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Liquid Crystalline Polymers XIII Main Chain Thermotropic Copoly (Arylidene-Ether)s Containing 4-Teriary Butyl-Cyclohexanone Moiety Linked with Polymethylene Spacers

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ABSTRACT

A new homologous series of thermotropic liquid crystalline copoly(arylidene-ether)s based on 4-teriary butyl cyclohexanone moiety were synthesized by solution polycondensation of 4,4'-diformyl-α,ω-diphenoxyalkanes, $\mathbf{I_{a-d}}$ or 4,4'-diformyl-2,2'-dimethoxy-α,ω-diphenoxyalkanes $\mathbf{II_{a-d}}$ with the 4-teriary butyl-cyclohexanone **III** and cyclopentanone. A model compound **I**V was synthesized from the monomer **III** with benzaldehyde and characterized by elemental and spectral analyses. The inherent viscosities of the resulting polymers were in the range 0.22 - 0.92 dI/g. All the copoly(arylidene-ether)s were insoluble in common organic solvents but dissolved completely in concentrated H_2SO_4 and formic acid. The mesomorphic properties of these polymers were studied as a function of the diphenoxyalkane space length. Their thermotropic liquid crystalline properties were examined by DSC and optical polarizing microscopy and demonstrated that the resulting polymers form nematic mesophases over wide temperature ranges. The thermogravimetric analyses of those polymers were evaluated by TGA and DSC measurements and correlated to their structural units. X-ray analysis showed that copolymers having some degree of crystallinity in the region $2\theta = 5^{\circ}$ - 60°. In addition, the morphological properties of selected examples were tested by Scanning electron microscopy.

Keywords: Liquid Crystal; Thermotropic; Synthesis; Characterization; Poly(Arylidene-Ether)s

1. Introduction

Thermotropic 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 liquid phases [4]. These thermotropic liquid crystalline (mesomorphic) polymers have two basic types [5]: one type has flexible aliphatic spacer groups, used to insulate the delicate intermolecular interactions in the liquid crystalline portions from small, but disruptive motions of the main chain. The other type of thermotropic mesogenic polymer is one in which the liquid crystalline moiety is incorporated in the main polymer chain. The introduction of long aliphatic segments "spacers" was avoided to retain the relative rigidity and high axial ratio of the macromolecules which seem to be necessary, not only to stabilize the mesophase, but also to obtain superior mechanical properties [6,7]. On the other hand, the anisotropy of the liquid crystalline mesophase offers the possibility of production of novel high performance materials, exhibiting excellent properties due to a proper arrangement of macromolecules in the mesophase during the processing. The spacer length can cause periodic changes in the thermodynamic properties of a material (in particular, the transition properties) based on whether there are an even or odd number of unit in the LC polymer spacers [8-13]. Our previous papers described how thertropic liquid crystal homo- and copoly(arylidene-ether)s containing cycloalkanone moieties were synthesized [14-17] 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. In this paper, attention was addressed to 4-teriary-butyl-cyclohexanone moiety to prepare new thermotropic liquid crystal homo- and copoly(arylidene-ther)s. A major purpose of this work was to study the effect of inclusion of the 4-teriary butyl cyclohexanone moiety in the polymer main chain on the LC properties of these polymers. In addition, other cha-

racterization of these polymers such as thermostability, solubility, morphology, and crystallinity were discussed.

2. Experimental

2.1. Measurements

Elemental analyses were carried out using an Elemental Analyses system GmbH, VARIOEL, $V_{2.3}$ July 1998 CHNS Mode. 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 ^{1}H-NMR spectra were recorded on a GNM-LA 400-MHz NMR spectrophotometer at room temperature in DMSO or $CDCl_3$ using TMS as the internal reference. Mass spectra were recorded on a Jeol JMS_{600} mass spectrometer. The inherent viscosity was measured with an Ubbelhode Viscometer in DMSO at 25˚C (0.5 g/L). The solubility of polymers was examined using 0.02 g of polymer in 3 - 5 ml of solvent at room temperature. The X-ray diffractographs of the polymers were obtained with a Philips X-ray pw 1710 diffractometer, and Ni-filtered CuK_α radiations. Thermogravimetric analysis (TGA) and differential thermalgravimetric (DTG) were carried out in air with TA 2000 thermal analyzer at heating rate of 10˚C/min. in air. The maximum position of the melting endotherms was taken to be the m.p.s. The isotropization temperatures were determined by observing polymer melts with a polarizing microscope, GARL-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 mesophase. The morphologies of polymers were examined by scanning electron microscopy (SEM) using a Jeol JSM-5400 LV instrument.

