

This article was downloaded by:

On: 24 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



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

LIQUID CRYSTALLINE POLYMERS. IV. THERMOTROPIC LIQUID CRYSTALLINE POLY(ARYLIDENE-ETHER)S AND COPOLYMERS CONTAINING N-METHYLPYRROLIDONE LINKED TO THE MAIN CHAIN THROUGH SPACERS OF VARIOUS LENGTHS

Kamal I. Aly^a; Hussein S. El-Kashef^b

^a Polymer Lab 507, Chemistry Department, Faculty of Science, Assiut University, Egypt

Online publication date: 31 July 2001

To cite this Article Aly, Kamal I. and El-Kashef, Hussein S.(2001) 'LIQUID CRYSTALLINE POLYMERS. IV. THERMOTROPIC LIQUID CRYSTALLINE POLY(ARYLIDENE-ETHER)S AND COPOLYMERS CONTAINING N-METHYLPYRROLIDONE LINKED TO THE MAIN CHAIN THROUGH SPACERS OF VARIOUS LENGTHS', *Journal of Macromolecular Science, Part A*, 38: 8, 785 – 806

To link to this Article: DOI: 10.1081/MA-100104448

URL: <http://dx.doi.org/10.1081/MA-100104448>

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 CRYSTALLINE POLYMERS. IV.
THERMOTROPIC LIQUID CRYSTALLINE
POLY(ARYLIDENE-ETHER)S AND COPOLYMERS
CONTAINING N-METHYLPYPERIDONE LINKED
TO THE MAIN CHAIN THROUGH SPACERS OF
VARIOUS LENGTHS**

Kamal I. Aly* and Hussein S. El-Kashef

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

ABSTRACT

Two novel series of poly(arylidene-ether)s and copoly(arylidene-ether)s were synthesized from N-methylpiperidone and/or cyclohexanone respectively. The first series (homopolymers) was derived from 4,4'-diformyl- α,ω -diphenoxyalkane or 4,4'-diformyl-2,2' dimethoxy- α,ω -diphenoxyalkane with N-methylpiperidone. The second series (copolymers) was derived from the diphenoxyalkanes (I-VIII) with N-methylpiperidone and cyclohexanone. The inherent viscosities of the polymers thus prepared were in the range of 0.37–0.98 dl/g. The majority of the polymers and copolymers are soluble in chlorinated hydrocarbons. DSC measurements and microscope observation under polarized light demonstrate that this type of poly(arylidene-ether)s form nematic mesophase over a wide temperature range in contrast to the corresponding copoly(arylidene-ether)s. All of the polymers and copolymers exhibited thermotropic liquid crystalline properties. In most cases, the mesophase extends up to 315°C, where thermal decomposition prevents further observation. The morphology of polymer IXb and copolymer XIb as a selected example was examined by scanning electronic microscope.

*Corresponding author. E-mail: k.i.aly@aun.eun.eg

Key Words: Thermotropic; Liquid crystal; Piperidone; Poly(arylidene-ether)s; Cycloalkanone; Copolymers; Flexible spacers.

INTRODUCTION

Our previous papers described how thermotropic liquid crystal homo- and copoly(arylidene-ether)s containing cyclopentanone and cyclohexanone moieties were synthesized [1-4] and the relationship between structure and liquid crystallinity was evaluated. It was found that the copolymers showed stable mesophases over the entire range of composition [3].

In this paper, attention was addressed to N-methylpiperidone, as heterocyclic ring, to prepare new thermotropic liquid crystal homo- and copoly(arylidene-ether)s. The first series (homopolymers) was prepared from 4,4'-diformyl- α,ω -diphenoxyalkane or 4,4'-diformyl-2,2' dimethoxy- α,ω -diphenoxyalkane with N-methylpiperidone. The second series (copolymers) was derived from the diphenoxyalkanes (I-VIII) with N-methylpiperidone and cyclohexanone as shown in Schemes 1 and 2.

A major purpose of this work was to study the effect of inclusion of the heterocyclic ring in the polymer and copolymer chain on the LC properties of these polymers. In addition, other characterization of these polymers such as thermostability, solubility, morphology, and crystallinity were discussed.

EXPERIMENTAL

Measurements

Infrared spectra from 4000-600 cm^{-1} of solid samples of the synthesized monomers and polymers were obtained by the KBr method using a Shimadzu 2110 PC Scanning Spectrophotometer. The inherent viscosity were measured with an Ubbelohde Viscometer in methane sulphonic acid at 25°C (0.5g/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 a 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 [5]. Thermal gravimetric analyses (TGA) of the polymers were examined in air atmosphere using a thermal analyzer DuPont 2000 at a heating rate of 10°C/min. Differential Scanning Calorimetry (DSC) was examined in nitrogen atmosphere using a Shimadzu 501 TA (Thermal Analyzer). 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 250-500nm 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, N-methyl-piperidone and cyclohexanone (Merck) were freshly distilled before using. Potassium hydroxide and all other solvents were of high purity and were further purified by standard methods [6].

Monomer Synthesis

4,4'-Diformyl- α,ω -diphenoxyalkanes I-IV and 4,4'-diformyl-2,2'-dimethoxy- α,ω -diphenoxyalkane (V-VIII). These monomers were prepared as described in our previous papers [1-4].

Polymerization

The polycondensation of the dialdehydes and N-methylpiperidone were carried out using the high-temperature solution method under the following conditions: 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, washed with hot ethanol, acetone, and then dried under reduced pressure (1 mm/Hg) at 60°C for 24 hours.

