This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Liquid crystalline polymers V. Thermotropic liquid crystalline poly(azomethine-ether)s containing a cycloalkanone moiety in the polymer backbone

Kamal I. Aly; Ragaa A. Ahmed

Online publication date: 06 August 2010

To cite this Article Aly, Kamal I. and Ahmed, Ragaa A.(2000) 'Liquid crystalline polymers V. Thermotropic liquid crystalline poly(azomethine-ether)s containing a cycloalkanone moiety in the polymer backbone', Liquid Crystals, 27: 4, 451 — 458

To link to this Article: DOI: 10.1080/026782900202633

URL: http://dx.doi.org/10.1080/026782900202633

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

LIQUID CRYSTALS, 2000, VOL. 27, NO. 4, 451–458

Liquid crystalline polymers V. Thermotropic liquid crystalline poly(azomethine-ether)s containing a cycloalkanone moiety in the polymer backbone

KAMAL I. ALY* and RAGAA A. AHMED

Polymer Lab. 507, Chemistry Department, Faculty of Science, Assiut University,
Assiut 71516 Egypt

(*Received 17 August 1999; accepted 12 November 1999*)

A new homologous series of thermotropic liquid crystalline poly(azomethine-ether)s was synthesized by solution polycondensation of various diformyl-α,ω-diphenoxyalkanes, **I–VIII** with 2,5-bis(*m*-aminobenzylidene)cyclopentanone, **XI** and 2,6-bis(*m*-aminobenzylidene)cyclohexanone, **XII**. The inherent viscosities of the polymers were in the range 0.34–0.75 $\mathrm{dl\,g^{-1}}$. The mesomorphic properties were studied as a function of the diphenoxyalkane spacer length. Analyses by DSC and optical polarized microscopy demonstrated that the poly(azomethine-ether)s form nematic mesophases over wide temperature ranges. The poly(azomethine-ether)s based on the cyclohexanone moiety had better thermal stabilities than the corresponding poly(azomethine-ether)s based on cyclopentanone.

1. Introduction

Polymers incorporating mesogenic moieties in the main chain are known to exhibit liquid crystalline behaviour. The direct study of mesomorphic homopolymers is however frequently hampered by their high melting points. Lowering of the solid crystal to liquid crystal transition temperature may be effected by separation of the rigid mesogenic moieties with regularly spaced sequences of flexibilizing groups or by copolycondensation [1–4]. However, most wholly aromatic poly(azomethine)s have high softening temperatures which make melt spinning and injection moulding impracticable [5–8]. These polymers may start to decompose before reaching the melting point. One method for lowering the high melting point of rod-like polymers is to introduce flexible aliphatic units into the main chain [9]. This lowering may be also achieved by using substituent groups to reduce the coplanarity of adjacent mesogenic groups, thereby increasing the diameter or decreasing the axial ratio of the mesogenic units [10].

Morgan *et al.* [11] described the preparation and properties of a variety of wholly aromatic melt-anisotropic poly(azomethine)s. However, a literature survey revealed that few poly(azomethine-ether)s had been synthesized [12–14]. The first poly(azomethine-ether)s were prepared by Guillon and Skoulios [12] from benzidine and 4,4′-diformyl-α,ω-diphenoxydecane. Also, terephthalaldehyde was reacted with 4,4′-diamino-α,ω-diphenoxyalkanes to obtain poly(azomethine-ether)s [13]. Li and Chang [15] synthesized a series of poly(azomethine-ether)s by the condensation of 1,4 phenylenediamine and 4,4′-diformyl-α,ω-diphenoxyalkane derivatives and studied their LC properties.

In continuation of our interest in the study of the liquid crystal properties of arylidene polymers, we wish to report here a route for the synthesis of some new poly(azomethine-ether)s containing cyclohexanone or cyclopentanone moieties in the main chain by the simple solution polycondensation of 2,5-bis(*m*-aminobenzylidene)cyclopentanone, **XI** or 2,6-bis(*m*-aminobenzylidene)cyclohexanone, **XII** with two series of diformyldiphenoxyalkane derivatives under mild conditions. The major purpose of this work was to examine these systems for liquid crystallinity, and in addition to characterize them for thermal stability, solubility, and spectroscopy.

