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Thermotropic Liquid Crystalline Poly(Azomethine-Ether)s Containing Dibenzylidene Derivatives in the Main Chain

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A new homologous series of thermotropic liquid crystalline poly (azomethine-ether)s based on dibenzylidene derivatives were synthesized by solution polycondensation of various diformyl- α,ω -diphenoxyalkanes, I–VIII with 2,6-bis(m-aminobenzylidene)-4-phenylcyclohexanone X, and characterized by ¹H-NMR, IR and elemental analyses. The inherent viscosities of the polymers were in the range 0.29–0.58 dl/g. All the poly (azomethine-ether)s were insoluble in common organic solvents but dissolved completely in concentrated H₂SO₄ and methanesulphonic acid. The mesomorphic properties were studied as a function of the diphenoxyalkane space length. Analysis by DSC and optical polarized microscopy demonstrated that the poly (azomethine-ether)s from nematic mesophases over wide temperature ranges.

Keywords poly(azomethine-ether)s, dibenzylidene, thermotropic, texture observation

Introduction

Thermotropic (heat-induced) liquid crystalline behavior of polymeric materials is of considerable current interest, not only because of their potential as high-strength fibers, plastics, moldings, etc. (1–3), but also because of their unique position in the theoretical scheme of structural order in fluid phases (4). Morgan et al. (5) described the preparation and properties of a variety of wholly aromatic melt-anisotropic poly (azomethine)s. However, a literature survey revealed that many poly(azomethine-ether)s had been synthesized (6–11). The first poly(azomethine-ether)s were prepared by Guillon and Skoulios (6) from benzidine and 4,4'-diformyl- α,ω -diphenoxy-decane. Also, terephthalaldehyde was reacted with 4,4'-diamino- α,ω -diphenoxyalkanes to obtain poly(azomethine-ether)s (7). Li and Chang (12) 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 liquid crystalline (LC) properties. The first successful synthesis of high molecular mass, wholly aromatic polyazomethines by the solution polycondensation technique, was that reported by Suematsu et al. (13). This was followed by the work of Saegusa et al. (14) who synthesized a series of polyazomethines containing heterocyclic

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moieties. In continuation of our interest in the study of the liquid crystal properties of arylidene polymers (15), we wish to report here a route for the synthesis of some new poly(azomethine-ether)s containing dibenzylidene derivatives in the main chain by the simple solution polycondensation of 2,6-bis(*m*-aminobenzylidene)-4-phenylcyclohexanone X with two series of diformyl-diphenoxyalkane derivatives under mild conditions. The liquid crystallinity of the systems was examined.

Experimental

Reagents and Solvents

p-Hydroxybenzaldehyde (Aldrich), 4-hydroxy-3-methoxybenzaldehyde (Aldrich) 4-phenylcyclohexanone (Merck), nitrobenzaldehyde (Fluka) m.p. 54–57°C and dihaloalkanes (Aldrich) were used without purification. Ethanol (95%), and all other solvents were of high purity but were further purified by standard methods (16).

Measurements

Infrared spectra in the range 4000–600 cm⁻¹ of solid samples of the synthesized monomers and polymers were obtained using KBr discs and a Shimadzu IR-470 scanning spectrophotometer. The ¹H-NMR spectra were recorded on a GNM-LA 400 MHz NMR spectrophotometer and a Varian EM-390 90 MHz NMR spectrophotometer at room temperature in DMSO or (CF₃COOH) using TMS as the internal reference. The inherent viscosities were measured with an Ubbelohde viscometer using a solution in DMF at 25°C (0.5 g/L). Thermogravimetric analysis (TGA) and differential thermal gravimetry (DTG) of the polymers were carried out in air using a DuPont 2000 thermal analyzer at a heating rate of 10°C·min⁻¹. Differential scanning calorimetry (DSC) analysis was carried out in a nitrogen atmosphere using a Shimadzu DSC-50 thermal analyzer. 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 (Ti). 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 H₂SO₄ in the region of 250–500 nm with a Shimadzu 2110C scanning spectrophotometer.