Copolymerization

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

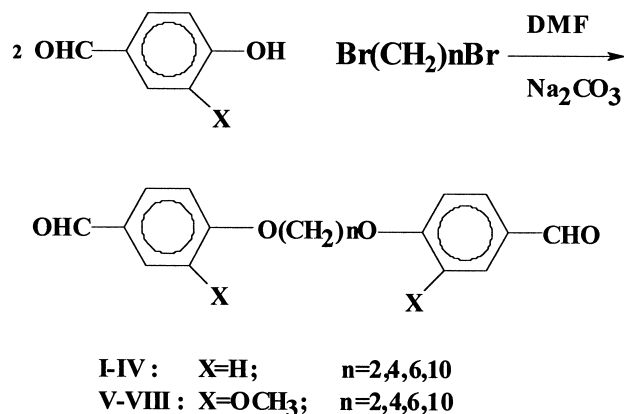
RESULTS AND DISCUSSION

Preparation and Elemental Analyses

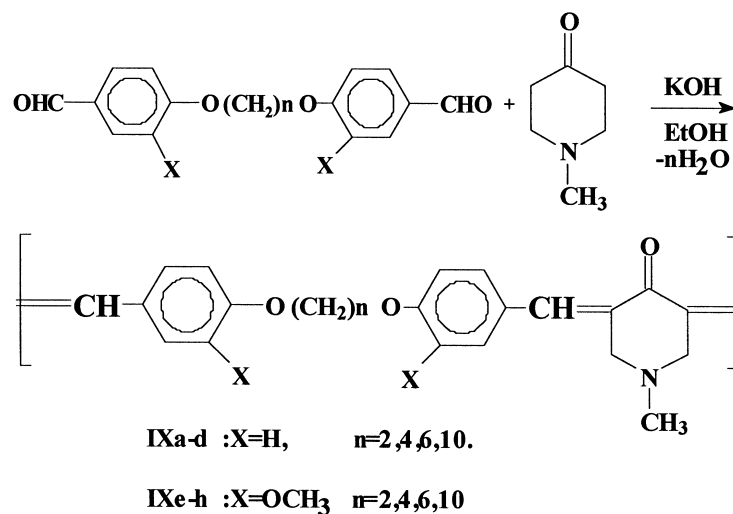
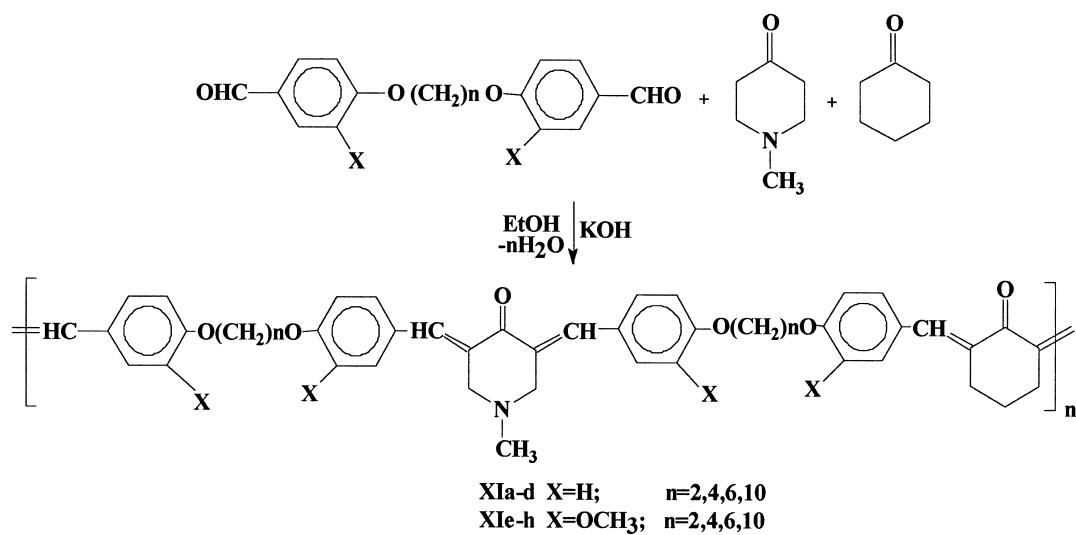
New thermotropic liquid crystal poly(arylidene-ether)s IXa-h and copoly(arylidene-ether)s XIa-h were synthesized in high yields by the solution polycondensation of the two series of dialdehydes namely 4,4'-diformyl- α,ω -diphenoxyalkanes I-IV and 4,4'-diformyl-2,2'-dimethoxy- α,ω -diphenoxyalkanes V-VIII with N-methylpiperidone and/or cyclohexanone, respectively. Ethanol (95%) was used as a solvent for the polycondensation 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 [1-4, 7, 8]. The model compounds of these polymers were carried out in our previous papers [7, 9, 10]. The expected structures of these resulting poly(arylidene-ether)s and copoly(arylidene-ether)s were confirmed from elemental analyses, IR, and ¹H-NMR spectra. Tables 1 and 2 show 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 gave the highly yellowish-orange precipitate and separated during the stirring on hot, in ethanol. The yield of poly(arylidene-ether)s IXa-h were in the range 79-96%, except polymer IXg,h which are 58% and 63%, respectively and the inherent viscosity were in the range 0.53-0.82 dl/g, while the yields of copoly(arylidene-ether)s XIa-h were in the range of 75-95% and the inherent viscosity were in the range 0.37-0.98 dl/g.

Elemental analyses were performed on all the monomers, as well as the new polymers. It should be noted that the analyses of the polymers (Tables 1, 2) deviated from 1.2 to about 2.5% of the theoretical values. However, it is not uncom-



Scheme 1.

*Scheme 2.**Scheme 3.*

mon for the polymers to trap solvent molecules within the polymer matrix, especially polymers of high molecular weight and those polymers containing polar groups which are capable of hydrogen bonding with solvent molecules [11].

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 2940-2865 cm⁻¹, C=O of cyclohexanone and N-methyl-

Table 1. 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			
				Calcd	C%	H%	N%
IXa	87	0.68	$C_{22}H_{21}NO_3$ (347.41)	Calcd	76.05	6.1	4.03
				Found	74.62	5.03	3.84
b	96	0.87	$C_{24}H_{25}NO_3$ (375.47)	Calcd	76.77	6.71	3.73
				Found	75.38	6.07	3.39
c	83	0.53	$C_{26}H_{29}NO_3$ (403.21)	Calcd	77.38	7.25	3.47
				Found	76.45	7.11	3.22
d	79	— ^{b)}	$C_{30}H_{37}NO_3$ (459.28)	Calcd	78.38	8.12	3.05
				Found	76.74	8.01	2.98
e	84	— ^{b)}	$C_{24}H_{25}NO_5$ (407.47)	Calcd	70.75	6.18	3.44
				Found	69.23	6.65	3.12
f	92	0.82	$C_{26}H_{29}NO_5$ (435.52)	Calcd	71.70	6.71	3.22
				Found	70.23	6.45	3.53
g	58	0.75	$C_{28}H_{33}NO_5$ (463.57)	Calcd	72.55	7.18	3.02
				Found	71.34	7.57	2.86
h	63	0.66	$C_{32}H_{41}NO_5$ (519.68)	Calcd	73.96	7.95	2.70
				Found	71.59	7.14	2.14

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

^{b)}Insoluble.

Table 2. Elemental Analyses, Yields, and Inherent Viscosity of Copoly(Arylidene-ether)s XIa-h

Copolymer Formula	Yield (%)	η_{inh}^a (dl/g)	Elemental Formula (Mol. Wt)	Elemental Analyses			
				Calcd	C%	H%	N%
XIa	86	0.98	$C_{44}H_{41}NO_6$ (679.29)	Calcd	77.74	6.08	2.06
				Found	76.34	5.89	2.12
b	95	0.57	$C_{48}H_{49}NO_6$ (735.36)	Calcd	78.33	6.72	1.90
				Found	77.98	6.35	1.78
c	91	0.76	$C_{52}H_{57}NO_6$ (791.42)	Calcd	78.85	7.26	1.77
				Found	77.08	7.12	1.56
d	79	0.54	$C_{60}H_{73}NO_6$ (903.54)	Calcd	79.69	8.14	1.55
				Found	78.23	7.76	1.85
e	87	0.78	$C_{48}H_{49}NO_{10}$ (799.34)	Calcd	72.06	6.18	1.75
				Found	70.78	6.01	1.54
f	92	0.37	$C_{52}H_{57}NO_{10}$ (855.40)	Calcd	72.95	6.72	1.64
				Found	71.19	6.45	1.32
g	73	0.73	$C_{56}H_{65}NO_{10}$ (911.46)	Calcd	73.73	7.19	1.54
				Found	74.92	7.09	1.16
h	76	0.61	$C_{64}H_{73}NO_{10}$ (1015.52)	Calcd	75.63	7.24	1.38
				Found	73.74	7.83	1.22

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

piperidone at $1660\text{-}1690\text{ cm}^{-1}$, C=C at $1605\text{-}1610\text{ cm}^{-1}$ phenylene at $1590\text{-}1500\text{ cm}^{-1}$ and C-O-C (ether-linkage) at $1230\text{-}1270\text{ cm}^{-1}$ (Figures 1, 2).

^1H NMR for polymer IXb (in CDCl_3) showed signals at δ : 6.85-7.80 (m, 8 Ar-H and 2H, 2 CH=C); at 3.75-4.45 (m, 8 H of 4 CH_2 aliphatic space; at 2.5 (s, 3 H, CH_3); and at 2.2 (s, 4H, 2 CH_2 , cyclopiperidone) ppm (Figure 3).