2. Experimental procedure

2.1. *Measurements*

Infrared spectra in the range 4000–600 $\mathrm{cm^{-1}}$ of solid samples of the synthesized monomers and polymers were obtained using KBr discs and a Schmidzu 2110 PC scanning spectrophotometer. The inherent viscosities were measured with an Ubbelohde viscometer using solutions in concentrated sulfuric acid at 25°C ($c = 0.5\,\mathrm{g\,l^{-1}}$). ^{1}H NMR Spectra were run on a GNM-LA 400 MHz NMR spectrophotometer at room temperature with DMSO or CHCl$_3$ as solvent and using TMS as an internal reference. Thermal gravimetric analyses (TGA)

---

*Author for correspondence; e-mail: k.i.aly@aun.eun.eg

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2000 Taylor & Francis Ltd
http://www.tandf.co.uk/journals/tf/02678292.html

of the polymers were carried out in air using a Du Pont 2000 thermal analyser at a heating rate of 10°C min^{-1}. Differential scanning calorimetry (DSC) was carried out in a nitrogen atmosphere using a Schmidzu TA 501 thermal analyser. The maxima of the melting endotherms were taken to be the melting points. The isotropization temperatures were determined by observing the polymer melts with a polarizing microscope, Carl-Zeiss (Jena) equipped with a hot-stage Chaixmeca (Nancy, France). The temperature at which initial formation of the isotropic phases occurred was taken as the isotropization temperature T_i. At the same time, the optical textures of the polymer melts were closely examined to determine the nature of the mesophases. Electronic spectra were recorded for solutions in conc. H_2SO_4 in the region 250–500 nm with a Shimadzu 2110 PC scanning spectrophotometer.

2.2. *Reagents and solvents*

p-Hydroxybenzaldehyde (Aldrich) was used without purification. 4-Hydroxy-3-methoxybenzaldehyde (vanillin) (EL-Nassr Chemical Company, Egypt) was used as supplied. Dihaloalkanes (Aldrich) were used without purification. Cyclohexanone and cyclopentanone (Merck) were freshly distilled: cyclohexanone (b.p. 155°C) and cyclopentanone (b.p. 130–131°C). *m*-Nitrobenzaldehyde (Fluka) m.p 54–57°C was used without purification. Ethanol (95%) and all other solvents were of high purity but were further purified by standard methods [16].

2.3. *Monomer syntheses*

4,4′-Diformyl-α,ω-diphenoxyalkanes **I–IV** and 4,4′-diformyl-2,2′-dimethoxy-α,ω-diphenoxyalkanes **V–VIII** were prepared as described in the literature [17]. Arylidene monomers were synthesized as described in our previous work [18].

2.4. *Polymerization*

A typical example of the polycondensation for poly(azomethine-ether)s **XIIIa–h** and **XIVa–h** is now described.

2,6-Bis(*m*-aminobenzylidene)cyclohexanone **XII** (0.3045 g, 1 mmol) was dissolved in absolute ethanol (20 ml) and to the solution was added the dialdehyde **I** (0.2704 g, 1 mmol) at 25°C. The mixture was then stirred at this temperature for 20 min under dry nitrogen, and then at ~ 80°C for 2–3 h; during this time, the viscosity of the solution increased rapidly and the polymer began to precipitate in the early stages of the reaction. The polymer precipitate was isolated by filtration, then washed with hot methanol and hot acetone and dried in vacuum. The yield was 85%. The inherent viscosity was 0.71 dI g^{-1}, measured at a concentration of 0.5 g dl^{-1} in conc. H_2SO_4 at 25°C. IR (KBr): 1690 cm^{-1} (C=O of cyclohexanone) and at 1620–1605 cm^{-1} (C=C of benzylidene and CH=N of azomethine overlapping). All the other poly(azomethine-ether)s were synthesized by an analogous procedure. The yields, inherent viscosities, and some physical properties of the poly(azomethine-ether)s are listed in tables 1 and 2.

3. Results and discussion

3.1. *Synthesis of poly(azomethine-ether)s*

The present work had as its aim the synthesis of new thermotropic liquid crystal poly(azomethine-ether)s **XIIIa–h** and **XIVa–h** by the solution of polycondensation of the two arylidene monomers **XI** and **XII** with the two

Table 1. Elemental analyses, yields, and inherent viscosities of poly(azomethine-ether)s **XIIIa–h**.

					Elemental analyses		
Polymer **XIII**	Yield/%	$\eta_{inh}{}^{a}$/dI g^{-1}	Molecular formula (mol.wt)		C/%	H/%	N/%
a	79	0.38	$C_{35}H_{28}N_2O_3$	Calc.	80.12	5.38	5.34
			(524.21)	Found	78.35	5.02	4.98
b	83	0.62	$C_{37}H_{32}N_2O_3$	Calc.	80.41	5.84	5.07
			(552.67)	Found	79.13	5.64	4.75
c	95	0.54	$C_{39}H_{36}N_2O_3$	Calc.	80.65	6.25	4.83
			(580.27)	Found	78.95	6.13	4.32
d	68	0.48	$C_{43}H_{44}N_2O_3$	Calc.	81.09	6.97	4.40
			(636.36)	Found	80.32	6.49	4.19
e	85	0.75	$C_{37}H_{32}N_2O_5$	Calc.	76.01	5.52	4.79
			(584.67)	Found	74.33	5.18	4.22
f	91	0.49	$C_{39}H_{36}N_2O_5$	Calc.	76.45	5.92	4.57
			(612.73)	Found	75.12	5.43	4.19
g	77	0.57	$C_{41}H_{40}N_2O_5$	Calc.	76.85	6.29	4.37
			(640.78)	Found	75.47	5.96	4.09
h	82	0.34	$C_{45}H_{48}N_2O_5$	Calc.	77.56	6.94	4.02
			(696.89)	Found	75.89	6.34	3.44

[a] Measured for solutions in concentrated sulphuric acid, with $c = 0.5$ g/100 ml at 25°C.