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).

2,6-Bis(*m*-nitrobenzylidene)-4-phenylcyclohexanone (IX)

A 250 ml flask was charged with a mixture of *m*-nitrobenzaldehyde (40 mmol), 4-phenylcyclohexanone (20 mmol), and ethanol (95%, 100 ml). The mixture was warmed at about 50°C. A few drops of KOH as a catalytic (20%) were added with stirring. An exothermic reaction was observed while a highly yellowish solid was precipitated. It was filtered off, washed thoroughly with water, and dried to afford monomer IX. A purified sample

(mp 163°C, 95% yield) was obtained in the form of yellow crystals by recrystallization from ethanol. Anal. Calcd. for $C_{26}H_{20}O_5N_2$: C, 71.07; H, 4.32; N, 6.37%. Found: C, 71.15; H, 4.03; N, 6.94%. IR (KBr, cm^{-1}): 2990 (cyclohexanone C-H stretching); 1660 (C=O); 1600 (C=C); 1340, 1530 (NO_2); 1435 (cyclohexanone C-H deformation). 1H -NMR (DMSO- d_6 , ppm): 7.2–8.1 (m, 13H of Ar-H and 2H of 2CH=C), 3.1 (4H of 2CH₂ of cyclohexanone).

2,6-Bis(m-aminobenzylidene)-4-phenylcyclohexanone (X)

A flask was charged with a mixture of compound IX (3.22 g, 8.52 mmol), ethanol (95% 40 ml), and a catalytic quantity of 10% palladium on activated carbon. Hydrazine hydrate (4 ml) diluted with ethanol (10 ml) was added dropwise to the stirred mixture at 60°C. It was subsequently kept at this temperature for 30 min. The solid gradually dissolved during hydrogenation. The reaction mixture was filtered off and the filtrate was concentrated by a rotary evaporation. The residue was dried in a vacuum oven to yield a compact pale yellow solid. An analytical sample was obtained by recrystallization from ether/THF (1 : 1) in the form of yellowish crystals (m.p. 110°C, 90% yield). Analysis Calculated for $C_{26}H_{24}ON_2$: C, 82.32; H, 6.06; N, 7.38%. Found: C, 82.11; H, 6.63; N, 7.54%. IR (KBr, cm^{-1}): 3390–3195 (NH stretching); 2850–2940 (C-H of cyclohexanone); 1685 (C=O of cyclohexanone); 1600 (C=C); 680 (NH deformation). 1H -NMR (DMSO- d_6 , ppm): 6.39–7.04 (m, 13H of Ar-H and 2H of 2CH=C); 4.98 (s, 4H of 2NH₂); 2.85–3.3 (m, 4H of 2CH₂ cyclohexanone).

Polymerization

A typical example of the polycondensation for poly(azomethine-ether)s XIa–h is described. The details as follows will be: Bis-(m-aminobenzylidene)-4-phenylcyclohexanone X (0.379 g, 1 mmol) was dissolved in absolute ethanol (20 ml) and to this solution, the dialdehyde I was added (0.270 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, washed with hot methanol and hot acetone and then dried in vacuum. The yield was 84% and the inherent viscosity was 0.58 dLg⁻¹ (measured at a concentration of 0.5 dLg⁻¹ in dimethylformamide at 25°C).

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 were studied.