Polymers Characterization

The solubility properties of the poly(arylidene-ether)s IXa-h and copoly (arylidene-ether)s XIa-h containing N-methylpiperidone were tested in various solvents including DMF (dimethylformamide), NMP (N-methylpyrrolidone), THF (tetra-hydrofuran), CHCl_3 -acetone mixture, CH_2Cl_2 , TFA (trifluoroacetic acid) and conc. H_2SO_4 . A 5% (w/v) solution was taken as a criterion for solubility. The homo- and copoly(arylidene-ether)s show good solubility in protonic solvents like sulphuric acid and trifluoroacetic acid at room temperature, but are insoluble in DMSO or DMF (except polymers IXd,h and copolymers XI f,g,h). In chlorinated

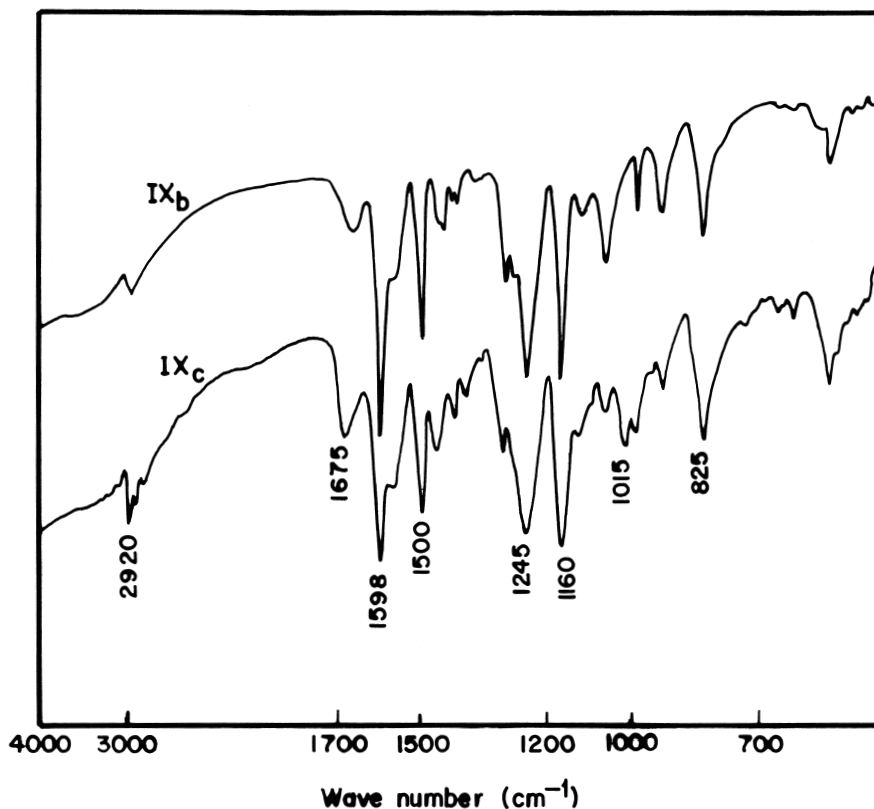


Figure 1. IR spectra of polymers IXb,c.

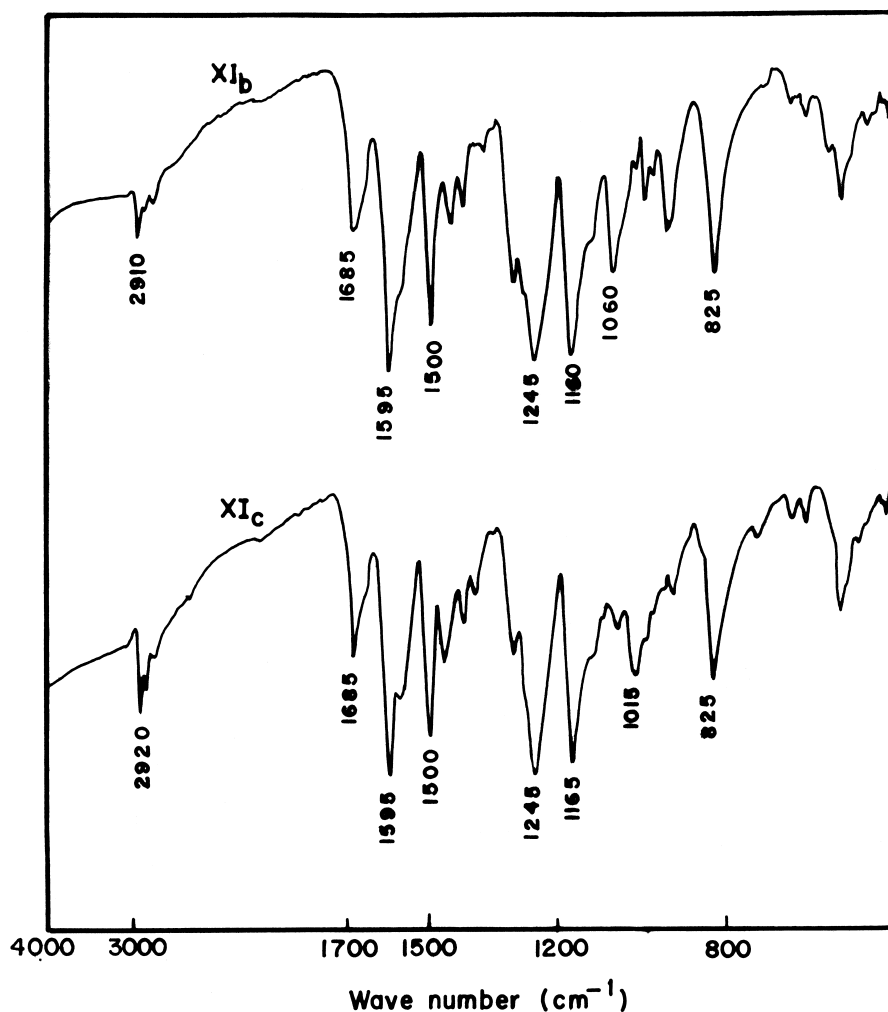


Figure 2. IR spectra of copolymers XIb,c.

hydrocarbons like CHCl_3 and CH_2Cl_2 , the majority of homo-polymers and copolymers are freely soluble as shown in Tables 3 and 4. Brittle films were cast from CH_2Cl_2 solutions of the polymer IXb and copolymer XIc.

We compared the solubility of these polymers and copolymers which contain N-methylpiperidone, as heterocyclic moiety, with those poly(arylidene-ether)s containing cyclopentanone and cyclohexanone, in previous works [1, 2], and we found that the inclusion of piperidone moiety enhanced the solubility of such kind of polymers. This may be attributed to the presence of CH_3 group attached by the N-atom in piperidinone moiety, this increases the polarity of the molecules in the chain towards the solvent molecules.

The electronic spectra of selected examples of polymers IXb,e,g and copolymers XIa,b,c were obtained in conc. H_2SO_4 at a concentration 2.6×10^{-6} M. The

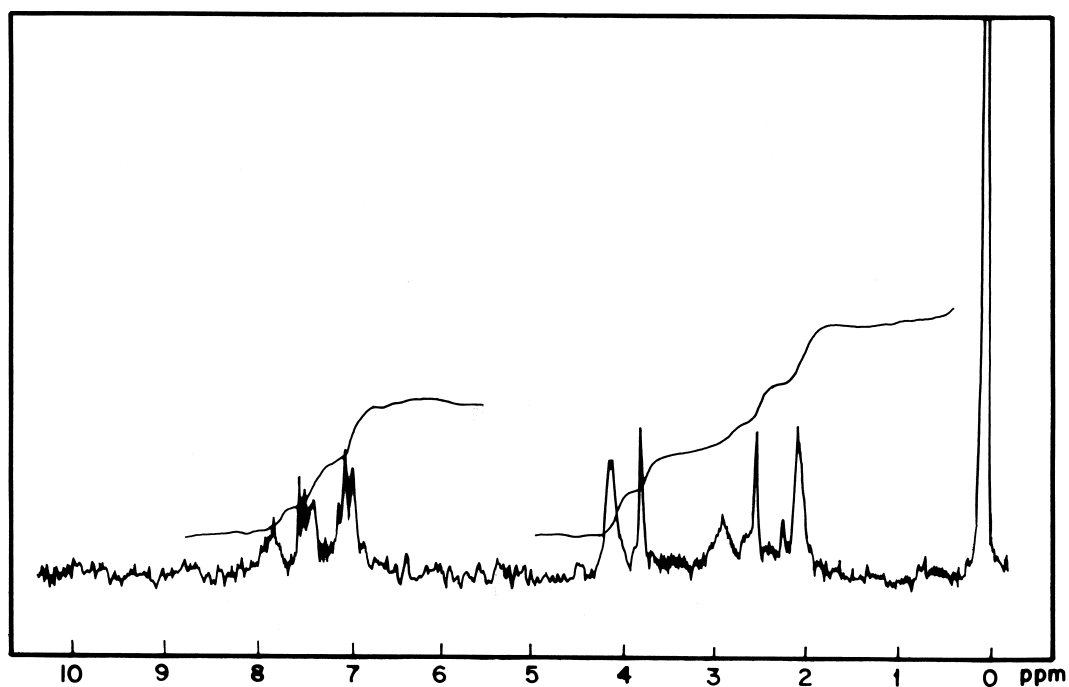


Figure 3. ^1H NMR spectrum of polymer IXb.