Table 2. Elemental analyses, yields and inherent viscosities of poly(azomethine-ether)s **XIVa–h**.

				Elemental analyses			
Polymer **XIV**	Yield/%	$\eta_{inh}{}^{a}$/dl g^{-1}	Molecular formula (mol.wt)n		C/%	H/%	N/%
a	85	0.71	$C_{36}H_{30}N_2O_3$	Calc.	80.26	5.62	5.2
			(538.65)n	Found	78.73	5.33	4.85
b	96	0.56	$C_{38}H_{34}N_2O_3$	Calc.	80.54	6.05	4.94
			(566.7)n	Found	79.67	5.86	4.75
c	78	0.48	$C_{40}H_{38}N_2O_3$	Calc.	80.78	6.44	4.71
			(594.75)n	Found	79.29	6.12	4.22
d	82	0.69	$C_{44}H_{46}N_2O_3$	Calc.	81.20	7.12	4.30
			(650.86)n	Found	80.08	6.86	4.08
e	79	0.36	$C_{38}H_{34}N_2O_5$	Calc.	76.24	5.20	4.68
			(598.70)n	Found	75.83	4.84	5.12
f	83	0.45	$C_{40}H_{38}N_2O_5$	Calc.	76.66	6.11	4.47
			(626.75)n	Found	75.15	5.54	4.06
g	86	0.61	$C_{42}H_{42}N_2O_5$	Calc.	77.04	6.47	4.28
			(654.81)n	Found	76.16	6.11	4.03
h	69	0.57	$C_{46}H_{50}N_2O_5$	Calc.	77.72	7.09	3.94
			(710.91)n	Found	75.87	6.56	3.67

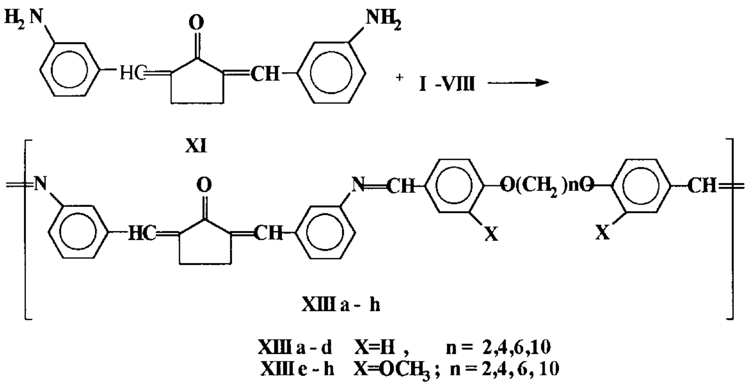
[a] Measured for solutions in concentrated sulphuric acid, with $c = 0.5$ g/100 ml at 25°C.

series of diformyl α,ω diphenoxyalkanes **I–VIII**, because it is a convenient method for the preparation of conjugated polyazomethine arylidene polymers [18].

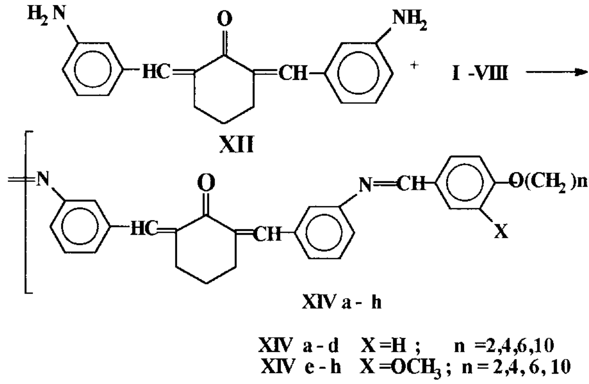
The expected structures of the resulting poly(azomethine-ether)s **XIIa–h** and **XIVa–h** were confirmed from elemental analyses, IR, and ^{1}H NMR. Results for the properties of the polymers are listed in tables 1, 2. The direct polycondensation easily affords high to moderate molecular mass polymers in quantitative yields. The monomers used and the polymers are depicted in schemes 1 and 2.

