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LIQUID CRYSTALLINE POLYMERS. 3. SYNTHESIS AND LIQUID CRYSTAL PROPERTIES OF THERMOTROPIC POLY(ARYLIDENE-ETHER)S AND COPOLYMERS CONTAINING CYCLOALKANONE MOIETY IN THE POLYMER BACKBONE

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Key Words: Thermotropic Liquid Crystal, Poly(arylidene-ether), Cycloalkanone, Copolymers

ABSTRACT

Two novel series of poly(arylidene-ether)s and copoly(arylidene-ether)s were synthesized by polycondensation of 4,4'-diformyl- α,ω -diphenoxyalkane and 4,4'-diformyl-2,2'-dimethoxy- α,ω -diphenoxyalkane with cyclohexanone and/or cyclopentanone. The inherent viscosity of the polymers and copolymers thus prepared were in the range of 0.42–1.27 dL/g. The phase behavior of these polymers was studied by differential scanning calorimetry (DSC), optical polarizing microscopy using a heated stage, and thermogravimetric analyses. Almost all the polymers and copolymers exhibited thermotropic liquid crystalline properties. In most cases, the mesophase extends up to 310°C, where thermal decomposition prevents further observa-

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tion. Methoxy substituents, on the benzene ring of these polymers, lower the transition temperature significantly. The morphology of polymer IX_f was examined by scanning electronic microscope.

INTRODUCTION

Much of the research activity involving liquid crystalline polymers (LCPs) has until recently focused on the development of high-strength, high-temperature fibers and thermoplastics [1, 2]. Other work has resulted in the development of novel elastomeric materials with unusual optical and mechanical properties [3, 4]. Moreover, thermotropic main chain polymers that melt to form a structural fluid phase have been of considerable interest for the past two decades [5]. These thermotropic materials are becoming more prominent in the development of high-performance materials, such as fibers, film, and molded parts [6]. Synthetically, a variety of polymerization methods have been employed in the preparation of (LCPs) [7].

The polycondensation is one possible way for modification of polymer properties. For polymers exhibiting liquid crystalline properties, copolycondensation of appropriate monomers allows us to influence the temperature of mesophase formation and the temperature range of the mesophase [8]. On the other hand, one method for lowering the high melting points 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 group and to increase the diameter or decrease the axial ratio of mesogens [7].

In the proceeding paper in this series [10], the synthesis and liquid crystal properties of poly(arylidene-ether)s prepared from 4,4'-diformyl- α,ω -di-*i*-phenoxyalkane and 4,4'-diformyl-2,2'-dimethoxy- α,ω -diphenoxyalkane with cyclopentanone were reported. Such liquid crystalline polymers are of interest because they have relatively flexible chains and corresponding low melt viscosity.

The purpose of this study is:

- (1) to synthesize poly(arylidene-ether)s and copoly(arylidene-ether)s with rod-like segments connected by a short alkylene oxide spacer or insertion of a methoxy group; and
- (2) to examine these systems for liquid crystallinity

EXPERIMENTAL

Characterization of Polymers

Infrared spectra from 4000-600 cm^{-1} of solid samples of the synthesized monomers and polymers were obtained by KBr method using a Shimadzu 2110 PC Scanning Spectrophotometer. The inherent viscosity were measured with an Ubbelohde Viscometer in methanesulphonic acid at 25°C ($C=0.5\text{g/L}$). $^1\text{H-NMR}$ Spectra were run on a GNM-LA 400 MHz NMR spectrophotometer at room temperature in DMSO or CHCl_3 using TMS as an internal reference. X-ray diffractographs were obtained with a Philips X-ray PW 1710 diffractometer using Ni-filtered $\text{CuK}\alpha$ radiation. The morphology of polymers was examined by Scanning electron microscope (SEM) using a JEOL JSM-5400 LV instrument. The SEM sample was prepared by evaporating a dilute solution of the polymer on a smooth surface of aluminum foil and subsequently coating with a gold palladium alloy. SEM images were taken using a Pentax Z 50 voltage of 15 KV using a low dose technique [11]. Thermal properties of the polymers were examined in air or nitrogen atmosphere using a thermal analyzer Du Pont 2000 at a heating rate of 10°C/min. The maximum position of the melting endotherms were taken to be the m.p.s. The isotropization temperatures were determined by observing polymer melts with a polarizing microscope, CARL-ZEISS (JENA) equipped with a hot-stage Chaixmeca (Nancy, France). The temperature at which initial formation of isotropic phases occurred was taken as the isotropization temperature, T_i . At the same time, optical textures of the polymer melts were very closely followed to determine the nature of their mesophases. Electronic spectra were recorded in DMF in the region 250-600 nm with a Shimadzu 2110 PC Scanning Spectrophotometer.

Reagents and Solvent

p-Hydroxybenzaldehyde from (Aldrich) was used without crystallization. 4-Hydroxy-3-methoxybenzaldehyde (vanillin) from EL-Nassr Chemical Company, Egypt, was used as is. Dihaloalkanes (Aldrich), was used without purification. Cyclohexanone and cyclopentanone (Merck) were freshly distilled: cyclohexanone (b.p. 155°) and cyclopentanone (b.p. 130-131°). Potassium hydroxide and all other solvents were of highly purity and were further purified by standard methods [12].

Monomers Syntheses

4,4'-Diformyl- α,ω -diphenoxyalkanes I-IV

Anhydrous sodium carbonate (0.25 mol) and appropriate dibromoalkane (0.1 mol) dissolved in dimethylformamide (DMF) (25 ml) were added to a solution of 4-hydroxybenzaldehyde (0.2 mol) in DMF (25 ml) with stirring and then refluxed at 120° for 4 hours. The reaction mixture was cooled to 50°, then poured into cold water (about 500 ml) and allowed to stand overnight in a refrigerator. The precipitate was filtered off, washed with water and dried under vacuum and recrystallized from appropriate solvents.

By a similar procedure, 4,4'-diformyl-2,2'-dimethoxy- α,ω -diphenoxyalkane (V-VIII) were prepared from vanillin and dihaloalkanes. The yield, melting point and elemental analyses of the monomers (I-VIII) are listed in Table 1.