Results and Discussion

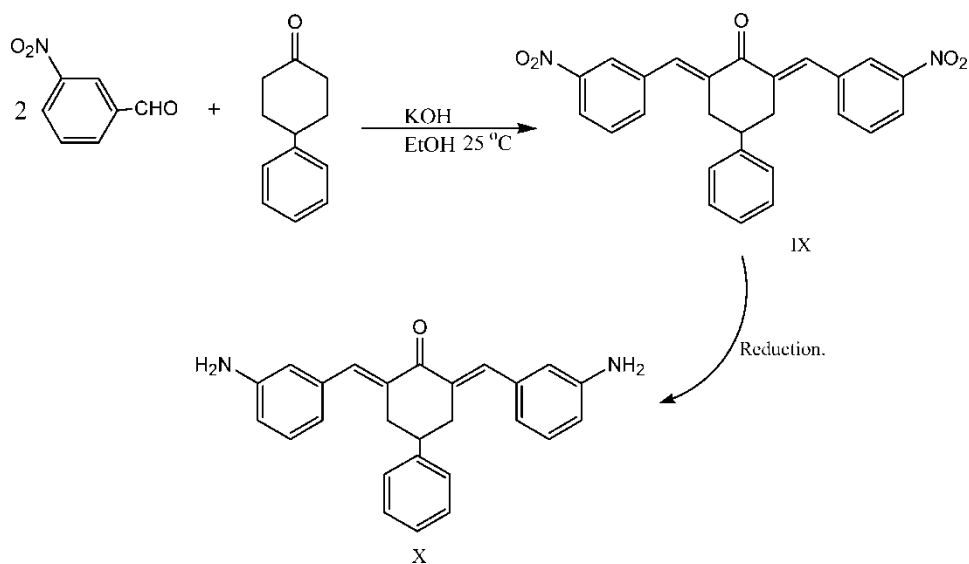
The aim of the present work was the synthesis of new thermotropic liquid crystal poly(azomethine-ether)s XIa–h, by solution polycondensation of the one dibenzylidene monomer X with two series of diformyl- α,ω -diphenoxyalkanes I–VIII. Scheme 1 formulates the methods utilized for the preparation of the diarylidene cycloalkane. As shown, this monomer was prepared by the base-catalyzed condensation of two moles of m-nitrobenzaldehyde with one mole of 4-phenylcyclohexanone followed by hydrogenation using palladium on activated carbon in ethanol at 50°C. This hydrogenation should not be excessively prolonged, because the benzylidene olefinic bonds, as well as

the 4-phenylcyclohexanonecarbonyl group might also be hydrogenated. The IR and $^1\text{H-NMR}$ spectra of these three monomers did not show detectable hydrogenation of these segments under the particular experimental conditions employed. Moreover, a literature survey revealed that hydrogenation of the cyclohexanone carbonyl group requires an acidic medium, a platinum catalyst, and a pressure of 30–45 psi to preferentially give the axial alcohol (18).

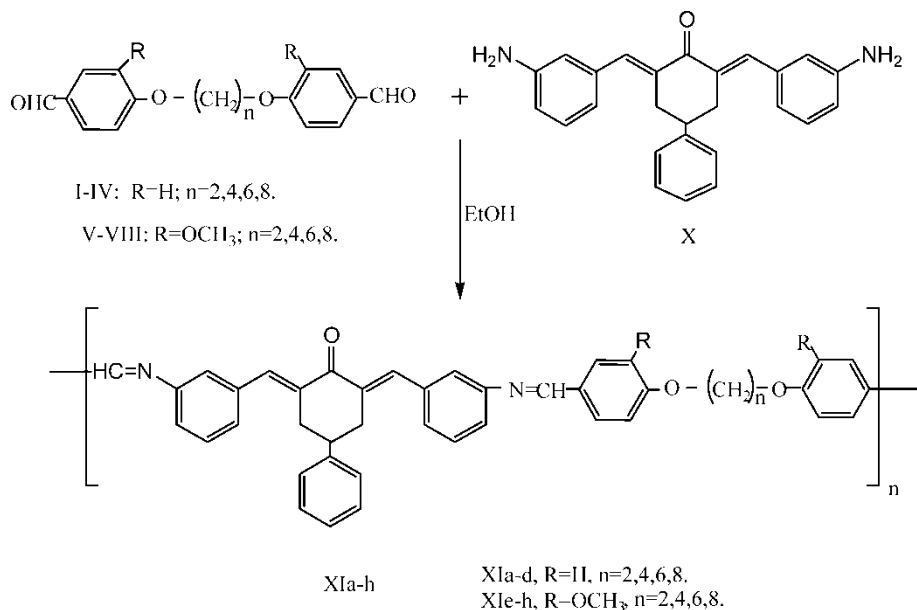
This method was used for the preparation of conjugated polyazomethine arylidene polymers (19). The expected structures of the resulting poly(azomethine-ether)s XIa–h were confirmed by elemental analyses, IR and $^1\text{H-NMR}$ spectra. The monomers used and the polymers are depicted in Schemes 1 and 2.