Table 3. Solubility Characteristics of Poly(Arylidene-ether)s IXa-h

Polymer Number	DMSO	DMF	NMP	THF	CHCl_3 +acetone (1:1)	CH_2Cl_2	Conc. H_2SO_4	TFA
IXa	I	I	I	I	I	Sw	S	S
b	Sw	I	Sw	I	S	S	S	Sw
c	I	Sw	I	I	Sw	S	S	S
d	S	Sw	I	Sw	Sw	S	S	S
e	Sw	I	Sw	I	Sw	S	S	S
f	Sw	I	S	Sw	S	S	S	S
g	Sw	Sw	S	Sw	S	S	S	S
h	S	S	S	Sw	S	S	S	S

^a)S: Soluble at room temperature (RT).

I: Insoluble at RT.

Sw: Swells.

Table 4. Solubility Characteristics of Copoly(Arylidene-ether)s XIa-h

Polymer Number	DMSO	DMF	NMP	THF	CHCl ₃ +acetone (1:1)	CH ₂ Cl ₂	Conc. H ₂ SO ₄	TFA
Ixa	Sw	I	Sw	I	Sw	Sw	S	S
b	Sw	I	Sw	I	S	S	S	S
c	Sw	S	S	S	S	S	S	Sw
d	Sw	Sw	I	Sw	Sw	S	S	S
e	Sw	I	Sw	I	Sw	Sw	S	S
f	S	S	S	S	Sw	Sw	S	S
g	S	S	S	I	S	S	S	S
h	S	S	S	Sw	S	S	S	S

^a)S: Soluble at room temperature (RT).

I: Insoluble at RT.

Sw: Swells.

electronic spectra in Figure 4 showed absorption bands brooding, and also small bathochromic shifting with λ_{\max} near 265-283 nm due to π - π^* transition within the benzenoid system, and that λ_{\max} near 310-376 nm due to π - π^* of C=C groups.

The crystallinity of selected examples for the poly(arylidene-ether)s IXb,c,g was examined by wide-angle X-ray diffraction in the region of $2\theta = 5$ - 65° as shown in Figure 5, all the polymers show 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 [1- 4] for liquid crystalline polymers (LCP) based on cyclopentanone and cyclohexanone. 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 [12, 13]. In particular, Figure 5 shows that the polymers IXc have higher degree of crystallinity than the polymers IXb,g.

The morphology of the synthesized poly(arylidene-ether)s IXb, and copoly (arylidene-ether)s XIb as selected examples was examined by scanning electron microscopy. SEM photomicrographs in Figure 6a,b show that the polymer surface (IXb) appears as a Fibrous structure. In Figure 6c,d, the Fibrous structure is very clear in the main chain of the polymers. For the copoly(arylidene-ether)s XIb, SEM photomicrographs in Figure 7a-d show that the polymer surface, also like the Fibrous structure, but irregular. This may be attributed to the irregularity in the chain of the repeating units of the copolymer.

Thermotropic Liquid Crystalline Properties

The thermal properties of the polymers and copolymers were characterized by DSC, TGA and by optical polarizing microscopy (OPM) with heating stage.

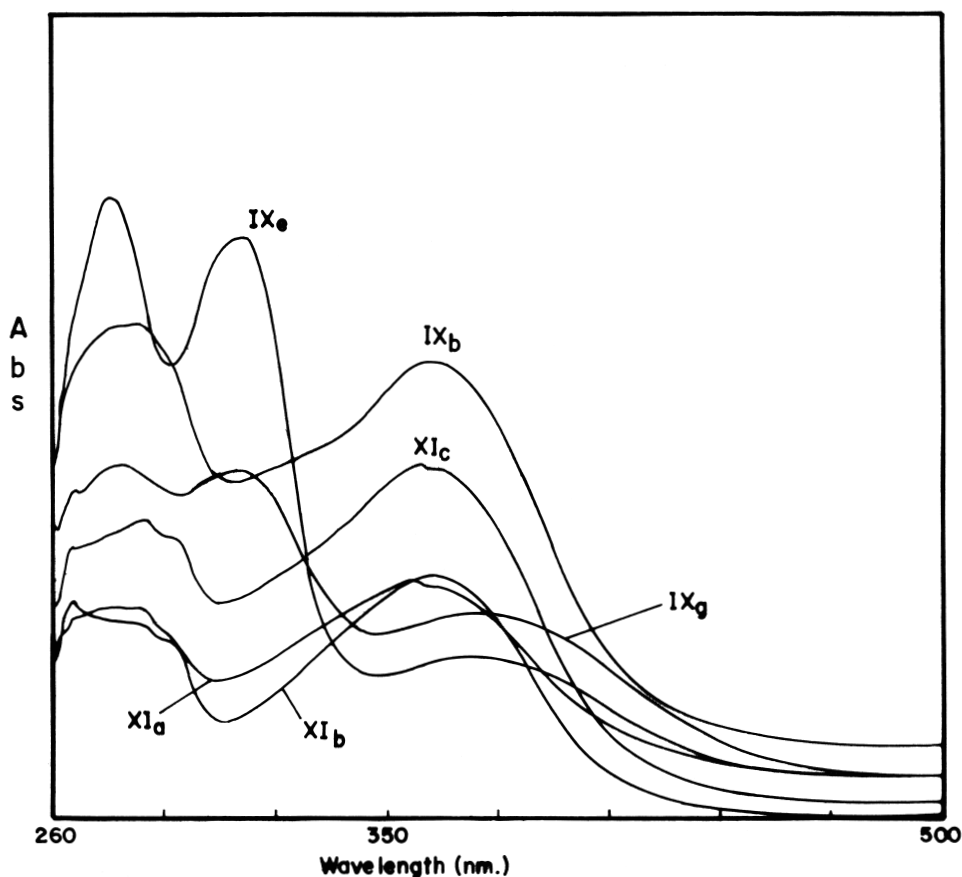


Figure 4. Electronic absorption of polymers IXb,e,g and copolymers XIa-c.

The poly(arylidene-ether)s and copoly(arylidene-ether)s exhibited melt birefringence and stirred opalescence during polarized microscope observation. The phase transition temperatures of the polymers and copolymers are shown in Tables 5 and 6.