2.2. Reagents and Solvents

4-Teriary butyl cyclohexanone (Merk) was used without purification. p-Hydroxy-benzaldehyde (Aldrich) was used without crystallization. 4-Hydroxy-3-methoxybenzaldehyde (vanillin) from EL-Nassr Chemical Company (Egypt) was used as it is. Dihaloalkanes (Aldrich) were used without purification. All solvents and other reagents were of high purity and were further purified by standard methods [18].

2.3. Monomers Syntheses

4,4'-Diformyl-α,ω-diphenoxyalkanes $\mathbf{I_{a-d}}$ and 4,4'-diformyl-2,2'-dimethoxy-α,ω-diphenoxyalkane $\mathbf{II_{a-d}}$. These monomers were prepared as described in our previous papers [16, 19].

2.4. Polymerization

The polycondensation of the dialdehydes and 4-teriary butyl cyclohexanone 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˚C - 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. All the poly(arylidene-ether)s were synthesized by an analogous procedure. Their yields, inherent viscosities, and elemental analyses are listed in **Table 1**.

3. Results and Discussion

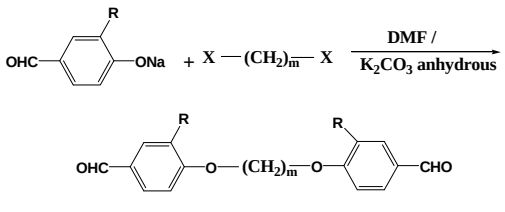
3.1. Synthesis of Dialdehyde Monomers I_{a-d} and II_{a-d}

Two series of dialdehydes, namely of 4,4-diformyl-α,ω-diphenoxyalkanes $\mathbf{I_{a-d}}$ and 4,4-diformyl-2,2-dimethoxy-α,ω-diphenoxyalkanes $\mathbf{II_{a-d}}$ were prepared by interaction of one mole of dihaloalkanes with two moles of the sodium salt of 4-hydroxybenzaldehyde or sodium salt of 4-hydroxy-3-methoxy benzaldehyde respectively, in DMF in the presence of anhydrous potassium carbonate, as mentioned previously in our previous papers [13-16] as shown in **Scheme 1**.

The structures of these monomers were confirmed by elemental and spectral analyses as shown in the experimental part.

3.2. Synthesis of Model Compound 2, 6-Dibenzylidene-4-Tert-Butylcyclo-Hexanone IV

Before attempting the polymerization process, model compound IV for the desired poly(arylidene-ether)s was synthesized by the interaction of 1 mole of the monomer named 4-tert-butyl-cyclohexanone with 2 moles of benzaldehyde in absolute ethanol and in the presence of few drops of (30%) alcoholic KOH as basic catalyst according to **Scheme 2**.



I_a , R=H, m=2 , X=Cl
I_b , R=H, m=6 , X=Cl
I_c , R=H, m=8 , X=Cl
I_d , R=H, m=10 , X=Cl

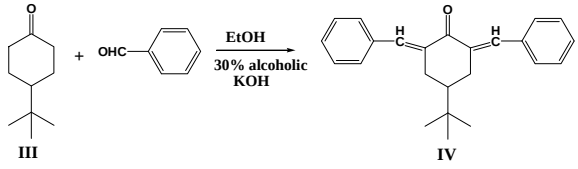
II_a , R=OCH_3, m=2 , X=Cl
II_b , R=OCH_3, m=6 , X=Cl
II_c , R=OCH_3, m=8 , X=Cl
II_d , R=OCH_3, m=10 , X=Cl

Scheme 1. Synthesis of dialdehydic monomers I_{a-d}, II_{a-d}.

Table 1. Solubility characteristic and inherent viscosity of copoly(arylidene-ether)s containing 4-tertiary butyl cyclohexanone moiety in the main chain V_{a-d} and VI_{a-d}.