As mentioned in our previous work [18], the first successful synthesis of high molecular mass, wholly aromatic polyazomethines by the solution polycondensation technique was that reported by Suematsu *et al.* [7]. This was followed by the work of Saegura *et al.* [22] who synthesized a series of polyazomethines containing heterocyclic moieties. Both groups used *m*-cresol as solvent. Hui-Li and Chang [15] prepared a series of poly(azomethine-ether)s in a mixture of *m*-cresol an *o*-chlorophenol at room temperature. In this work, *m*-cresol and *o*-chlorophenol were not the solvents of choice, not only because it was difficult to remove water during the polymerization, but also because the heterogeneity of the reaction medium might have resulted in the formation of low molecular mass polymers. Experimentation led us to believe that ethanol was a better solvent for this purpose, because the monomers easily dissolved in it and poly(azomethine-ether)s with inherent viscosities up to 0.75 dl g^{-1} were readily obtained in high yields after a few minutes. The polycondensation results are summarized in tables 1 and 2.

The results of elemental analyses for the poly(azomethine-ether)s **XIIIa–h** and **XIVa–h** agree with the calculated values as shown in tables 1 and 2. It should be noted that the elemental analysis results for the polymers deviated up to 1.77% from the theoretical values. However, it is not uncommon for polymers to



Scheme 1.



Scheme 2.

trap solvent within the matrix, especially for polymers of high molecular mass and those containing polar groups which are capable of hydrogen bonding with solvent molecules.

Spectral data support the structural assignment for the poly(azomethine-ether)s and the IR data from KBr disks for all the polymers showed characteristic absorptions due to CH stretching of CH_2 groups (aliphatic spacers) at 2940–2860 cm^{-1}; C=O of cyclohexanone and cyclopentanone at 1660–1690 cm^{-1}, C=C and CH=N (azomethine groups) at 1605–1620 cm^{-1}, phenylene rings at 1590–1510 cm^{-1} and C–O–C bonds (ether linkages) at 1235–1275 cm^{-1}. The ^{1}H NMR data for polymer **XIVe** are quoted as an example: (in $CDCl_3$) signals at δ 9.75 (s, 2H of CH=N); at 6.85–7.55 14H Ar–H and (2H, 2CH=C); at 4.5 (s, 4H, $2CH_2$ of $O(CH_2)_2O$); at 3.85 (s, 6H 2 OCH_3); at 0.75–1.65 (*m* 6H, $6CH_2$ cyclohexanone) ppm.

3.2. *Polymer characterization*

The solubility characteristics of the poly(azomethine-ether)s **XIIIa–h** and **XIVa–h** were tested using various solvents including DMF (dimethylformamide), NMP (*N*-methylpyrrolidone), THF (tetrahydrofuran), $CHCl_3$–acetone mixture, TCA (tetrachloroacetylene), methane-sulphonic acid and conc. H_2SO_4. A 5% (w/v) solution was taken as a criterion for solubility. It can be seen from tables 3 and 4 that all the poly(azomethine-ether)s are soluble in protonic acids, e.g. conc. H_2SO_4 and methanesulphonic acid. In polar aprotic solvents, such as DMF, DMSO, or NMP, the polymers showed poor solubility, except polymers **XIIIa,c,d,f** and **XIVa,d,h** which dissolved partially in DMSO. In common organic solvents and halogenated hydrocarbons all the polymers are insoluble.

The electronic spectra of selected examples, namely polymers **XIIIa,b,g** and **XIVb,e,f** were obtained for conc. H_2SO_4 solutions at a concentration of 2.6×10^{-6} M. The electronic spectra showed absorption band broadening and also small bathochromic shifts with λ_{max} near 225–284 nm due to π-π* transitions within the benzenoid system and at λ_{max} near 339–474 nm due to π-π* transition of C=C groups.

3.3. *Liquid crystal behaviour of poly(azomethine-ether)s XIIIa–h and XIVa–h*

The liquid crystalline properties of the poly(azomethine-ether)s **XIIIa–h** and **XIVa–h** were investigated by combined DSC, TGA and optical polarized microscopy (OPM) analyses. It is concluded that poly(azomethine-ether)s **XIIIa–h** and **XIVa–h** except **XIIIa,b,e** and **XIVa,e** exhibit thermotropic liquid crystalline properties. The

Table 3. Solubility characteristics of poly(azomethine-ether)s **XIIIa–h**. ++: Soluble at room temperature (RT). +: Partially soluble at RT. —: Insoluble.

Polymer **XIII**	DMSO	DMF	NMP	THF	$CHCl_3$ + acetone (1:1)	TCA	Conc. H_2SO_4	Methane sulphonic acid
a	+	—	—	—	—	—	++	++
b	—	—	—	—	—	—	++	++
c	+	+	—	—	—	+	++	++
d	+	+	+	+	+	—	++	++
e	—	—	—	—	—	+	++	++
f	+	+	+	+	++	++	++	++
g	—	—	—	—	—	—	++	++
h	++	+	+	+	++	++	++	++

Table 4. Solubility characteristics of poly(azomethine-ether)s **XIVa–h**. ++: Soluble at room temperature (RT). +: Partially soluble at RT. —: Insoluble.