The microscopic observations by OPM allowed detection of the beginning of the melting process and the subsequent transition to the fully isotropic liquid, while the DSC measurements give the temperatures determined at the endothermic maxima [9]. The isotropic temperature of these polymers was observed by using a polarizing microscope equipped with a heating stage in the temperature range of 185-315°C for the polymers IXa-h and in the temperature range of 170-305°C for the polymers XIa-h. In DSC studies, most of the polymers and copolymers revealed multiple or more endotherms on DSC thermograms, probably due to polymorphism [15, 16]. In some cases, the peaks in DSC are broad, especially

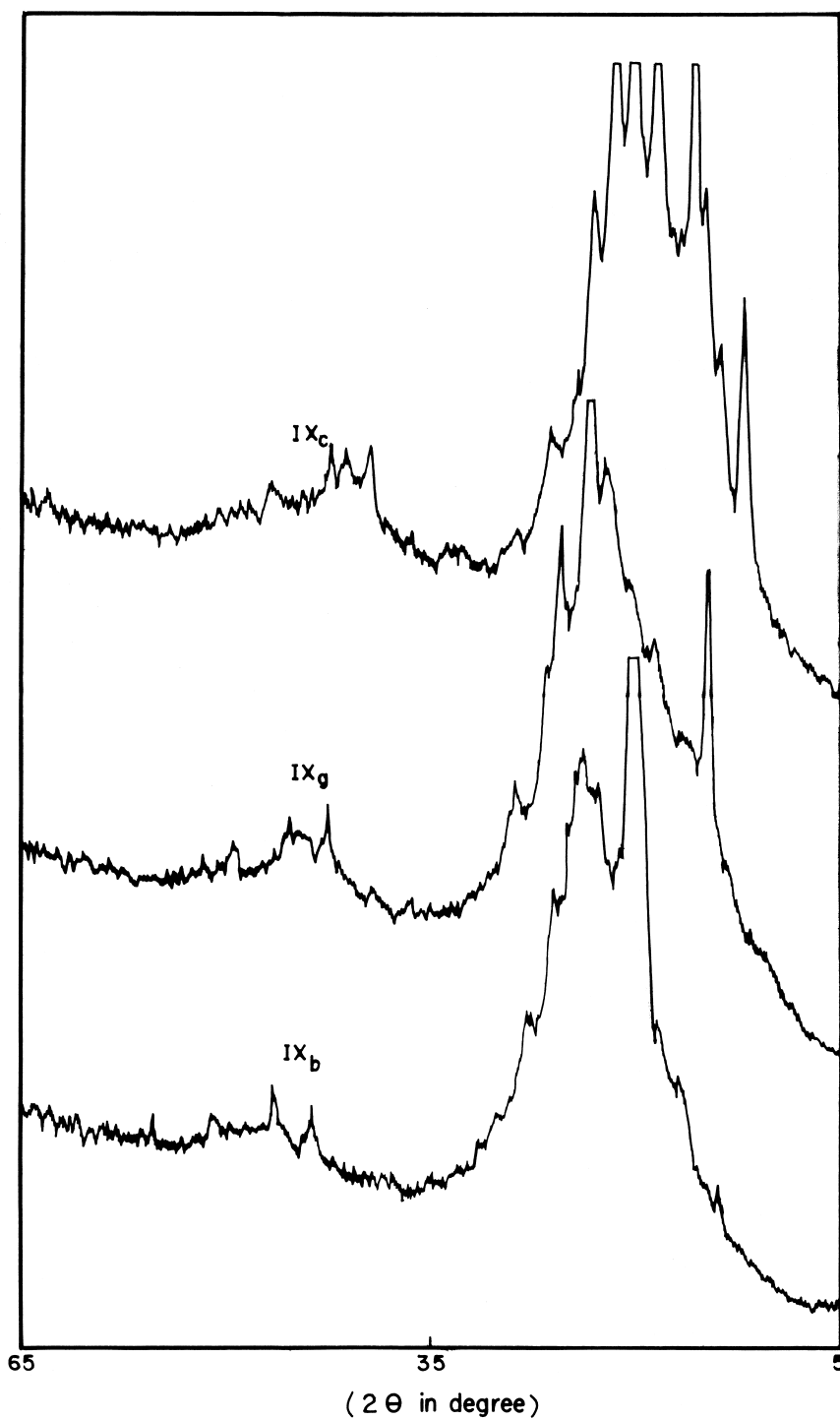


Figure 5. X-ray diffraction patterns of polymers IX_b,c,g.

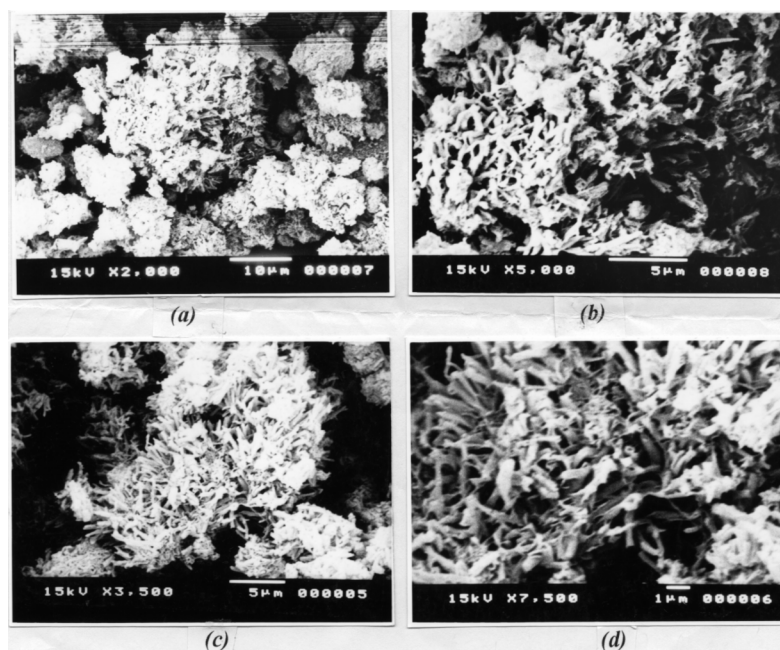


Figure 6(a-d). SEM images of polymer IXb (a,X 2000; b, X 5000; c, X 3500; d, X 7500).

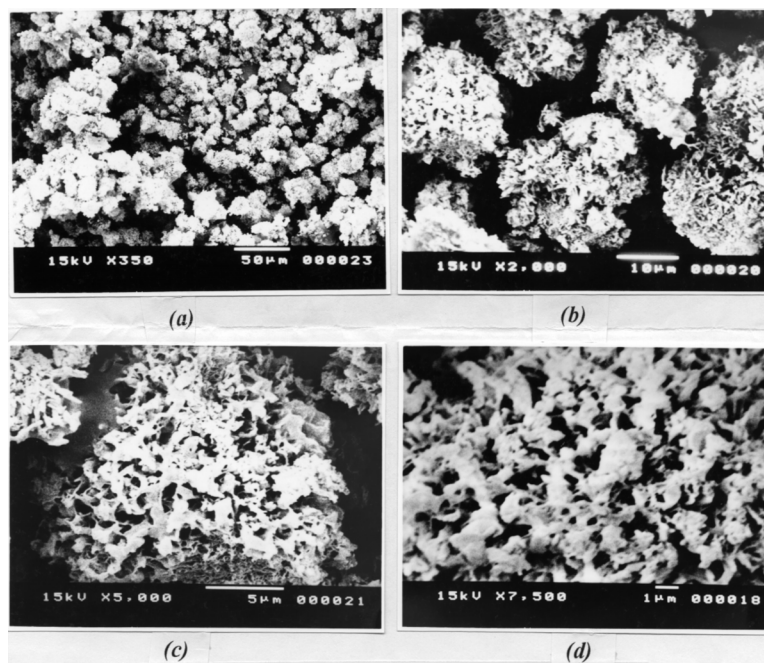


Figure 7(a-d). SEM images of copolymer XIb (a,X 350; b, X 2000; c, X 5000; d, X 7500).

Table 5. Phase Transition Temperature of Poly(Arylidene-ether)s IXa–h

Polymer Number		X	Phase Transition Temperature (C°, Microscope) ^{a)}			Phase Transition Temperature (C°, DSC) ^{b)}		
			T _m	T _i	ΔT	T _m	T _i	ΔT
IXa	2	H	220	280	60	212	316	104
b	4	H	179	273	94	158	307	149
c	6	H	156	287	131	146	276	130
d	10	H	256	315	59	—	—	—
e	2	OCH ₃	163	265	102	171	285	114
f	4	OCH ₃	123-	185	62	129	196	67
g	6	OCH ₃	187	286	99	—	—	—
h	10	OCH ₃	175	234	59	—	—	—

^{a)}Measured by a polarizing microscope equipped with a heating stage.

^{b)}Measured by DSC, heating rate 10°C/min.

in the 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.

All the poly(arylidene-ether)s and copoly(arylidene-ether)s were characterized by DSC measurements (except IXd,g,h and XIe,e,h) 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 IXa-h (Figures 8, 9), and is difficult to identify in the case of copolymers XIa-h.