Polymerization

The polycondensations of the dialdehydes and cyclohexanone were carried out using the high-temperature solution method under the following condi-

TABLE 1. Yield and Properties of the Synthesized Monomers I-VIII

Monomer	Formula	Yield (%)	Melting Point (°C)	Analysis	
				C%	H%
I	C ₁₆ H ₁₄ O ₄	59	113-4	Found	71.02 5.12
				Calcd	71.11 5.19
II	C ₁₈ H ₁₈ O ₄	63	104-5	Found	72.3 5.95
				Calcd	72.48 6.04
III	C ₂₀ H ₂₂ O ₄	90	116-8 ^a	Found	73.51 6.72
				Calcd	73.62 6.75
IV	C ₂₄ H ₃₀ O ₄	91	111-2 ^b	Found	75.05 7.79
				Calcd	75.39 7.85
V	C ₁₈ H ₁₈ O ₆	75	175-7	Found	65.18 6.38
				Calcd	65.45 6.67
VI	C ₂₀ H ₂₂ O ₆	82	157-8	Found	66.80 6.123
				Calcd	67.04 6.15
VII	C ₂₂ H ₂₆ O ₆	92	154-5	Found	68.12 6.49
				Calcd	68.39 6.74
VIII	C ₂₆ H ₃₄ O ₆	87	98-9 ^c	Found	70.31 7.63
				Calcd	70.59 7.69

^a Reference 23. 112°C

^b Reference 24. 112°C

^c Reference 24. 98°C

tions: the concentration of the monomers was 0.2 mol/L in ethanol (95%) in the presence of KOH (few drops) as a catalyst. The reaction temperature was 75-80°C. Polymers were precipitated during the reflux, filtered off, and extracted with boiling ethanol (Soxhlet apparatus) for 10 hours, and then dried under reduced pressure (1mm/Hg) at 60°C for 24 hours.

Copolymerization

The copolycondensation of the dialdehydes with cyclohexanone and cyclopentanone were carried out under the same conditions described in the polymerization procedure in ratio (1 mole dialdehyde, 0.5 mole cyclohexanone, 0.5 mole cyclopentanone).

RESULTS AND DISCUSSION

Preparation of Poly(arylidene-ether)s IX a-h and Copoly(arylidene-ether)s XI a-h

New thermotropic liquid crystal poly(arylidene-ether)s IXa-h and copoly(arylidene-ether)s XIa-h were synthesized, in high yields, by the solution polycondensation of the two series of dialdehydes namely: 4,4'-diformyl- α,ω -diphenoxyalkanes I-IV and 4,4'-diformyl-2,2'-dimethoxy- α,ω -diphenoxyalkanes V-VIII with cyclohexanone and/or cyclopentanone, respectively, in ethanol (95%) at 75-80°C and in the presence of basic catalyst (20% aq. KOH) to the direct polycondensation, which is a convenient method for the preparation of conjugated arylidene polymers and LCP in our laboratory [10, 13, 14].

The expected structures of these resulting poly(arylidene-ether)s and copoly(arylidene-ether)s were confirmed from elemental analyses, IR, and 400 MHz-NMR. Results for preparation of the monomers I-VIII are listed in Table 1, while Tables 2 and 3 shows some properties of polymers IXa-h and copolymers XIa-h. The direct polycondensation easily affords high to moderate molecular weight polymers and copolymers in quantitative yields. The synthesized monomers, polymers and copolymers are depicted in Schemes 1-3.

The polymerization and copolymerization proceeded easily, the highly yellowish-orange precipitate separated during the stirring on hot in ethanol. The yield of poly(arylidene-ether)s IXa-h were in the range 68-94% and the inherent viscosity were in the range 0.42-1.27dL/g, while the yields of co-poly(arylidene-ether)s XIa-h except XIg and XIh were in the range of 78-98%, and the inherent viscosity in the range 0.48-1.12 dL/g.

TABLE 2. Elemental Analyses, Yields and Inherent Viscosity of Poly-(arylidene-ether)s IXa-h

Polymer Formula	Yield (%)	η_{inh}^a (dl/g)	Elemental Formula (mol.wt)	Elemental analyses	
				C%	H%
IXa	68	--- ^b	C ₂₂ H ₂₀ O ₃ (332.14)	Calcd	79.50 6.06
				Found	79.28 6.18
b	82	0.42	C ₂₄ H ₂₄ O ₃ (360.46)	Calcd	79.97 6.71
				Found	79.63 6.82
c	85	0.73	C ₂₆ H ₂₈ O ₃ (388.51)	Calcd	80.38 7.26
				Found	80.03 7.19
d	83	0.65	C ₃₀ H ₃₆ O ₃ (444.26)	Calcd	81.04 8.16
				Found	81.36 8.02
e	78	0.58	C ₂₄ H ₂₄ O ₅ (392.44)	Calcd	73.45 6.16
				Found	73.27 6.08
f	94	1.27	C ₂₆ H ₂₈ O ₅ (420.49)	Calcd	74.27 6.71
				Found	74.12 6.82
g	91	0.96	C ₂₈ H ₃₂ O ₅ (448.54)	Calcd	74.98 7.19
				Found	74.65 7.09
h	86	0.91	C ₃₂ H ₄₀ O ₅ (504.65)	Calcd	76.16 7.99
				Found	75.83 7.93

^a) Measured in Methanesulphonic acid, with C= 0.5 g/ 100 ml at 25°C.

^b) Insoluble.

The results of elemental analyses for these poly(arylidene-ether)s IXa-h and copoly(arylidene-ether)s XIa-h agree with calculated values as shown in Tables 2 and 3. Spectral data support the structural assignment for the poly(arylidene-ether)s and copoly(arylidene-ether)s and the IR data in KBr disks for all the polymers and copolymers showed characteristic absorption due to CH stretching of CH₂ (aliphatic spacers) at 2940-2860 cm⁻¹, C=O of cyclohexanone and cyclopentanone at 1660-1690 cm⁻¹, C=C at 1605-1610 cm⁻¹, phenylene at 1590-1500 cm⁻¹ and C-O-C (ether-linkage) at 1230-1270 cm⁻¹ (Figures 1, 2).

¹H NMR for copolymer XI_f (in CDCl₃) showed signals at δ : 6.85-7.75 (m, 12 Ar-H and 4H, 4CH=C); at 4.25 (s, 12 H, 4 OCH₃); at 3.85 (s, 16 H, 8 CH₂); at 3.00 (s, 4H, 2CH₂, cyclopentanone); and at 2.00 (s, 6H, 3CH₂, cyclohexanone) ppm (Figure 3).

As described in a previous paper, [10] the polymers and copolymers were unstable to some degree in conc. H₂SO₄ and so the inherent viscosity were measured in methanesulphonic acid and ranged from 0.42-1.27dl/g as shown in Tables 2 and 3.

