5; 10; 15. The recorded temperatures of exothermal peak at cooling were (°C): 231.7; 230.6; 227.2, respectively. Since there was only 4.5 °C as temperature difference between scans, we consider that these data could sustain a monotropic behaviour for the monomer **M**.

OPM observations of the model compound **MC** showed a birefringence texture after 135 °C and mechanical stress applied on lamellae revealed a viscous fluid phase (Fig. 4b). By heating further the birefringence disappeared completely at 195 °C. At cooling, the sample showed the instantaneous appearance of a mosaic like texture at 186 °C which

Table 3
Thermal behaviour of monomer **M**, model compound **MC** and polymer fractions **P1–P4**

Sample code	OPM transition temperatures (°C)	DSC		
		Scan/rate (°C/min)	Transition temperatures (°C)	Corresponding enthalpies[b] (J/g)
M		1H[a]/5	K 243 I	ΔH_{m}: 98.6
		1C/5	I 231.7 LC[c]	$\Delta H_{\text{i-lc}}$: 136.8
	K[a] 243 I	2H/10	K 242.7 I	–
	I 226 LC[c]	2C/10	I 230.6 LC[c]	–
		3H/15	K 245.4 I	ΔH_{m}: 97.0
		3C/15	I 227.2 LC[c]	$\Delta H_{\text{i-lc}}$: 114.0
MC		1H[a]/1	K 133 LC 190 I	$\Delta H_{m} + \Delta H_{\text{lc-i}}$: 26.0
		1C/1	I 181 LC[c]	$\Delta H_{\text{i-lc}}$: 20.1
	K 135 LC 195 I	2H/5	K 133 LC 191 I	$\Delta H_{m} + \Delta H_{\text{lc-i}}$: 34.2
	I 186 LC[c]	2C/5	I 176 LC[c]	$\Delta H_{\text{i-lc}}$: 38.4
	ΔT[d]: 60	3H/15	K 133 LC 193 I	$\Delta H_{m} + \Delta H_{\text{lc-i}}$: 39.8
		3C/15	I 172 LC[c]	$\Delta H_{\text{i-lc}}$: 36.6
P1	K 85 LC 113 I ΔT[d]: 20	2H/10	G 35 K 95 LC 115 I	ΔH_{m}: 1.9
P2	K 105 LC 121 I	1H/10	K 105 LC 128 I	ΔH_{m}: 6.6
	ΔT[d]: 23	2H/10	G 62 K	
P3	K 126 LC 165 I ΔT[d]: 32	2H/10	G 78 K 135 LC 167 I	ΔH_{m}: 11.0
P4	K 165 LC 207 I ΔT[d]: 45	2H/10	G 100 K 162 LC 207 I	ΔH_{m}: 24.9

[a] G = glassy; K = crystalline; LC = liquid crystalline; I = isotropic; 1H = first heating scan; 1C = first cooling scan.

[b] Enthalpies subscript: m = melting; lc-i = liquid crystalline to isotropic transition; i-lc = isotropic to liquid crystalline transition.

[c] Sample remained frozen into liquid crystalline state up to the room temperature.

[d] Mesophase range = $T_{\text{lc-i}} - T_{m}$.

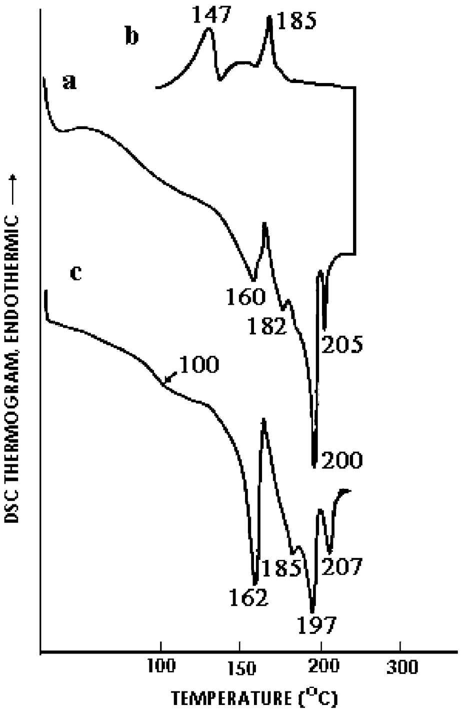


Fig. 2. DSC thermograms of polymer fraction **P4**: (a) first heating scan 10 °C/min; (b) first cooling scan 10 °C/min and (c) second heating scan 10 °C/min.

does not change up to room temperature, whatever from the cooling rate used (Fig. 4c).