Table 6. Phase Transition Temperature of Copoly(Arylidene-ether)s XIa–h

Polymer Number	n	X	Phase Transition Temperature (C°, Microscope) ^{a)}			Phase Transition Temperature (C°, DSC) ^{b)}		
			T _m	T _i	ΔT	T _m	T _i	ΔT
XIa	2	H	236	285	49	223	305	82
b	4	H	195	246	51	206	268	62
c	6	H	136	170	34	162	278	116
d	10	H	185	268	83	—	—	—
e	2	OCH ₃	—	—	—	—	—	—
f	4	OCH ₃	149	185	36	169	276	107
g	6	OCH ₃	212	297	85	223	341	118
h	10	OCH ₃	192	305	13	—	—	—

^{a)}Measured by a polarizing microscope equipped with a heating stage.

^{b)}Measured by DSC, heating rate 10°C/min.

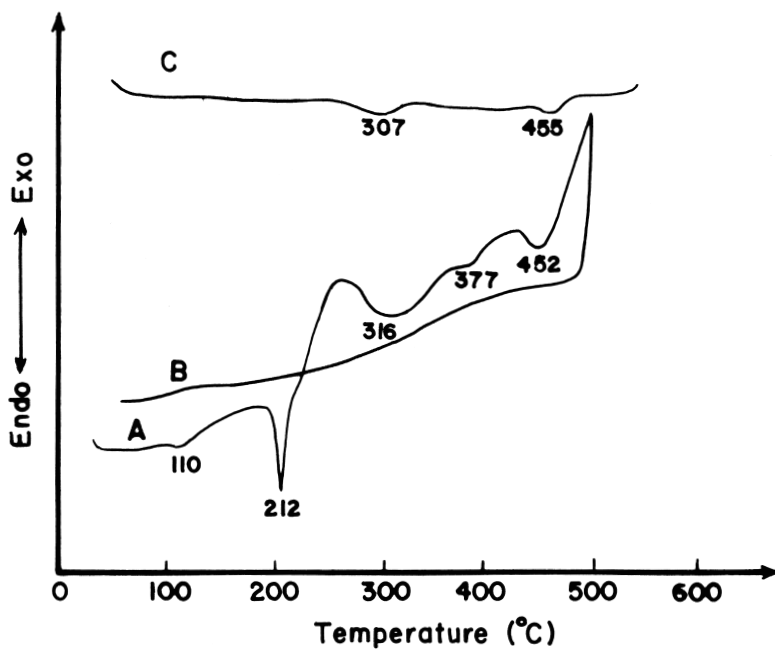


Figure 8. DSC thermograms of polymer IXa. (A) First heating. (B) First cooling. (C) Second heating. Rate 10°C/min.

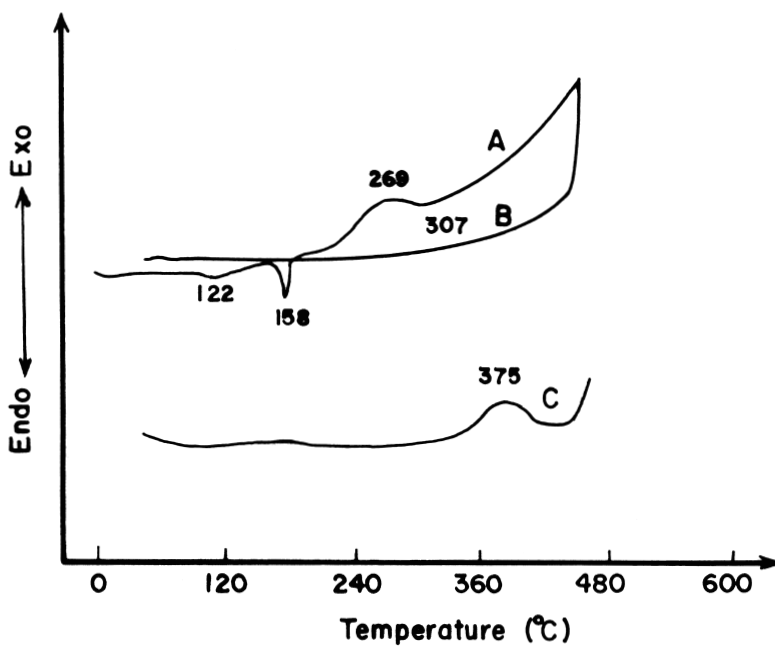


Figure 9. DSC thermograms of polymer IXb. (A) First heating. (B) First cooling. (C) Second heating. Rate 10°C/min.

It can be seen from the DSC curve (Figure 8) that polymer IXa showed endotherms at 212°, 316°, 377°, and at 452°. When the sample was cooled after preheating to 500°, there was no exothermal or endothermal peaks. On a second heating cycle, there were endotherms at 307° and 455°. From the DSC curve (Figure 9) for polymer IXb, there were endotherms at 158° and 307°, and an exothermal at 269°. When the sample was cooled after preheating at 450°, there was no exothermal peak. On a second heating cycle, there was an endotherm at 375°. This behavior suggests that degradation occurred up to 320° for polymers IXa,b. The DSC curve for copolymer XIc shows in Figure 10 that there were endotherms at 162° and at 335°, and an exothermal at 278°. When the sample was cooled after preheating to 450° there was an exotherm at 360° due to some crystallization. On a second preheating cycle, there was a reproducible peak at 338°. In the DSC in Figure 11 for copolymer XI_p, there were two endotherms at 169° and at 425° and an exothermal at 276°. When the sample was cooled after preheating to 450° there was no exothermal peak. On the second heating, there was a reproducible peak at 348°. This effect might be due to solid-to-solid (T_{ss}), solid-to mesophase (T_m) and mesophase to-solid (T_i) [17] transitions, which are observed from an optical microscope.

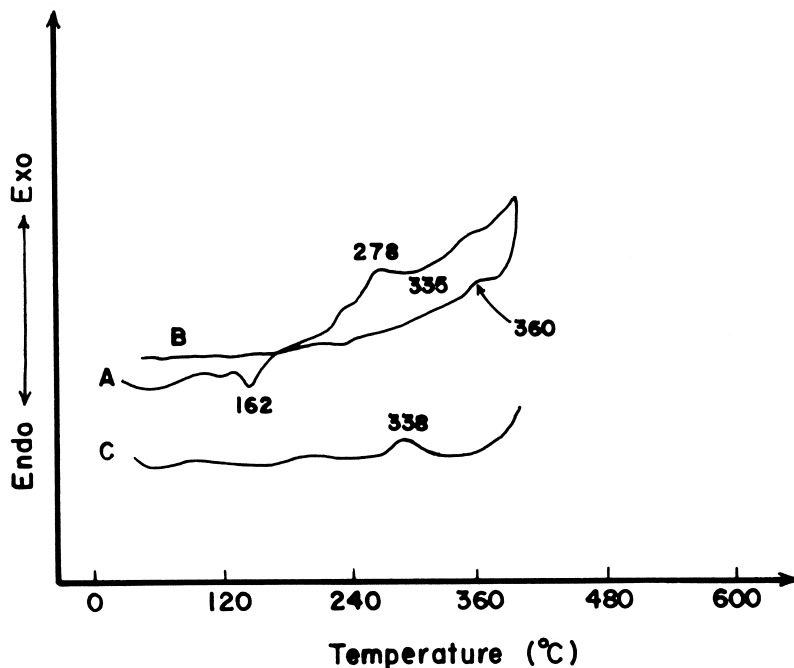


Figure 10. DSC thermograms of copolymer XIc. (A) First heating. (B) First cooling. (C) Second heating. Rate 10°C/min.