TABLE 3. Elemental analyses, Yield and Inherent Viscosity of Copoly (arylidene-ether)s XIa-h

Copolymer Formula	Yield (%)	Elemental Formula (mol.wt)	$\eta_{inh}^{a)}$ (dl/g)	Elemental analyses	
				C%	H%
XIa	82	C ₄₃ H ₃₈ O ₆ (650.77)	0.48	Calcd	79.36 5.84
				Found	78.93 5.64
b	86	C ₄₇ H ₄₆ O ₆ (706.88)	0.67	Calcd	79.86 6.51
				Found	79.35 6.18
c	94	C ₅₁ H ₅₄ O ₆ (762.99)	0.82	Calcd	80.28 7.08
				Found	79.81 7.19
d	78	C ₅₉ H ₇₀ O ₆ (874.65)	0.96	Calcd	81.02 8.07
				Found	80.69 7.93
e	89	C ₄₇ H ₄₆ O ₁₀ (770.52)	0.84	Calcd	73.26 6.02
				Found	72.95 5.87
f	95	C ₅₁ H ₅₄ O ₁₀ (826.56)	1.12	Calcd	74.11 6.59
				Found	74.67 6.48
g	59	C ₅₅ H ₆₂ O ₁₀ (882.61)	0.53	Calcd	74.85 7.02
				Found	74.36 6.83
h	73	C ₆₃ H ₇₈ O ₁₀ (995.31)	0.74	Calcd	76.03 7.90
				Found	75.49 7.52

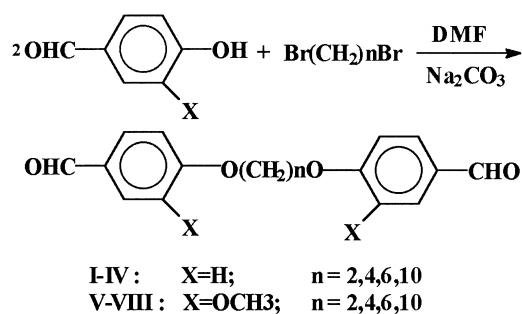
^{a)} Measured in Methanesulphonic acid , with C= 0.5 g/ 100 ml at 25°C.

Polymer Characterization

Solubility

The solubility characteristics of the poly(arylidene-ether)s IXa-h and copoly(arylidene-ether)s XIa-h were tested in various solvents including DMF (dimethylformamide), NMP(N-methylpyrrolidone), THF(tetrahydrofurane), CHCl₃-acetone mixture, CH₂Cl₂, methanesulphonic acid and conc. H₂SO₄. A 5% (w/v) solution was taken as a criterion for solubility. The copolymers have good solubility in organic solvents like halogenated hydrocarbons, while the polymers (except IX_{f,h}) not showed this properties.

In polar aprotic solvents, such as DMF, DMSO, or NMP, both polymers and copolymers showed partial solubility, except polymers IX_{b,f} and copolymers XI_{b,f} dissolved easily in DMSO. All the polymers and copolymers are freely soluble in conc. H₂SO₄ and methanesulphonic acid due to the unstability of the polymers , especially in the former one. Brittle films were casted from CH₂Cl₂ solutions of the polymer IX_f and copolymer IX_f.



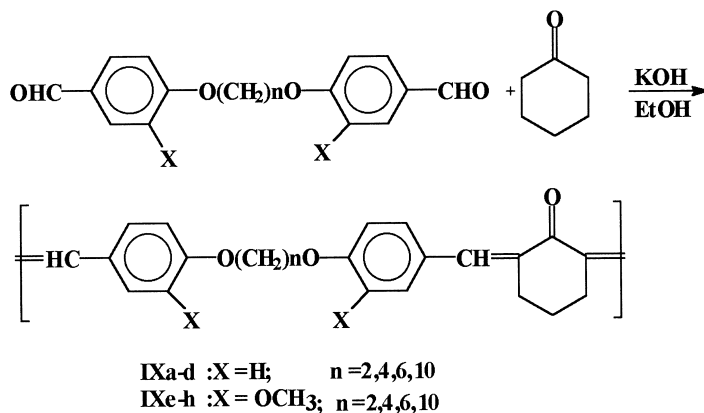
Scheme 1.

Electronic Spectra

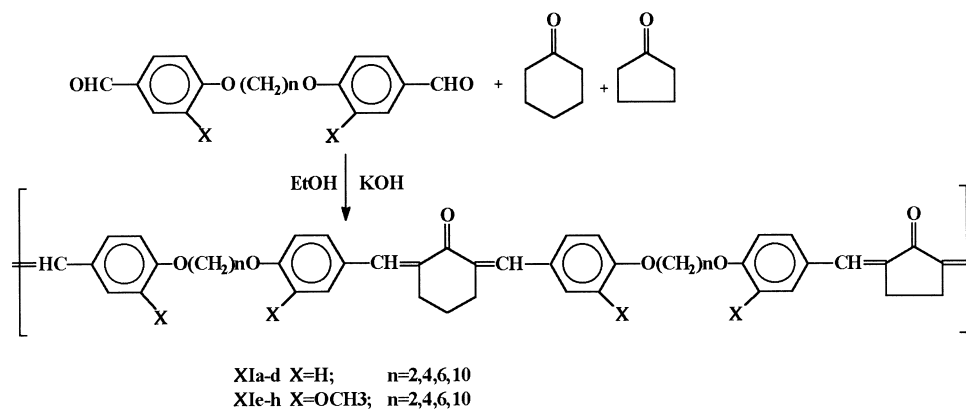
The electronic spectra of selected examples of polymers IXb,f,g and copolymers XIa,e,f were obtained in DMF at concentration 2.6×10^{-6} M. The electronic spectra in Figure 4 that showed absorption bands broadening, and also small bathochromic shifting with λ_{\max} near 272-284 nm due to $\pi-\pi^*$ transition within the benzenoid system, and that λ_{\max} near 312-398 nm due to $\pi-\pi^*$ of C=C groups. Moreover, the study kinetic oxidation by KMnO_4 and other oxidizing agents for this new ctageroy, will be published in the near future .

X-ray Analyses

The crystallinity of selected examples for the poly(arylidene-ether)s IXa-h and copoly(arylidene-ether)s XIa-h was examined by Wide-angle X-ray



Scheme 2.



Scheme 3.