Polymer code	DMF	DMSO	$CHCl_3$	$CHCl_3$ + acetone (1:1)	HCOOH	DMA	THF	DCM	Conc H_2SO_4	η_{inh}* (dL/g)
V_a	+	+	+	+	−	−	+	+	++	−
V_b	+	+	++	+	−	−	++	++	++	0.47
V_c	+	+	++	+	−	+	++	+	++	0.22
V_d	+	+	++	+	−	+	+	+	++	0.83
VI_a	+	+	+	+	−	+	+	+	++	−
VI_b	+	+	+	+	−	+	+	+	++	−
VI_c	+	+	++	+	−	+	++	++	++	0.92
VI_d	+	+	++	−	−	+	−	+	++	0.54

++: Soluble at room temperature (RT); +: Partially soluble at (RT); −: Insoluble; *Inherent viscosity was measured in $CHCl_3$ at 23˚C.



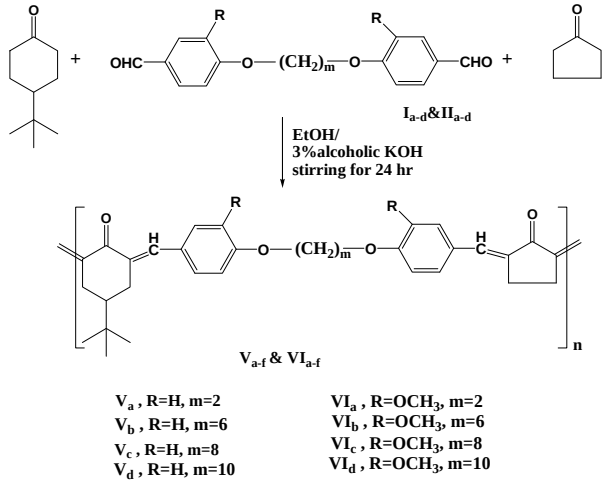
Scheme 2. Synthesis of model compound IV.

The structure of model compound **IV** was confirmed by elemental and spectral analyses. The FT-IR spectrum of [2,6-dibenzylidene-4-tertbutylcyclohexanone] **IV** showed characteristic absorption bands at 2995 cm^{-1} for (CH) stretching vibration of aromatic ring, at 1680 cm^{-1} for (C =O) of cyclohexanone and at 1595 cm^{-1} for (C=C) group of phenyl rings, beside other characteristics peaks were observed. 1H-NMR spectrum of **IV** in $CDCl_3$ showed singlet S at δ0.9 (9H of CH_3), multiple m at δ1.5 (1CH_2 cyclohexanone), multiple m at δ2.3 - 3.1 (2CH_2 cyclohexanone), multiple m at δ7.3 - 7.6 (2CH=C and 10 aromatic). The mass spectrum showed molecular ion peak at m/z = 330.45 (3.2%) which in agreement with its molecular formula ($C_{24}H_{26}O$), other peaks appeared at m/z = 273.52(M^+-$C_{20}H_{17}O$, 2%), at m/z = 57.91(M^+-C_4H_9 2.1%), and at m/z = 90.48 (M^+-C_7H_6 5.4%).

3.3. Synthesis of Copoly(Arylidene-Ether)s V_{a-d} & VI_{a-d}

The present work had as its aim the synthesis of new thermotropic liquid crystal copoly(arylidene-ether)s $\mathbf{V_{a-d}}$ and $\mathbf{VI_{a-d}}$ by the solution of polycondensation of the two series of diformyl-α,ω-diphenoxyalkane ($\mathbf{I_{a-d}}$) and diformyl-2,5-dimethoxy-α,ω-diphenoxyalkane ($\mathbf{II_{a-d}}$) with 4-teriary butyl-cyclohexanone **III** and cyclopentanone and as shown in **Scheme 3**.