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 the low molecular mass polymers. Experimentation led us to believe that ethanol was a better solvent for this purpose, because of the monomers easily dissolved in it and poly(azomethine-ether)s with inherent viscosities up to 0.58 dL/g were readily obtained in high yields after a few minutes. The results of elemental analyses for the poly(azomethine-ether)s XIa–h agree with the calculated values.

Spectral data support the structural assignment for the poly(azomethine-ether)s and the IR data from KBr disks for all the polymers showed disappearance of the amino groups at 3300 cm^{-1} and appearance of absorption bands at 1660 cm^{-1} ($\text{CH}=\text{N}$ of azomethine groups). In addition, other characteristic absorption due to CH stretching of CH_2 groups (aliphatic spacers) at $2940\text{--}2860\text{ cm}^{-1}$; $\text{C}=\text{O}$ of cyclohexanone at 1690 cm^{-1} ; $\text{C}=\text{C}$ at $1605\text{--}1620\text{ cm}^{-1}$ phenylene rings at $1590\text{--}1510\text{ cm}^{-1}$ and C-O-C bonds (ether linkages), at $1235\text{--}1275\text{ cm}^{-1}$. The $^1\text{H-NMR}$ data for polymer XIe (in CF_3COOH) showed signals at δ : 4.1–4.3 (s, 6H, 2OCH_3); at 4.6–4.9 (m, 4H, $-(\text{CH}_2)_2-\text{O}-$); at 6.9–8.0 (m, 19-Ar-H, 4H, $2\text{CH}=\text{CH}$ and 2H, $2\text{CH}=\text{N}-$) ppm.



Scheme 1. Synthesis of Monomers IX, X.



Scheme 2. Synthesis of poly(azomethine-ether)s XIa–h.

Polymer Characterization

The solubility characteristics of the poly(azomethine-ether)s XIa–h were tested using various solvents including (dimethylformamide) DMF, (N-methylpyrrolidone) NMP, (tetrahydrofuran) THF, CHCl₃-acetone mixture, methanesulphonic acid, tetrachloroacetylene (TCA), and conc. H₂SO₄. A 5% (w/v) solution was taken as a criterion for solubility. All the poly(azomethine-ether)s are soluble in protonic acids, e.g. (conc. H₂SO₄ and methanesulphonic acid). In polar aprotic solvents, such as DMF, DMSO or NMP, the polymers showed poor solubility (except polymers XIa,c,d,f which dissolved partially in DMSO). In common organic solvents and halogenated hydrocarbon, all the polymers are insoluble (except polymer XIh, is soluble in TCA, while, XI d,g are partially soluble).

The electronic spectra of selected samples of polymers XIa,d were obtained in sulphuric acid at a concentration 2.6×10^{-6} M. The electronic spectra showed absorption broad bands and also small bathochromic shifting with λ_{max} near 270–290 nm due to a $\pi-\pi^*$ transition within the benzenoid system, and with λ_{max} near 300–375 nm due to $\pi-\pi^*$ and $n-\pi^*$ excitation of C=C and C=O groups, respectively.

Thermotropic Liquid Crystalline Properties of Poly(azomethine-ether)s

The thermal properties of poly(azomethine-ether)s XIa–h were characterized by DSC, TGA and optical polarizing microscopy (OMP) at the heating stage. The poly(azomethine-ether)s XIa–h, exhibited melt birefringence and stirred opalescence during polarized microscope observation. The phase transition temperatures of the polymers are shown in Table 1. The isotropic temperature of these polymers was observed by using a polarizing microscope equipped with a heating stage in the temperature range of 274–310°C for the polymers XIa–h. In DSC studies, most of the polymers revealed multiple or more endothermic on DSC thermograms, probably due to polymorphism.