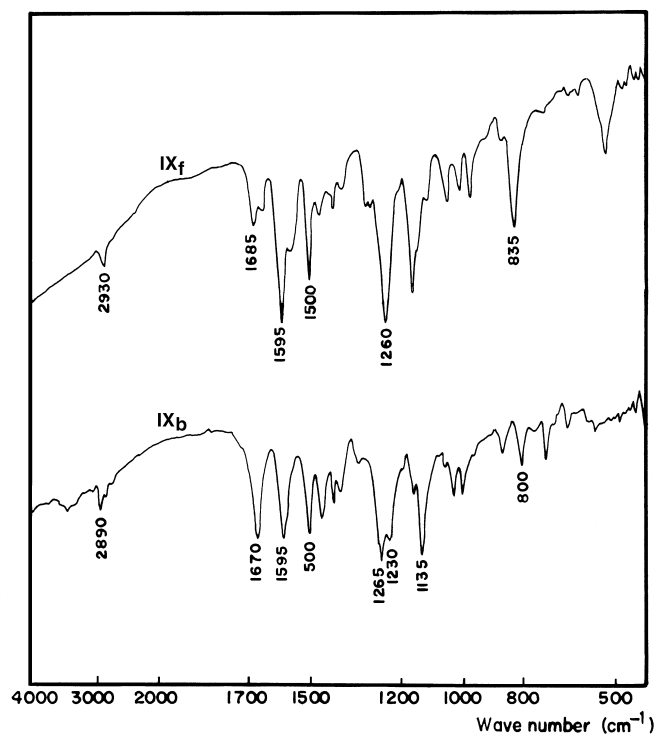


Figure 1. IR Spectra of polymers IXb,f.

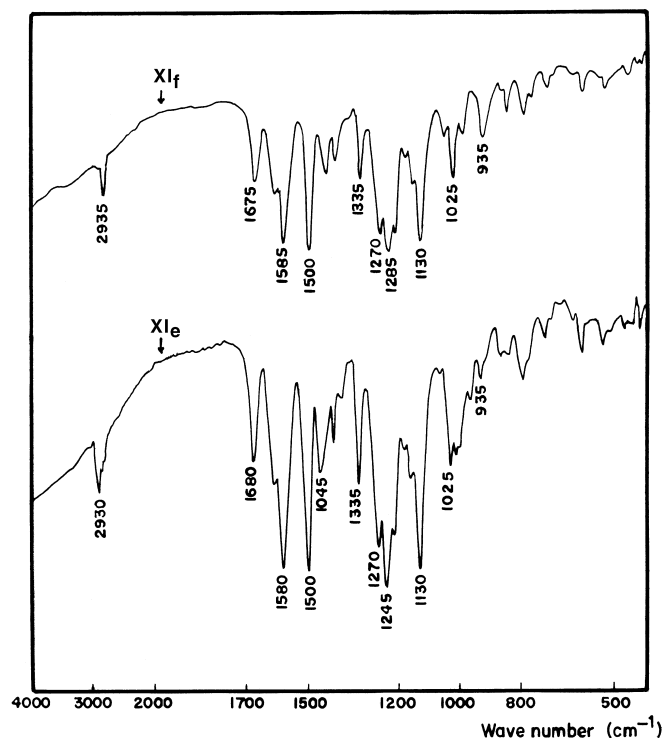


Figure 2. IR Spectra of copolymers XIe,f.

diffraction in the region of $2\theta = 5\text{-}65^\circ$. As shown in Figure 5, all the polymers and copolymers shows few reflections of sharpness peaks, indicating that there is a large class of structures in the polymer main chain in the ordered state. This observation is consistent with that observed in our previous work [10] for liquid crystalline polymers (LCP) based on cyclopentanone. Moreover, the degree of crystallinity in this type of LCP may be attributed to the presence of C=O as polar groups, in addition to a high level of C=C groups [15, 16]. More particularly, Figure 6 shows that the polymers IXe,f have high degree of crystallinity than the copolymers XI e,f, this attributed to the inclusion of cyclopentanone (as rigid moiety) into the polymer main chain.

Morphology Properties

The morphology of the synthesized poly(arylidene-ether)s Ixf, as selected example was examined by scanning electron microscopy. SEM study in

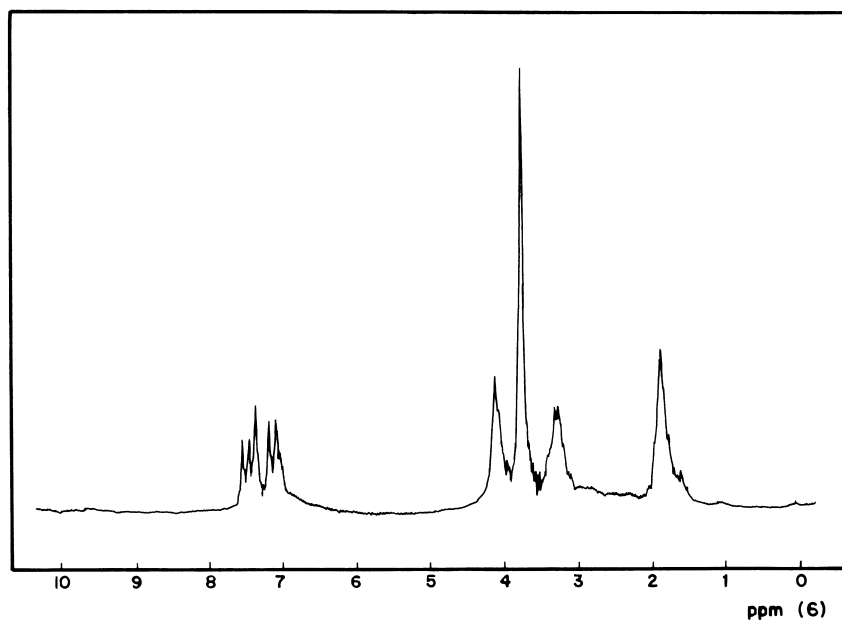


Figure 3. ¹H NMR Spectrum of polymer IXf.