Polymer **XIV**	DMSO	DMF	NMP	THF	$CHCl_3$ + acetone (1:1)	TCA	Conc. H_2SO_4	Methane sulphonic acid
a	+	—	—	—	—	—	++	++
b	—	—	—	—	—	—	++	++
c	—	—	—	—	—	+	++	++
d	+	+	+	+	+	—	++	++
e	—	—	—	—	—	+	++	++
f	—	—	—	—	+	++	++	++
g	—	—	—	+	+	+	++	++
h	+	+	+	+	+	+	++	++

isotropization temperatures of these polymers was also observed by using a polarizing microscope equipped with a heating stage in the temperature range of 318°C. The relevant results are presented below.

3.3.1. *DSC analyses*

The DSC measurements conducted at a heating and cooling rate of 10°C min^{-1} yielded the following information. The DSC heating curves of poly(azomethine-ether)s **XIIIa–h**, based on cyclopentanone as the pendant group, showed a set of endothermic transitions, of which the lowest temperature peak always corresponded to a solid → solid transition, whereas the highest temperature peak was due to the melting transition [19]. Figure 1 shows the DSC profiles of the melting process of sample **XIIIf** which revealed multiple endotherms at 168 (T_g), 228 and at 270°C, also probably with decomposition. When the sample was cooled after preheating to 450°C, there were no exothermal or endothermal peaks. On a second heating cycle there was an exotherm at 330°C. Figure 2 shows the DSC profiles of the melting process of sample **XIVf** which revealed multiple endotherms on the DSC thermogram at 110 (T_g), 175, and 263°C and an exotherm at 423°C, probably due to decomposition. When the sample was cooled after preheating to 450°C, there were no exothermal or endothermal peaks. On a second heating cycle there was an exotherm at 356°C.

The effect of spacer length on the thermal properties of the poly(azomethine-ether)s **XIIIa–h** is shown in table 5, while table 6 shows the same effect for the polymers **XIVa–h**; both melting point and isotropization temperature decreased as the length of the flexible aliphatic spacer in the polymer chain increased. The effect of substituents on the thermal properties of polymers **XIIIa–h** and **XIVa–h** is also shown in tables 5 and 6; both the melting point and the isotropization temperature were decreased by the introduction of methoxy groups into the polymer main chain [20]. Similar

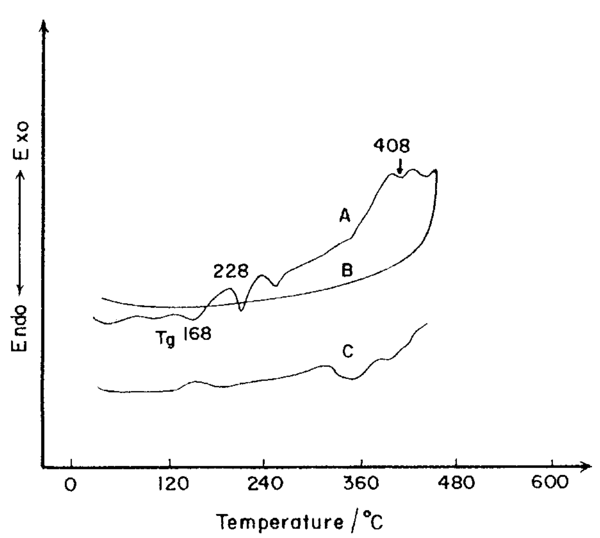


Figure 1. DSC thermograms of polymer **XIIIf** with heating and cooling rate 10°C min. (*a*) First heating (*b*) first cooling (*c*) second heating.

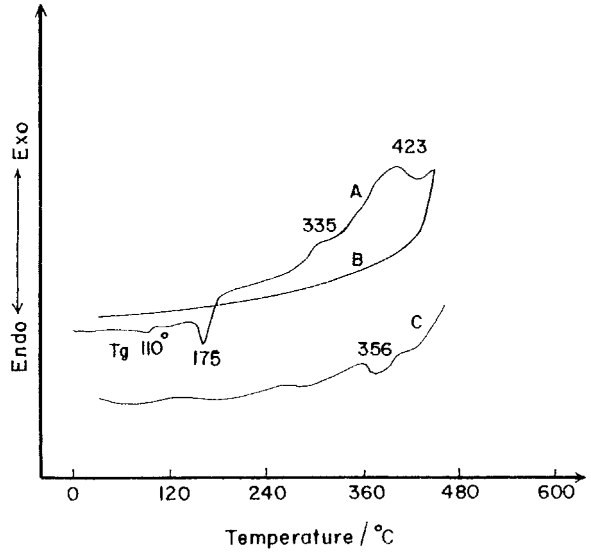


Figure 2. DSC thermograms of polymer **XIVf** with heating and cooling rate 10°C min. (*a*) First heating (*b*) first cooling (*c*) second heating.