The DSC heating scan of sample **MC** showed two endothermal peaks having different enthalpies: a small, broad one with onset at about 133 °C and a greater one at 191 °C. In the cooling scan a sharp peak at 176 °C was recorded. Three successive heating/cooling scans were done with different rates (°C/min): 1; 5; 15. The recorded exothermal peak temperatures were (°C): 181; 176; 172, respectively. Based on OPM observations we assigned the small peak from 133 °C to a solid to mesophase transition. Since the enthalpy differences between the endothermal peak from 191 °C and exothermal peak at 176 °C are small, and based on OPM observations, we assigned these peaks to disappearance and to appearance of the mesophase, respectively. Further investigations using SAXS measurements on samples **M** and **MC** are intended to understand the assignment of phase type and structure.

The polymer fractions **P1**, **P2**, when observed by OPM showed a fine texture (Fig. 4d), similar as reported for thermotropic polymers having stiff chains without flexible spacers [17,18]. The polymer **P3** showed two textures on cooling: a fine one and a mosaic one (Fig. 4e) [19].

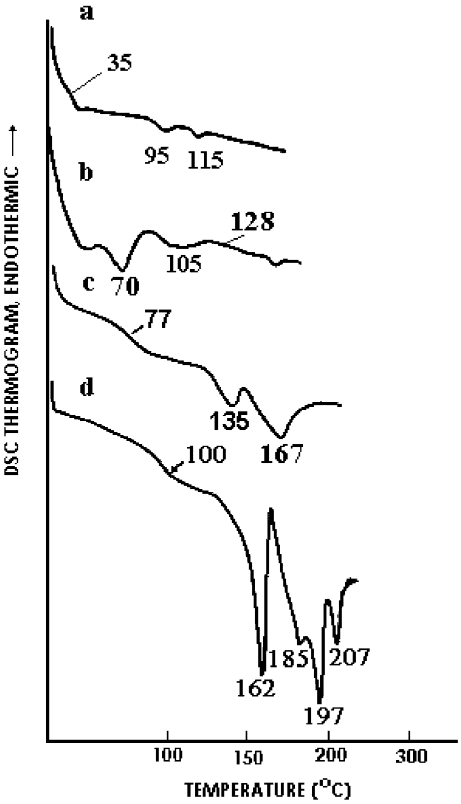


Fig. 3. Comparative DSC thermograms of polymer fractions: (a) **P1** second heating scan 10 °C/min; (b) **P2** first heating scan 10 °C/min; (c) **P3** second heating scan 10 °C/min and (d) **P4** second heating scan 10 °C/min.

The polymer fraction **P4** was investigated by OPM in two different ways: (a) during the cooling with 5 °C/min, showed three textures, difficult to ascribe. One of these is illustrated in Fig. 4f. (b) After annealing of the sample at 200 °C for 1 h, a kind of very interesting droplets appeared (Fig. 4g) and their population grew and transformed in a fine texture (Fig. 4h). The sample was than cooled at 194.5 °C, annealed for 75 min, cooled at 180 °C and annealed for 3 h. The fine texture described above transformed into a clear mosaic texture (Fig. 4i) [19]. On the basis of this observations, we can conclude that the liquid crystalline behaviour of this polymer strongly depends on its thermal history.

On cooling from the LC state the four fractions showed different behaviours: **P3**, **P4** crystallized (Fig. 4j), **P1** exhibited a frozen mesophase, while **P2** showed a glassy isotropic solid.

Wide-angle X-ray diffraction (WAXD) spectra of sample **P4** (Fig. 5), recorded at room temperature, showed a semicrystalline behaviour. Two more intense peaks were observed at $2\theta = 20°$ and 23° and