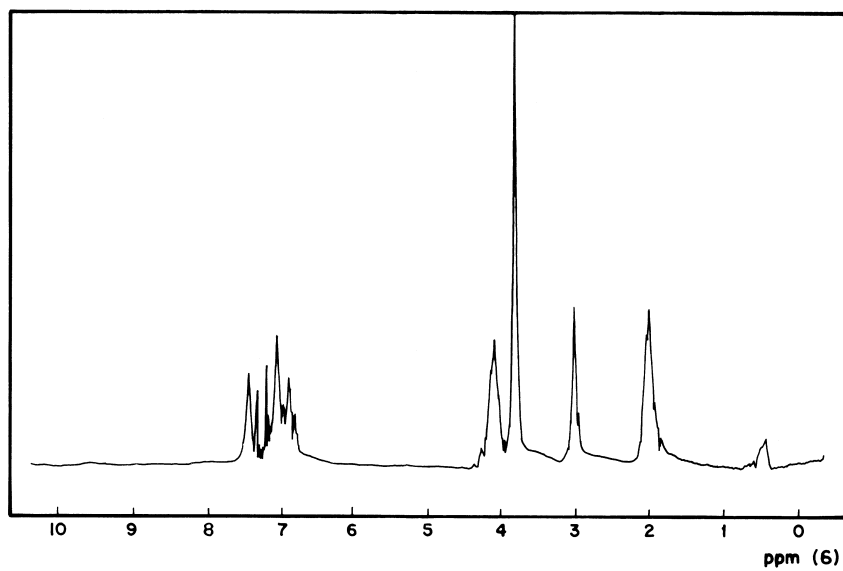


Figure 4. ¹H NMR Spectrum of copolymer XI f.

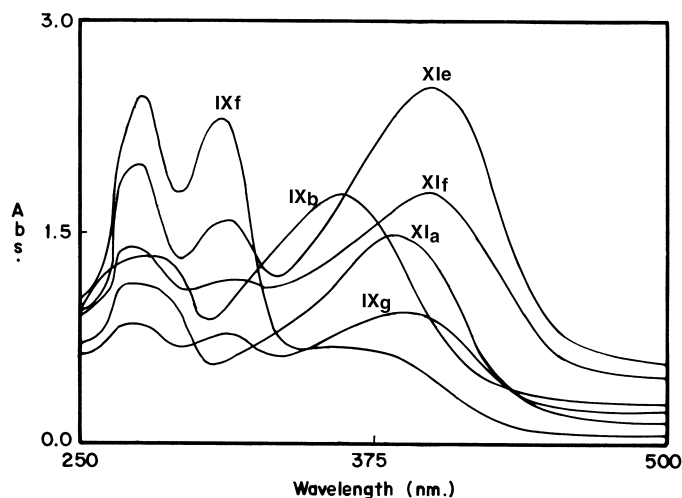


Figure 5. Electronic absorption of polymers Ib,f,g and copolymers XIa,e,f.

Figure 7 a,b (X 350, X 500) show that the polymer surface appears as a sub-hedral crystal aggregates, while in Figure 7 c,d (X3500, X 10,000) show that the polymer surface like Cabbage shape.

Thermotropic Liquid Crystalline Properties of Polymers and Copolymers

The phase behavior of the polymers and copolymers were measured by DSC, optical microscope and thermogravimetric analyses, and are summarized in Tables 4 and 5. According to our recent previous studies [10], the poly(arylidene-ether)s and copoly-(arylidene-ether)s, containing cyclohexanone except polymers IXa,b,e exhibited melt birefringence and stirred opalescence during polarized microscope observation. Therefore, it is concluded that poly(arylidene-ether)s IXa-h except IXa,b,e and copoly(arylidene-ether)s XIa-h exhibit thermotropic liquid crystalline properties. The mesophase-isotropic phase transition temperature could not be determined by DSC analyses. The isotropic temperature of these polymers was observed by using a polarizing microscope equipped with a heating stage in the temperature range of 135-310°C.

The effect of spacer length on the thermal properties of poly(arylidene-ether)s IX a-h is shown in Table 4, while Table 5 showed the same effect for the copolymers XI a-h; both the melting point and isotropic temperature increased as

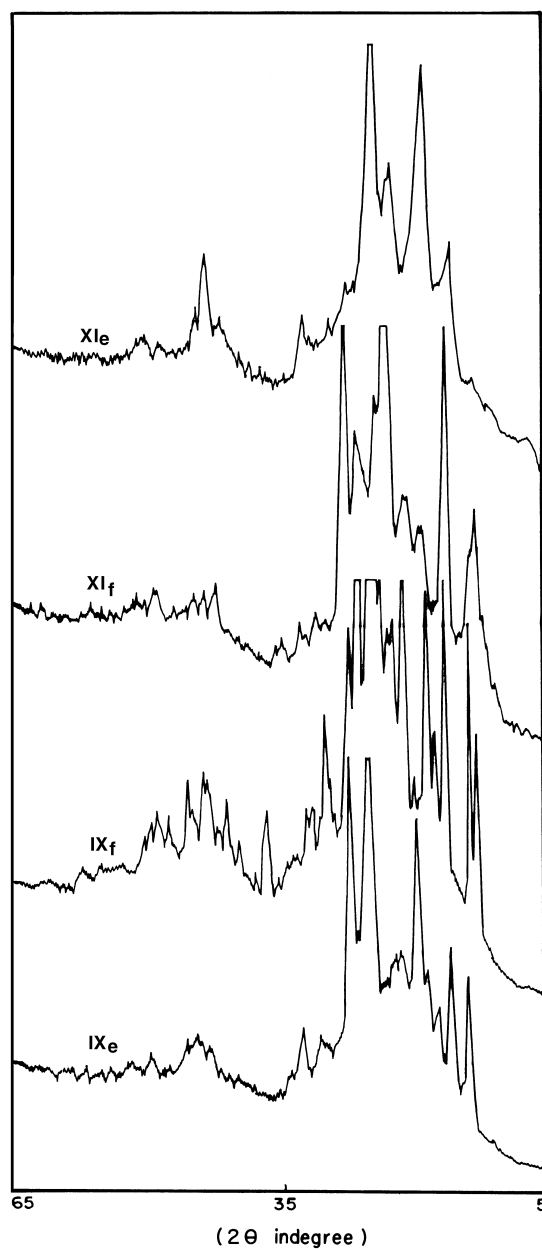


Figure 6. X-ray diffraction Patterns of polymers IX_{e,f} and copolymers XI_{e,f}.