Table 5. Transition behaviour of poly(azomethine-ether)s **XIIIa–h**.

				Anisotropic melt[a]		Weight loss temp./°C[b]	
Polymer **XIII**	*n*	*X*	Stirred opalescence	$T_m - T_i$/°C	ΔT/°C	5%	10%
a	2	H	None	—		297	316
b	4	H	None	—		305	338
c	6	H	Strong	231–257	26	298	342
d	10	H	Strong	228–295	67	285	325
e	2	OCH_3	None	—		310	345
f	4	OCH_3	Strong	185–263	78	295	330
g	6	OCH_3	Strong	205–310	105	303	325
h	10	OCH_3	Strong	195–276	81	280	310

[a] Measured using a polarizing microscope equipped with a heating stage.
[b] From TGA in air with heating rate 10°C min^{-1}.

Table 6. Transition behaviour of poly(azomethine-ether)s **XIVa–h**.

				Anisotropic melt[a]		Weight loss temp./°C[b]	
Polymer **XIV**	*n*	*X*	Stirred opalescence	$T_m - T_i$/°C	ΔT/°C	5%	10%
a	2	H	None	—		335	355
b	4	H	Strong	218–257	39	325	346
c	6	H	Strong	230–310	80	318	339
d	10	H	Strong	236–318	82	307	328
e	2	OCH_3	None	—		320	358
f	4	OCH_3	Strong	214–270	56	339	352
g	6	OCH_3	Strong	226–291	65	326	347
h	10	OCH_3	Strong	235–285	50	338	363

[a] Measured using a polarizing microscope equipped with a heating stage.
[b] From TGA in air with heating rate 10°C min^{-1}.

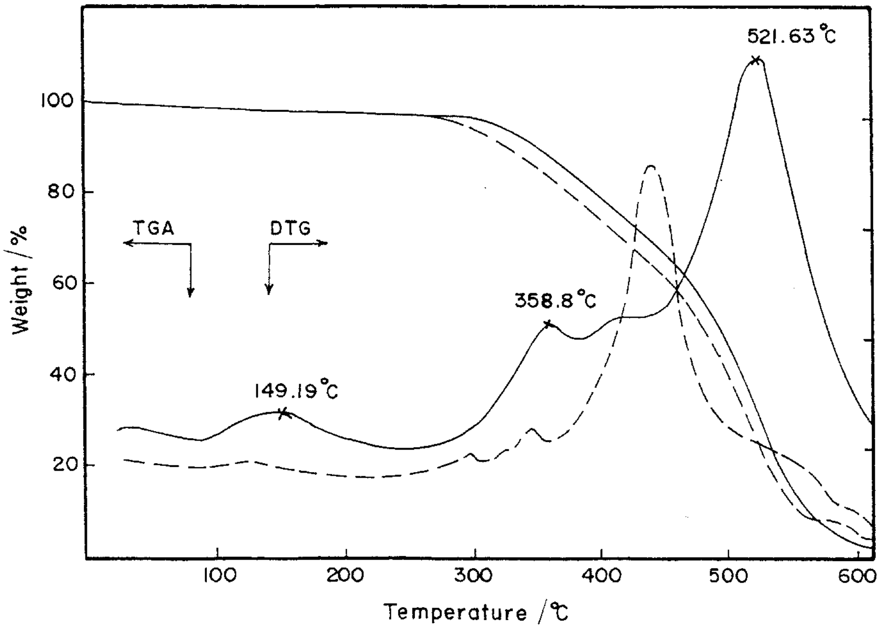


Figure 3. TGA and DTG thermograms of poly(azomethine-ether)s **XIIIf** (---) and **XIVf** (—) in air, heating rate 10°C min.

observations were reported in previous work [21]. It is known that substituents can reduce the coplanarity of adjacent mesogenic groups and increase the diameter or decrease the axial ratio of the mesogenic units [10]. Thus, the unsubstituted *para*-linked poly(azomethine-ether) **XIIIb** is infusible below its decomposition temperature, but fusibility is achieved by the introduction of a methoxy group in the benzene ring. The introduction of a methoxy group into the mesogenic moiety lowers the transition temperatures, but, of course, also decreases the orientational interactions thereby decreasing the mesophase stability [15]. In DSC studies, in some cases the peaks are broadened, especially in polymers **XIIIa–h** based on cyclopentanone, and this is attributed to overlapping with thermal decomposition temperature. For this reason, the isotropization temperatures of the polymers were obtained by observing the textures of the melt using the polarizing microscope.