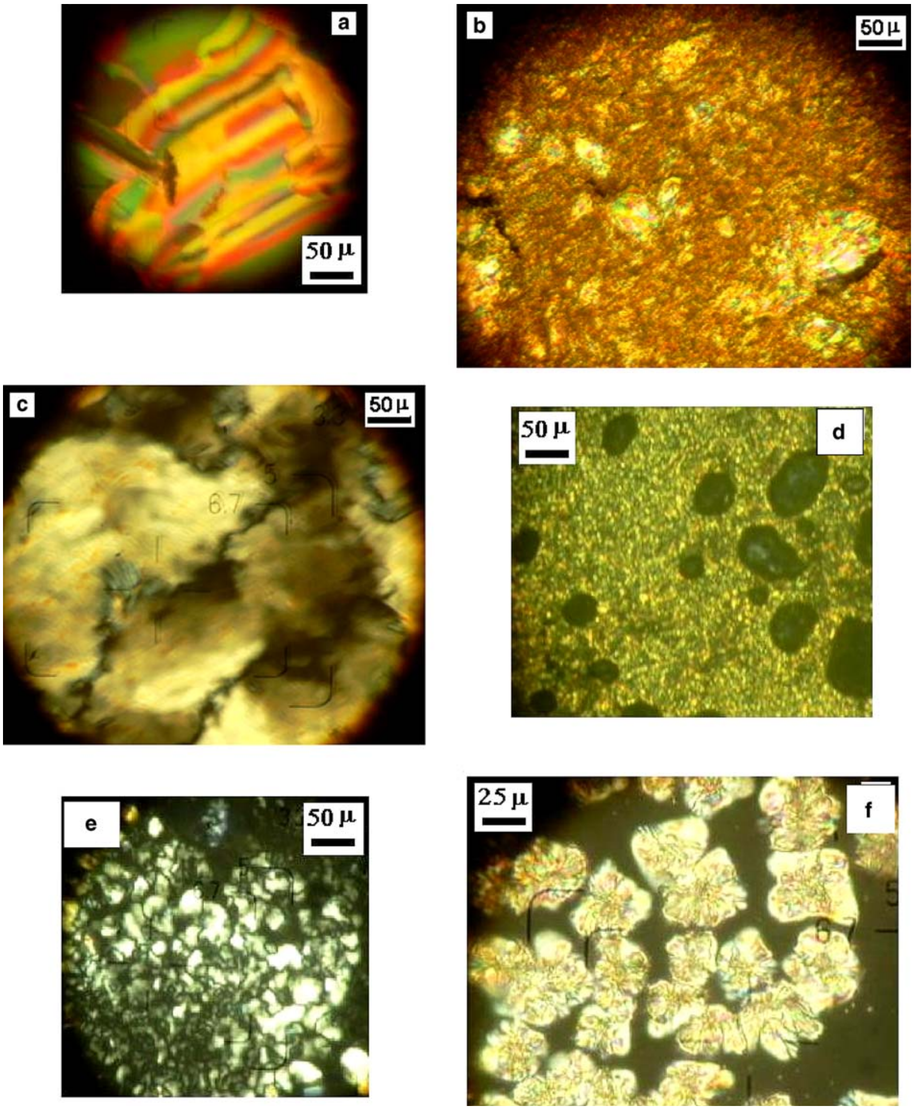


Fig. 4. Optical polarized microphotographs, crossed polarizers: (a) **M** first cooling 223 °C; (b) **MC** first heating 137 °C; (c) **MC** first cooling 158 °C; (d) **P1** first heating 103 °C; (e) **P3** first cooling 160 °C; (f) **P4** first cooling 187 °C; (g) **P4** first cooling 200 °C, annealed for 60 min; (h) **P4** first cooling 194.5 °C, annealed for 75 min; cooled at 180 °C, annealed for 3 h, (i) **P4** first cooling 180 °C and (j) **P4** first cooling 83 °C.

one more diffuse at 29°. Similar WAXD data for poly(azomethine-ester)s have been reported [6,16].

We observed that an increase of the molecular weight of the polymer fractions led to an enrichment of the mesomorphism.

The influence of the molecular weight on the transition temperatures of polymer fractions **P1–P4** is illustrated in Fig. 6. As can be seen, the incorporation of bisphenol A and monomer **M** units into the polymer backbone by polycondensation led to a decrease of melting (T_m) and isotropization ($T_{lc\text{-}i}$) temperatures for polymer fractions, in comparison with high values for **M**. One can see also the increasing tendency of transition temperatures and mesophase range with increasing of M_n values, as was reported in literature [20].

The geometrical features were studied by molecular modelling methods (MM+) [21] for a simple model molecule, (Fig. 7) to simulate the possible conformation of a poly(azomehine-ether). We observed that rotations around the ether bonds minimize the disruptive influence of the kinked bisphenol A units on the straightness of the chain.