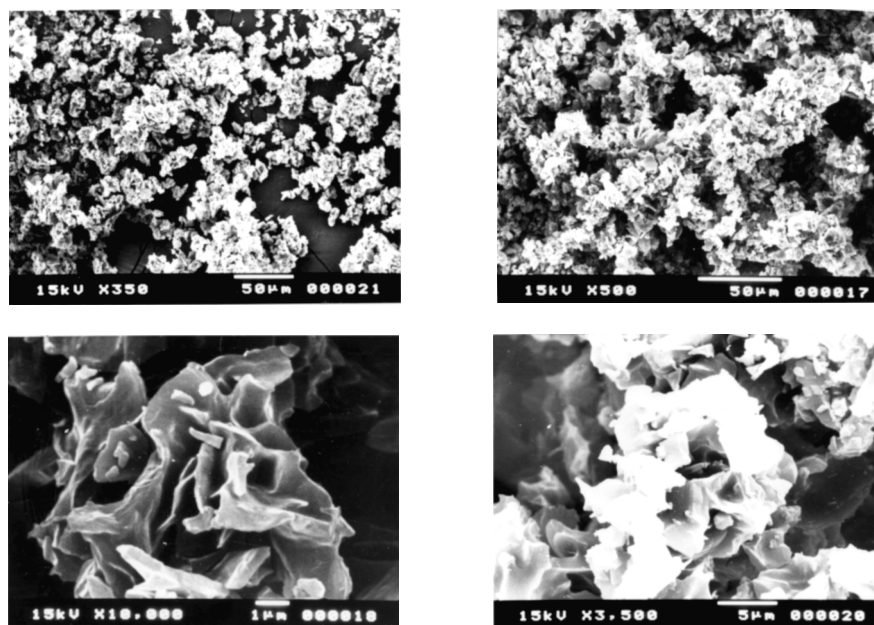


Figure 7. SEM images of Polymer IXf.

the length of the flexible aliphatic spacer in the polymers chain increased. It should be noted that poly(arylidene-ether)s IXa,b,e not showed this behavior, this attributed to the shortness of methylene spacers $-(CH_2)-$ especially polymers (IXa,e) and the rigidity of the chain. The effect of substituents on the thermal properties of polymers IXa-h and copolymers XIa-h is also,shown in Table 3, 4, both the melting point and the isotropic temperatures decreased by the introduction of methoxy groups into the polymer main chain [17]. Thus, unsubstituted, para-linked poly(arylidene-ether)s IXb, is infusible below the decomposition temperature but fusibility is achieved by the introduction of a methoxy group (polymer I f) in the benzene ring. The same observations were reported in previous work [10]. It is known that the substituents can reduce the coplanarity of adjacent mesogenic groups, i.e decrease the orientation interaction, and increase the diameter or decrease the axial ratio of the mesogens [18].

In DSC studies, all the polymers and copolymers (except XIa,e) revealed multiple endotherms on DSC thermograms, probably due to polymorphism [19, 20]. In some cases, the peaks in DSC are broad, especially in the

TABLE 4. Transition Behavior of Poly(arylidene-ether)s IXa-h

Polymer number	n	X	Stirred Opalescence	Anisotropic melt ^{a)}		Temperature (°C) for various % decomposition ^{b)}					
				T _m -T _i (°C)	ΔT (°C)	10%	20%	30%	40%	50%	
IXa	2	H	None	c)	-	-	380	395	413	425	440
b	4	H	None	c)	-	-	395	410	415	425	460
c	6	H	Yes	210-	295	85	365	390	420	430	445
d	10	H	Yes	218 -	269	51	330	345	380	395	430
e	2	OCH ₃	None	c)	-	-	305	345	360	375	380
f	4	OCH ₃	Yes	135	-148	13	285	310	345	395	415
g	6	OCH ₃	Yes	158-183		25	360	370	375	380	395
h	10	OCH ₃	Yes	180-235		55	295	320	325	360	380

^a Measured by a polarizing microscope equipped with a heating stage.

^b From TGA in air with heating rate 10°C/min.

^c Unmeltable.

TABLE 5. Transition Behavior of Copoly(arylidene-ether)s XIa-h

Copolymer number	n	X	Stirred Opalescence	Anisotropic melt ^{a)}		Temperature(°C)for various %Decomposition ^{b)}				
				T _m -T _i	ΔT	10%	20%	30%	40%	50%
XIa	2	H	Yes	218-256	38	315	355	370	395	415
b	4	H	Yes	235-310	75	370	390	410	415	455
c	6	H	Yes	246-279	33	330	360	385	395	420
d	10	H	Yes	206-258	52	265	290	310	360	375
e	2	OCH ₃	Yes	148-187	39	285	305	325	340	355
f	4	OCH ₃	Yes	157-182	25	365	380	485	390	405
g	6	OCH ₃	Yes	193-235	42	340	355	370	395	410
h	10	OCH ₃	Yes	225-276	51	255	270	294	320	350

^a Measured by a polarizing microscope equipped with a heating stage.

^b From TGA in air with heating rate 10°C.

copolymers, due to the overlapping with thermal temperature decomposition. For this reason, isotropization temperatures of the polymers and copolymers were identified by observing the textures of the melts on a cross-polarizing microscope. It can be seen from the DSC curves of some polymers IXa-h in Figure 8, 9, two or three sharp endotherms in addition to the glass transition (T_g) step on the first heating run. Figure 8 also shows that poly(arylidene-ether)s IX g has two sharp peaks (endotherms) at 146 and at 491°C and another exotherm at 231°C, (Figure 9). This effect might be due to solid- to- solid (T_{ss}), solid-to mesophase (T_m) and mesophase -to- solid (T_i) [21] transitions, which are observed from optical microscope. In the DSC curves of the copoly(arylidene-ether)s XI a,f weak and broad endotherms are observed (Figure 10). As known for other LC polymers [22], DSC curves of tend to become broader than those for the corresponding homopolymers and it is difficult to identify from these curves; the phase transitions and mesophase.

Further evidence of the thermal degradation was given by TGA and DTG which will be discussed below. The thermal behavior of Poly(arylidene-ether)s IX a-h and copoly(arylidene-ether)s IX a-h was evaluated by TGA and DTG in air at a heating rate 10°C/min. The thermographs of these polymers are given in Figures 11 and 12, while Table 4 and 5 give the temperature for various percentages of weight loss. The initial decomposition of polymers was observed to start at 295°C, while for copolymers at 255°C. In Figure 11, the thermograms

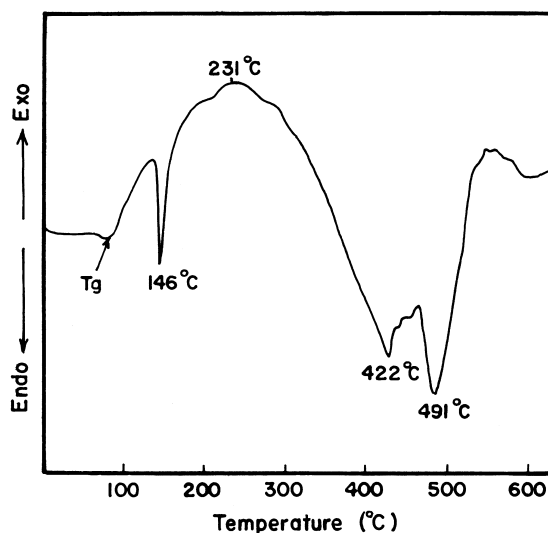


Figure 8. DSC thermogram of Polymer IX g.