Table 1
Transition behavior of pPoly(azomethine-ether)s XIa–h

Polymer XI	<i>n</i>	X	Stirred opalescence	T _g (DSC) ^a	Phase transition temperature (°C, microscope) ^b			Wt loss, temp. °C ^c	
					T _m	T _i	Δ _T	5%	10%
a	2	H	None	—	—	—	—	295	355
b	4	H	Strong	128	248	310	62	315	360
c	6	H	Strong	125	243	294	51	310	362
d	8	H	Strong	116	238	286	48	295	328
e	2	OCH ₃	None	—	—	—	—	300	340
f	4	OCH ₃	Strong	120	234	281	47	290	335
g	6	OCH ₃	Strong	113	227	277	50	305	333
h	8	OCH ₃	Strong	112	223	274	51	275	330

^aMeasured by DSC.

^bMeasured using a polarizing microscope equipped with a heating stage.

^cFrom TGA in air with heating rate 10°C min⁻¹.

In some cases, the peaks in DSC are broad, with thermal temperature decomposition. For this reason, isotropization temperatures of the polymers were identified by observing the textures of the melts on a cross-polarizing microscope. All the poly(azomethine-ether)s were characterized by DSC measurements except XIa,e,f and conducted at a heating rate of 10°C min. The heating traces of the polymers display a glass-transition (T_g), which is weak in the case of the polymers XI. If the DSC profiles of the melting process of sample XI_f which revealed multiple endotherms at 120.69 (T_g), 230.78 (T_m), 283.51 (T_i) and 360.54°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 endotherm at 388.39°C. This phenomena could be due to solid-to-solid (T_{ss}), solid-to mesophase (T_m) and mesophase to-solid (T_i) transitions (20), which are observed from an optical microscope.

The effect of spacer length on the thermal properties of the poly(azomethine-ether)s XIa–h is shown in Table 1, both melting point and isotropization temperature decrease as the length of the flexible aliphatic spacer in the polymer chain increased. The effect of substituents on the thermal properties of the polymers XIa–h is also shown in Table 1. Both the melting point and the isotropization temperature were decreased by the introduction of methoxy groups into the polymer main chain. Similar observations were reported in previous work (15). 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, 21). Thus, the unsubstituted para-linked poly (azomethine-ether)s is infusible below its decomposition temperature. However, fusibility is achieved by 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 (12). In DSC measurements, the peaks are broadened. In some cases, this is attributed to overlapping with thermal decomposition temperature. For this reason, the isotropization temperature of the polymers was obtained by observing the textures of the melt using the polarizing microscope.

TGA Measurements

TGA and DTG in air at a heating rate of 10°C min⁻¹. The thermographs of selected samples from these polymers are given in Figure 1, while the temperatures for various percentage of are reported (see Table 1). The initial decomposition of these polymers (5% loss) started at 275°C for series XIa–h, and all the polymers showed similar decomposition patterns. The expected nature of the decomposition of these polymers is through pyrolytic oxidation of C=C group and rupture of many bonds. The temperature for 10% wt loss is considered to be the polymer decomposition temperature (11, 22). It occurs in the range 328–362°C for polymers XIa–h and 315–450°C. In Figure 1, mass loss is seen to be rapid between ~300–390°C for the polymer XI_c in the first region, and between 400–550°C in the second region. For the polymer XI_b, the mass loss was rapid between ~300–400°C in the first region and between ~400–490°C in the second region.

Texture Observation

The character of the texture at a given temperature was fixed by quenching it in liquid nitrogen. Micrographs were then obtained on heating to room temperature (not shown). All the samples except XI_a, and XI_e appeared to have low melt viscosities, indicating that the presence of a nematic phase is possible.