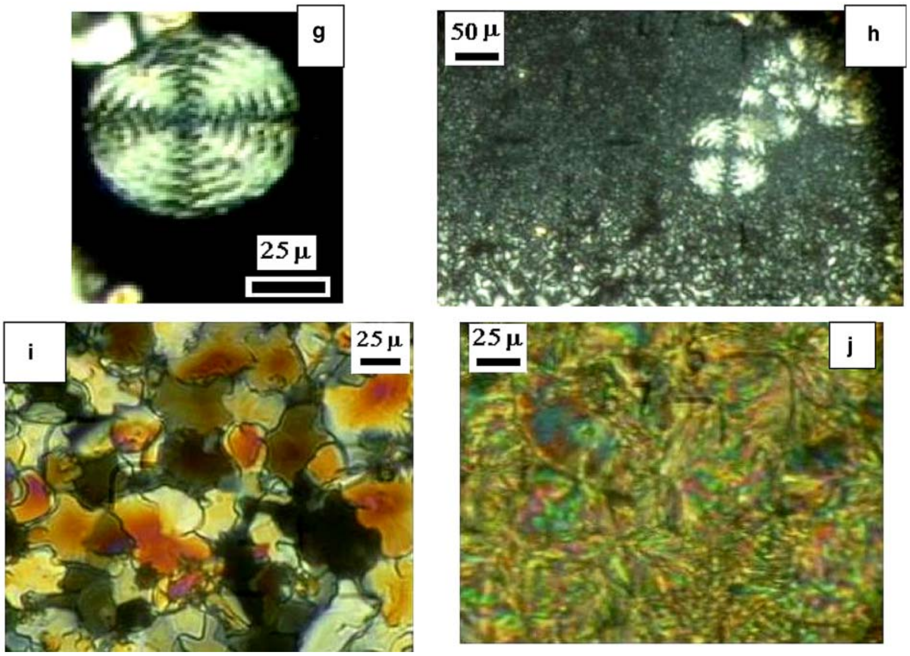


Fig. 4 (*continued*)

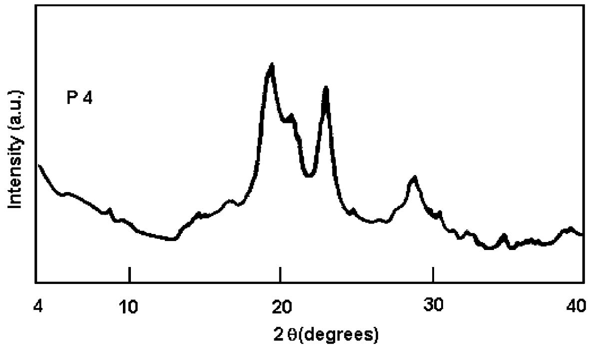


Fig. 5. WAXD diffractogram of polymer **P4** at room temperature.

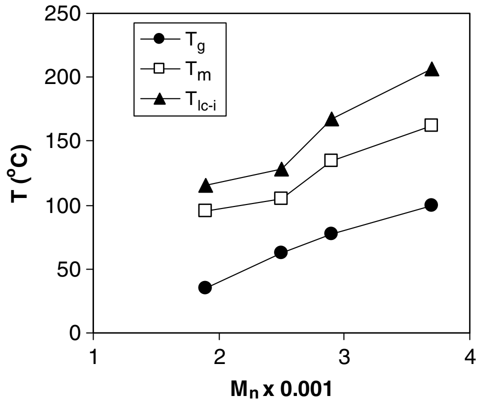


Fig. 6. The dependence of transition temperatures (T_g, T_m, $T_{lc\text{-}i}$) on the molecular weight for polymers **P1–P4**.

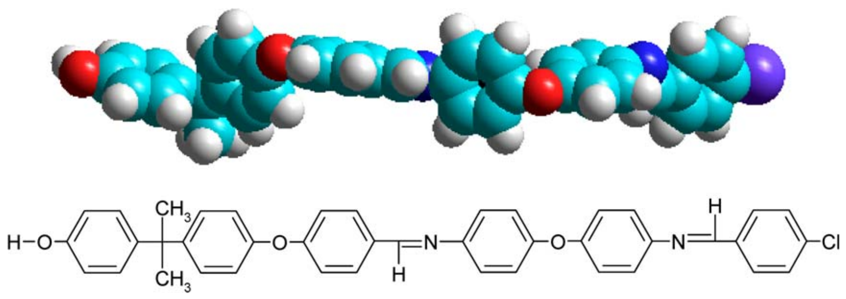


Fig. 7. Model molecule used for simulation of geometry conformation of poly(azomethine-ether)s.

4. Conclusions

A new poly(azomethine-ether) derived from an azomethine monomer 4,4′-oxy-bis(4-chlorobenzilideneiminophenylene) and bisphenol A was prepared in order to obtain more information about properties of polyazomethines containing bisphenol A, the relationship between molecular structure and mesomorphic behaviour in polyazomethines having different molecular weight.

Although the bisphenol A are not favourable for liquid crystalline behaviour, due to its structural and geometric features, thermotropic properties occurred when it was incorporated into polymeric backbone.

The melting and isotropization temperatures strongly decreased when the relatively rigid geometry of mesogenic monomer **M** is disturbed by the introduction of kinked units of bisphenol A and allowed us to obtain mesomorphic behaviour within rather large temperature range. The incorporation of bisphenol A by ether linkages into the main chain of a polymer is a suitable way for decreasing the transition temperatures.

When comparing four fractions of the poly(azomethine-ether)s, the effect of the length of the macromolecular chain on the thermotropic behaviour was proved to be significant. In addition, the polymers present good solubilities in common organic solvents, due to the presence of the bulky bisphenol A units.

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