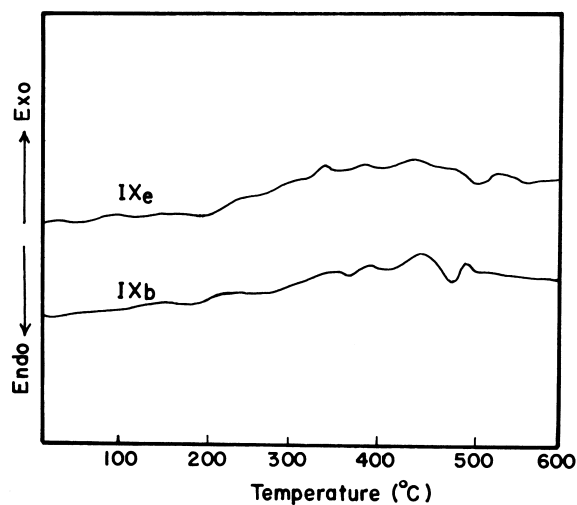


Figure 9. DSC thermograms of polymers IX b,e.

indicate that the Poly(arylidene-ether)s IXb,f decompose in two distinct steps. Mass loss was rapid between 385-425°C for polymer IXb and 280-345°C for polymer IXf. This was followed by a region of gradual mass loss between 430-495°C for the former and between 350-455°C for the latter one, and then another region of either rapid or slow mass depending on the methylene spacers and substituents (H or OCH₃) in the main chain of the polymers.

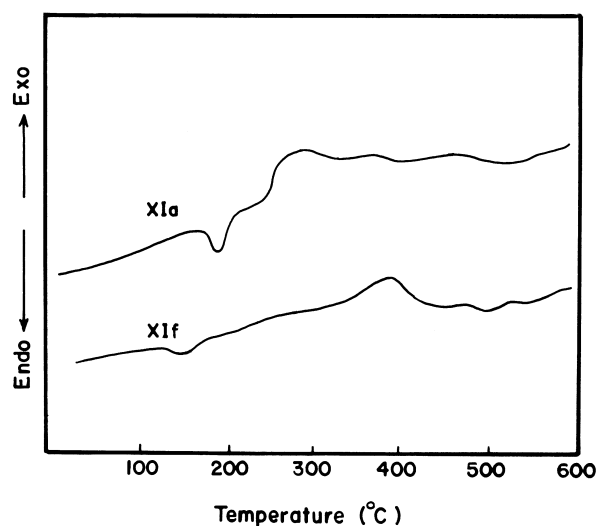


Figure 10. DSC thermograms of copolymers XI a,f.

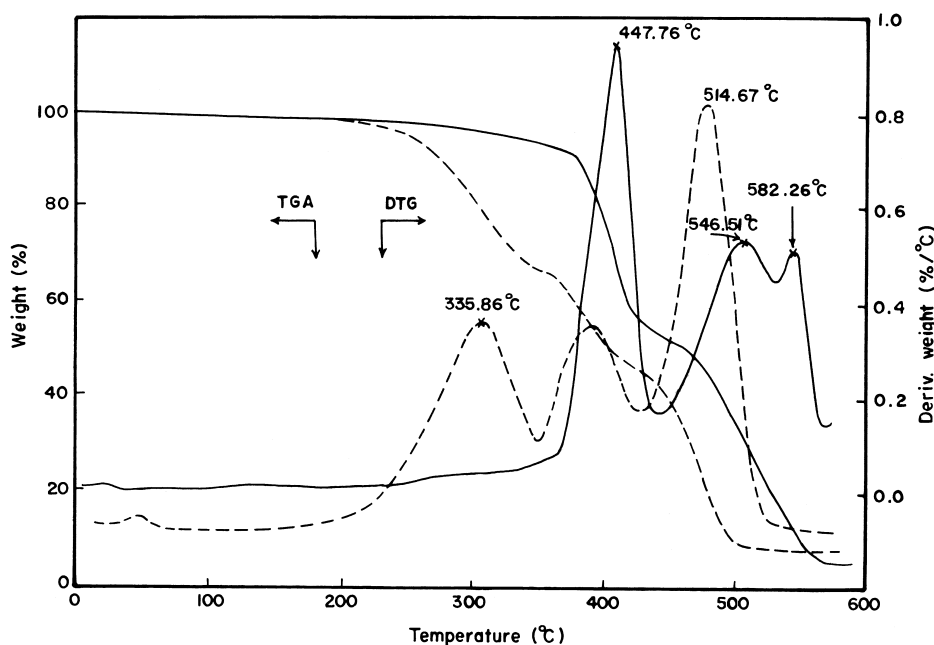


Figure 11. TGA and DTG thermograms of Polymers IXb (—), IXf (- - -); heating rate 10°C/min.

The behavior of all the polymers in the first region was nearly identical. In Figure 12, the thermographs show similar patterns of decomposition without well defined stages for the thermolysis of copoly((arylidene-ether)s IXa,f. Mass loss was rapid between 365-435°C for that copolymers. The expected nature of decomposition of this type of polymers is a pyrolytic oxidation of C = C, scission of many bonds, in addition to the formation of char as an end product.

Birefringence Texture

The character of the texture at a given temperature was fixed by quenching it in a liquid nitrogen. Micrographs were then obtained on heating to room temperature (not shown). Observation of poly(arylidene-ether)s IXf under a polarizing microscope revealed that this polymer exhibited well rounded with thick dark rim in Figure 13 a,b at 135°C (T_m) and the mesophases extend up to

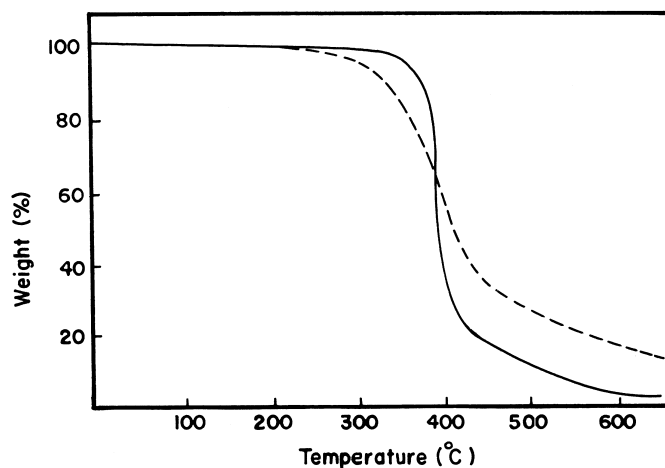


Figure 12. TGA thermograms of copolymers XIa,f; heating rate 10°C .

the isotropic phases at 138°C (T_i), showing subangular to subrounded (Figure 13 c,d).