3.3.2. *TGA measurements*

The thermal behaviour of the poly(azomethine-ether)s **XIIIa–h** and **XIVa–h** was evaluated by TGA and DTG in air at a heating rate of 10°C $\min^{-1}$. The thermographs of selected examples from these polymers are given in figure 3, while tables 5 and 6 give the temperatures for various % weight loss. The initial decomposition of these polymers (5% loss) started at 285°C for series **XIIIa–h**, and at 307°C for series **XIVa–h**. All the polymers

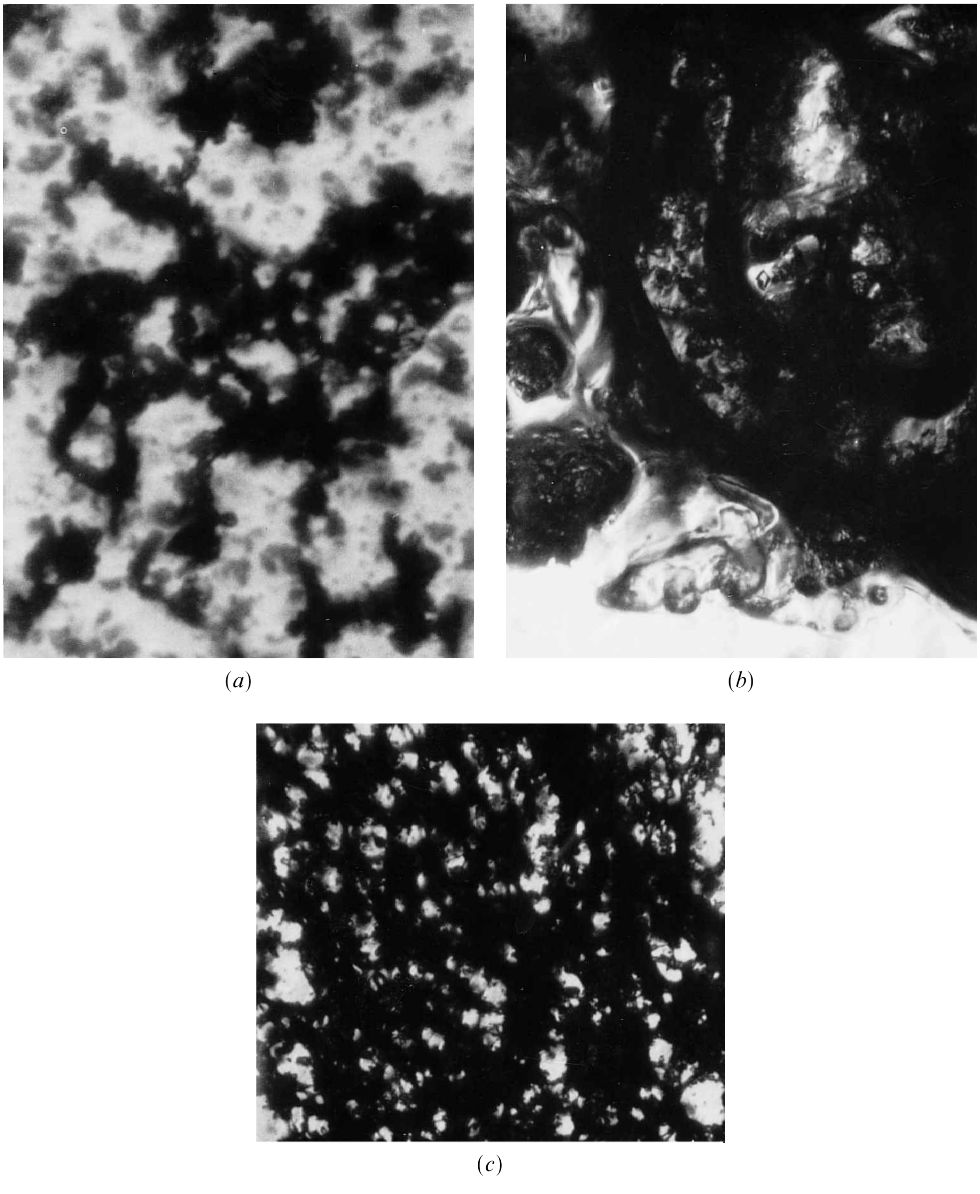

(*a*) (*b*) (*c*)

Figure 4. Photomicrographs of polymer **XIVf** in a heating cycle at (*a*) 200°C (before melting), (*b*) 270°C, (*c*) after cooling (magnification × 217).

showed similar decomposition patterns. The expected nature of the decomposition of these polymers is through pyrolytic oxidation of C=C and rupture of many bonds. The temperature for 10% weight loss is considered to be the polymer decomposition temperature [23]; it occurs in the range 310–345°C for polymers **XIIIa–h** and 328–362°C for polymers **XIVa–h**. In figure 3, mass loss is seen to be rapid between ∼300–480°C for polymer **XIVf** in the first region, and between 485∼550°C in the second region. For polymer **XIIIf**, the mass loss was rapid between ∼285–545°C in the first region and between 455–545°C in the second region. Unexpectedly, series **XIVa–h**, based on cyclohexanone, is higher in thermal stability than the first series **XIIIa–h**, based on cyclopentanone, although the latter polymers are more rigid than the former.