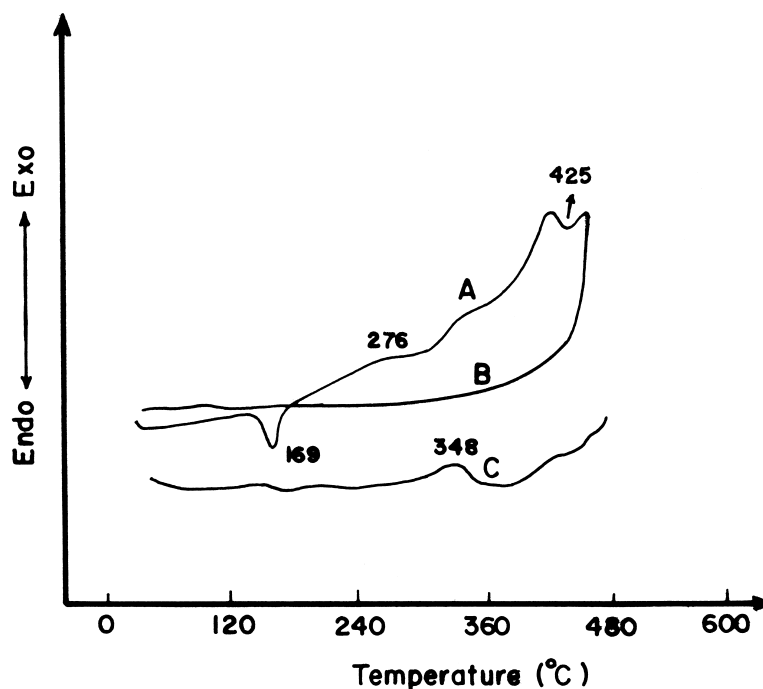


Figure 11. DSC thermograms of copolymer XIc. (A) First heating. (B) First cooling. (C) Second heating. Rate 10°C/min.

Further evidence of the thermal degradation was given by TGA and DTG. The thermal behavior of Poly(arylidene-ether)s IXa-h and copoly((arylidene-ether)s IXa-h) was evaluated by TGA and DTG in air at a heating rate 10°C/min. The thermographs of the polymers IXa,g are given in Figure 12, while Figure 13 shows the thermographs of copolymer XIc. The initial decomposition of the polymers was observed to start at 245°C, while for the copolymers it was 289°C. In Figure 12, the thermographs indicate that the Poly(arylidene-ether)s IXg decompose in two distinct steps. Mass loss was rapid between 308-460°C for polymer IXa and 328-385°C for polymer IXg. This was followed by a region of gradual mass loss between 460-495°C for the former and between 405-495°C for the latter one. These region of decomposition depend on the methylene spacers and substituents (H or OCH₃) in the main chain of the polymers.

The behavior of all the polymers in the first region was nearly identical. In Figure 13, the thermograph show a similar pattern of decomposition with two stages for the thermolysis of copoly((arylidene-ether)s XIc, mass loss was rapid between 403-485°C in the first step, and from 495-525°C in the second stage. The expected nature of decomposition of this type of polymers is a pyrolytic oxidation of C = C and scission of many bonds in the chain of the polymers.

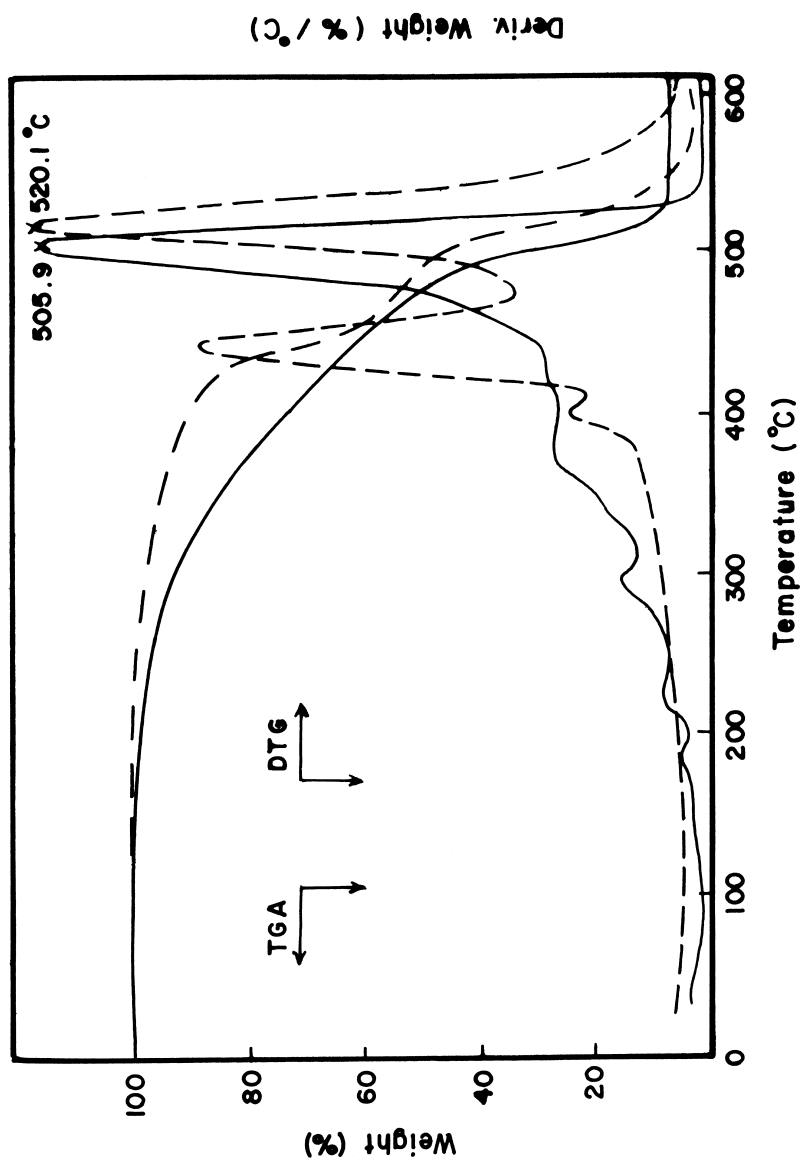


Figure 12. TGA and DTG thermograms of Polymers IXa (—), and IXg (---); heating rate 10°C/min.

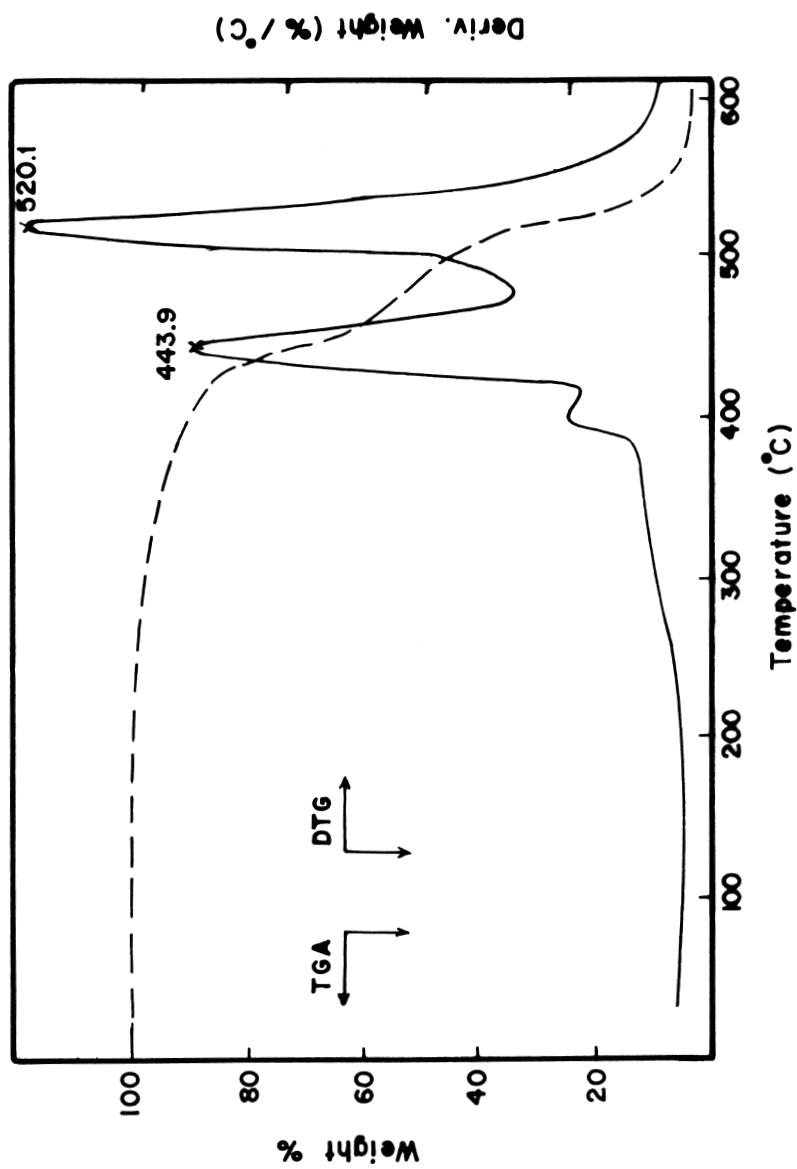


Figure 13. TGA and DTG thermograms of copolymer XIc; heating rate 10°C/min.