Observation of poly(arylidene-ether)s IXg under polarizing microscope reveal that this polymer exhibited like neck texture of the nematic phase at 183°C (Figure 14 a,b). Figure 15 show the changes which occurred in the appearance of copoly(arylidene-ether)s XI f on the polarizing microscope with increasing temperature. In Figure 15, it can be seen the change in the appearance of copolymer XI f from the threaded texture at 157°C (Figure 15b) to the highly spheroidal tex-

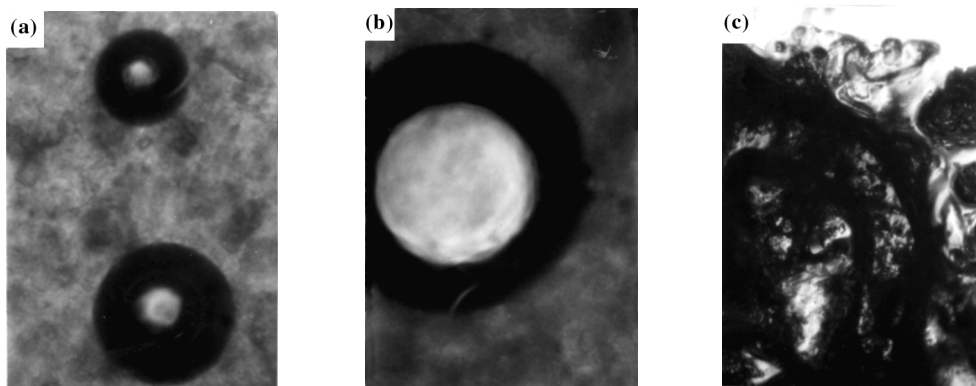


Figure 13(a-c). Photomicrographs of polymer IXf in the heating cycle at (a) 135°C ; (b) 148°C ; (c) after cooling (magnification X 217).

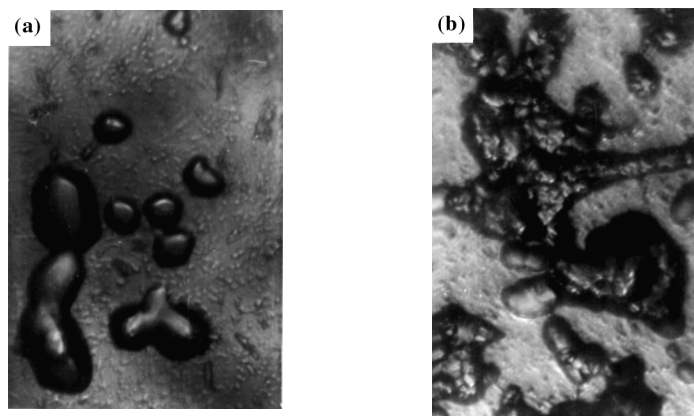


Figure 14 (a,b). Photomicrographs of polymer IXg in the heating cycle at (a) 158°C; (b) 185°C (magnification X 217).

ture at 182°C (Figure 15c), after cooling the spheroidal texture appear in a neck shape.

CONCLUSION

Two novel series of LC-poly(arylidene-ether)s and copoly(arylidene-ether)s containing cyclohexanone and/or cyclopentanone respectively have

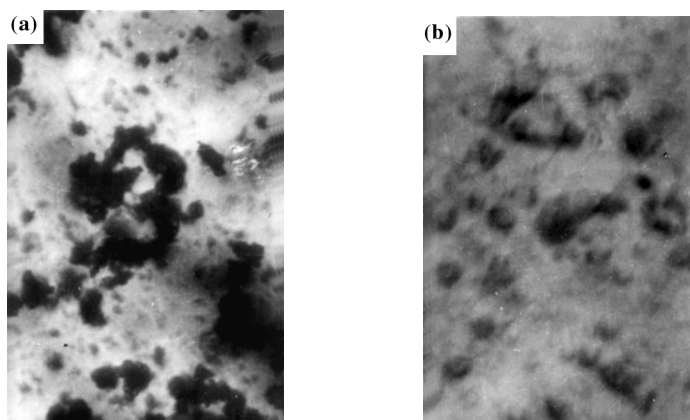


Figure 15 (a-d) Photomicrographs of polymer XIg in the heating cycle at (a) 25°C; (b) 157°C; (c) 182°C and; (d) after cooling (magnification X 217).

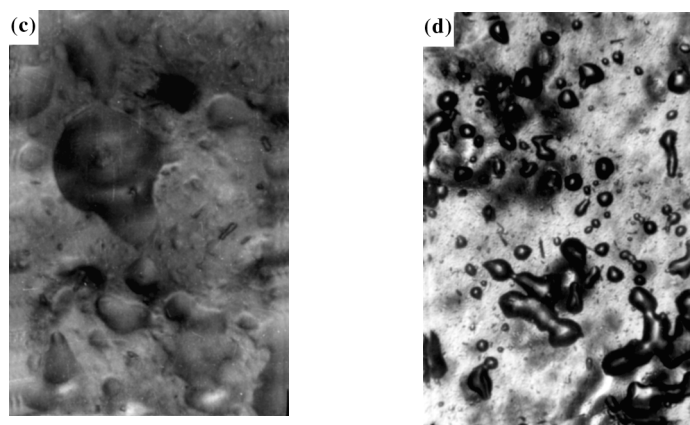


Figure 15. Continued.

been synthesized. a solution polycondensation technique at $\sim 80^{\circ}\text{C}$ was used. The majority of the polymers and copolymers reported, exhibited thermotropic nematic phases except poly(arylidene-ether)s IX a,b,e. Both the T_m and T_i increased as the length of the flexible aliphatic spacers increased, while decreased by introduction of methoxy groups, as substituents, into the polymer main chain. X-ray diffraction analyses showed that the polymers IX e,f have high degree of crystallinity than the copolymers XI e,f. SEM examination of poly(arylidene-ether)s IX f revealed that the polymer surface like cabbage shape.

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