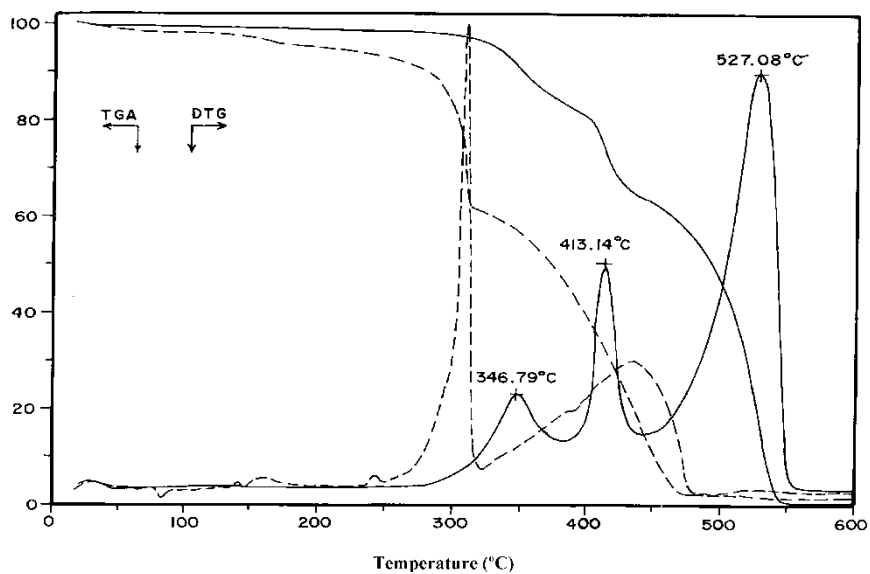
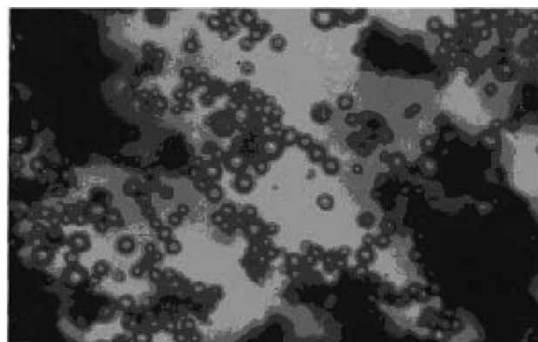
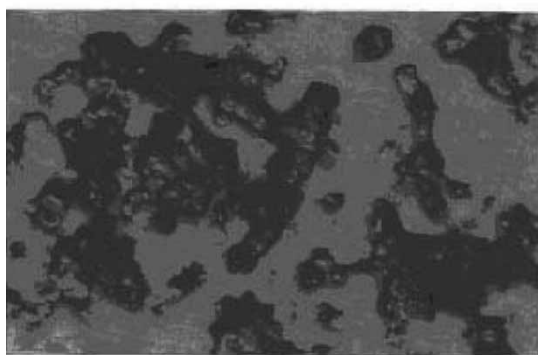


Figure 1. TGA and DTG thermogram of polymers XIb (—) and XIe (---); heating rate 10°C/min.



(A)



(B)

Figure 2. Photomicrographs of polymer XIi in the heating cycle, (A) at 234°C (before melting); (B) 281°C (Ti).

Observation of poly (azomethine-ether)s XI_f in the anisotropic melt displays the typical marbled textures (23) as shown in Figure 2(a) at 234°C and Figure 2(b) at 281°C (Ti). Similar textures were observed for XI_{d,h}. The other polymer samples in the mesomorphic state were highly birefringent and showed stirred opalescence, but did not exhibit typical nematic texture.

Conclusions

A new series of liquid crystalline poly (azomethine-ether)s containing 4-phenylcyclohexanone moiety were synthesized using solution polycondensation technique at ~80°C. The majority of the polymers are soluble in protonic acids. Most of them exhibited melt birefringence and stirred opalescence during polarized microscope observation. Both the T_m and T_i values increased as the length of the flexible aliphatic spacers increased and decreased with the introduction of the methoxy group as a substituent in the polymer main chain.

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