3.3.3. *Birefringence texture*

To support further the information gained by DSC on the thermotropic behaviour of the polymers, qualitative observation of the textures between crossed polarizers was carried out for polymers **XIIa–h** and **XIVa–h**. Optical microscopy showed that all the polymers melt to give viscous, birefringent liquid crystal phases (figure 4) except polymers **XIIIa**,**b**,**e** and **XIVa**,**e**. The molten polymers **XIIIa**,**b**,**e** and **XIVa**,**e** did not show any birefringence, providing direct evidence for the absence of mesomorphic behaviour for these polymers. The temperatures for T_m and T_i correspond roughly with those observed by DSC; differences may be due to variations in heating rates. The textures observed were generally grey, although annealing samples for long periods led to the formation of well developed schlieren textures [24].

4. Conclusions

Two novel series of liquid crystalline poly(azomethine-ether)s containing either cyclohexanone or cyclopentanone moieties have been synthesized. A solution polycondensation technique at ∼80°C was used. The majority of the polymers reported exhibited thermotropic nematic phases. Both the T_m and T_i values increased as the length of the flexible aliphatic spacers increased and decreased with introduction of the methoxy group as a substituent in the polymer main chain.

References

[1] Janneli, P., Roviello, A., and Sirigu, A., 1982, *Eur. polym. J.*, **18,** 745.

[2] Blumstein, A., Vilasagar, S., Pontrathnam, S., Clough, S. B., and Blumstein, R. B., 1982, *J. polym. Phys. Ed.*, **20,** 877.

[3] Jin, J. I., Antoun, S., Ober, C., and Lenz, R. W., 1980, *Br. polym. J.*, **12,** 132.

[4] Sek, D., 1984, *Eur. polym. J.*, **20,** 923.

[5] Adams, R., Bullock, R. E., and Wilson, W. C., 1923, *J. Am. chem. Soc.*, **45,** 521.

[6] D'Alelio, G. F., 1969, *Encyclopedia of Polymer Science and Technology*, Vol. 10, p. 659.

[7] Suematsu, K., Nakamurra, K., and Takeda, J., 1983, *Colloid polym. Sci.*, **261,** 493.

[8] Sek, D., 1982, *Polym. J.*, **14**(3), 173.

[9] Roviello, A., and Sirigu, A., 1975, *J. polym. Sci., polym. Edn.*, **13,** 455.

[10] Ober, C. K., Jin, J. I., and Lenz, R. W., 1984, *Liquid Crystal Polymer*, Vol. I (Berlin: Springer-Verlag), p. 103.

[11] Morgan, P. W., Kwolek, S. L., and Pletcher, T. C., 1987, *Macromolecules*, **20,** 729.

[12] Guillon, D., and Skoulios, A., 1978, *Mol. Cryst. liq. Cryst.*, **49,** 119.

[13] Milland, B., Thierry, A., Strazielle, C., and Skoulios, A., 1979, *Mol. Cryst. liq. Cryst.*, **49,** 299.

[14] Wojtkowski, P. W., 1987, *Macromolecules*, **20,** 740.

[15] Li, C. H., and Chang, T. C., 1991, *Eur. polym. J.*, **27,** 35.

[16] Perrin, D. D., Armarego, W. L. F., and Perrin, D. R., 1980, *Purification of Laboratory Chemicals*, 2nd Edn (New York: Pergamon).

[17] Date, R. W., Imrie, C. T., Luckhurst, G. R., and Seddon, J. M., 1992, *Liq. Cryst.*, **12,** 203.

[18] Aly, K. I., and Kalaf, A. A., 2000, *J. appl. polym. Sci.*, A37, 1 proof.

[19] Galli, G., Laus, M., Angeloni, A. S., Ferruti, P., and Chiellini, E., 1985, *Eur. polym. J.*, **21,** 727.

[20] Ozcayier, Y., and Blumstein, A., 1986, *J. polym. Sci. chem. Edn.*, **24,** 1217.

[21] Aly, K. I., *J. macromol. Sci. A Chem.* (to be published).

[22] Saegusa, Y., Kashikawa, T., and Nakamura, S., 1992, *J. polym. Sci. chem. Edn.*, **30,** 1369.

[23] Aly, K. I., 1998, *Polym. Int.*, **47,** 483.

[24] Demus, D., and Richter, L., 1978, *Textures of Liquid Crystals* (Weinheim: Verlag Chemie).