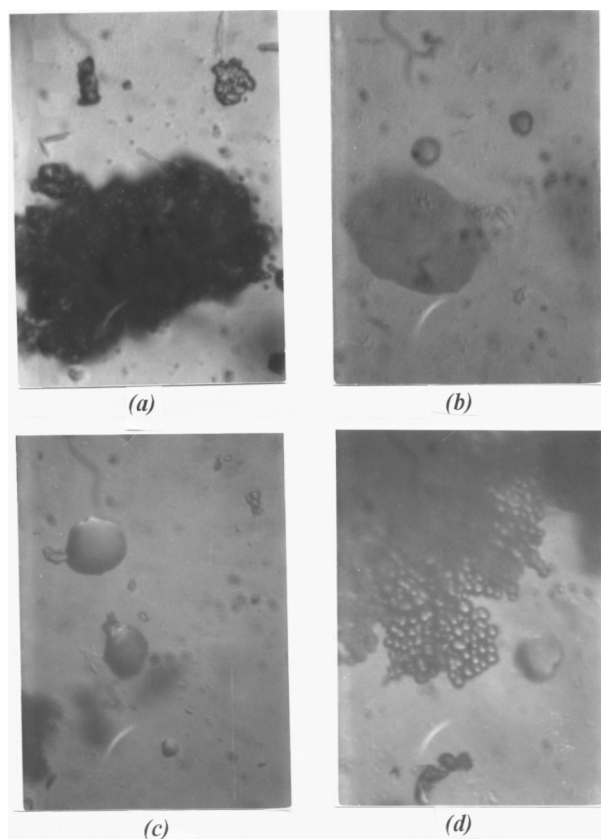


Figure 14(a-d). Photomicrographs of polymer IXf in the heating cycle (a) at 120°C (before melting); (b, c) at 185°C (Ti); (d) after cooling. (Magnification X 217).

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). Observation of poly(arylidene-ether)s IXf under a polarizing microscope revealed that this polymer exhibited a good spheroid structure with a thick dark rim in Figure 14a at 120°C (before melting), and the mesophases extend up to the isotropic phases at 185°C (Ti), (Figure 14b,c). After cooling to room temperature, a Botroidal structure appeared (Figure 14d).

Observation of poly(arylidene-ether)s IXg under polarizing microscope reveal that this polymer exhibited a Botroidal form of the nematic phase at 187°C (Figure 15b), the Botroidal structure change to spheroid at 286°C (Ti) Figure 15c, after cooling to room temperature, the spheroidal form changed to a sub-rounded structure, as shown in Figure 15d.

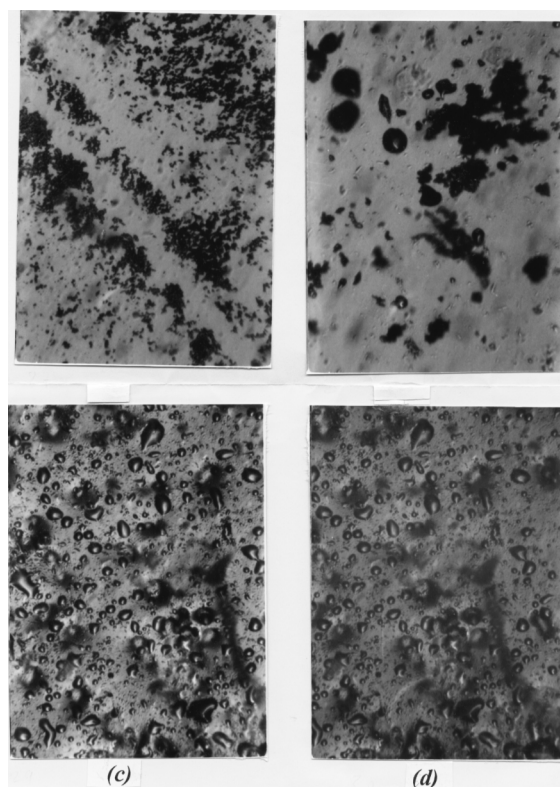


Figure 15(a-d). Photomicrographs of polymer IXg in the heating cycle (a) at 170°C (before melting); (b) at 187°C (T_m); (c) at 286 (T_i); (d) after cooling. (Magnification X 217.)

CONCLUSION

Liquid crystalline poly(arylidene-ether)s and copoly(arylidene-ether)s containing N-methylpiperidone and/or cyclohexanone moieties, respectively, pendant to the polymer backbone, were synthesized and characterized. A solution polycondensation technique at $\sim 80^\circ\text{C}$ was used. The majority of the polymers and copolymers are soluble in chlorinated hydrocarbons. Most of them exhibited melt birefringence and stirred opalescence during polarized microscope observation. X-ray diffraction analyses showed that the polymers IXc have a higher degree of crystallinity than the copolymers IXb,g. SEM examination of the polymer IXb and copolymer XIb revealed that the polymer surface appears as a Fibrous structure.

REFERENCES

1. Aly, K.I. High Perform. Polym. **1999**, *11*, 451.
2. Aly, K.I.; Hammam. A.S. Eurp. Polym. J. **1999**, *36*, 1933.

3. Aly, K.I. *Journ. Mac. Sci. Chem.* **2000**, *A37*, 39.
4. Aly, K.I.; Ahmed, R.A. *Liquid Crystals* **1999**, *27*, 451.
5. Tager, A. *Physical Chemistry of Polymers* **1972**, Mir, Moscow.
6. Perrin, D.D.; Armarego, W L.F.; Perrin, D.R. *Purification of Laboratory Chemicals*, 2nd Ed., Pergamon: New York, 1980.
7. Aly, K.I. *J. Appl. Polym. Sci.* **1999**, *74*, 2369.
8. Aly, K.I.; Khalaf, A.A. *J. Appl. Polym. Sci.* **2000**, *77*, 1218.
9. Aly, K.I. *High Perform. Polym.* **1994**, *6*, 149.
10. Aly, K.I.; Geies, A.A. *Ibid.* **1992**, *4*, 187.
11. Andrew, S.M.; Bass, R.G. *J. Polym. Sci.* **1989**, *A27*, 1225.
12. Mandelkern, L. *Crystallization of Polymers*, McGraw-Hill: New York, 1964.
13. Aly, K.I. *Polym. Intern.* 1998, *47*, 483.
14. Sek, D. *Eur. Polym. J.* **1984**, *20*, 923.
15. Antoun, S.; Lenz, R.W.; Jin, J.-I. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1901.
16. Roviello, A.; Sirigu, A. *Makromolek. Chem.* **1979**, *180*, 2543.
17. Sato, M.; Manabf, Y.; Sasaki, T.; Ohtomo, Y.; Komatsu, F. *Eur. Polym. J.* **1991**, *27*, 1391.

Received December 10, 2000

Revision received March 1, 2001