The structure of the resulting polymers was established from elemental and spectral analyses including (FT-IR and ^{1}H-NMR). The results of elemental analyses for the



Scheme 3. Synthesis of copoly (arylidene-ether)s V_{a-f} and VI_{a-f}.

copoly(arylidene-ether)s $\mathbf{V_{a-f}}$ and $\mathbf{VI_{a-f}}$ prepared agree with calculated values (see experimental part). It should be noted that the elemental analysis results from the polymer deviated by 2% - 5% for the proposed structures. These differences can be accounted for by: 1) poor solubility and hence poor reactivity in the initial stage of polymerization; 2) difference in the reactivity of monomers during the polymerization, which lead to polymers with different compositions, the so called "composition drift" [20-23].

The FT-IR spectra of the poly(arylidene-ether)s $\mathbf{V_{a-d}}$ and $\mathbf{VI_{a-d}}$ as examples, showed characteristic absorption bands at 3035 - 2926 cm^{-1} for (CH) stretching vibration of aromatic ring, at 2869 - 2852 cm^{-1} for (CH) stretching of (CH_2) groups, at 1691 - 1678 cm^{-1} for (C=O) of cyclohexanone, at 1600 - 1594 cm^{-1} for (C=C) group, at 1511 - 1465 cm^{-1} for phenyl rings and at 1266 - 1240 cm^{-1} for (C-O-C) bond (ether linkages). In addition, other characteristic bands, due to specific groups present in various

polymers were also shown.

^{1}H-NMR of polymers in $CDCl_3$ such as $\mathbf{V_a}$ showed singlet S at δ0.94 (9H of CH_3), weak multiple m at δ1.4 - 1.7 (H of CH and 2H of $2CH_2$ in cyclohexanone), multiple m at δ2.4 (H of CH_2 β to C=CH ph), weak multiple m at δ3 (2H of CH_2 near C=O bond), multiple m at δ4.3 (4H of CH_2 linked to oxygen in ether linkage) and multiple m at δ7 - 7.8 (8H of aromatic and H of CH=C).

^{1}H-NMR of polymers in $CDCl_3$ such as $\mathbf{VI_b}$ showed singlet S at δ0.94 (9H of CH_3), multiple m at δ1.4 - 1.7 (8H of middle methylene group, H of CH and 2H of 2 CH_2 in cyclohexanone), multiple m at δ2.3 (H of CH_2 β to C=CH ph), multiple m at δ3.1(2H of CH_2 near C=O bond), multiple m at δ3.9 (4H of CH_2 linked to oxygen in ether linkage) and multiple m at δ6.9 - 7.8 (8H of aromatic and H of CH=C).

4. Polymer Characterization

The various characteristics of the resulting polymers including solubility, viscometry, X-ray diffraction analysis, DSC, TGA, OPM and SEM were also determined and the data are discussed below.

4.1. Solubility

Room temperature solubility characterization of poly(arylidene-ether)s $\mathbf{V_{a-d}}$ and $\mathbf{VI_{a-d}}$ were tested using various solvents including: DMF, DMSO, $CHCl_3$, $CHCl_3$-acetone mixture, HCOOH, DMA, THF, DCM and conc. H_2SO4. A 0.5% (w/v) solution was taken as a criterion for solubility. It can be clarified from **Table 1** that poly(arylidene-ether)s $\mathbf{V_{a-d}}$ and $\mathbf{VI_{a-d}}$ are soluble in protonic acids, e.g. conc. H_2SO_4 (concentrated H_2SO_4 gave reddish-violet color).In polar aprotic solvents, such as DMF and DMSO all polymers dissolved partially. In DMA all polymers dissolve partially except $\mathbf{V_{a,b}}$, which are not soluble. In HCOOH all polymers are not soluble except $\mathbf{V_e}$, which are dissolved partially. In $CHCl_3$ all polymers dissolved partially except $\mathbf{V_d}$ not soluble and $\mathbf{V_{b-d}}$ and $\mathbf{VI_{c,d}}$ are completely soluble. In $CHCl_3$-acetone mixture all polymers dissolved partially except $\mathbf{VI_d}$ not soluble. In THF all polymers are partially soluble except $\mathbf{VI_d}$ not soluble but $\mathbf{V_b}$ and $\mathbf{VI_c}$ are completely soluble. In DCM all polymers are partially soluble except $\mathbf{V_{b,e}}$ and $\mathbf{VI_{c,d}}$ are completely soluble. They have good resistance to most Solvents. The difference in solubility can be attributed to the crystallinity associated with various LCPs. The presence of methoxyl group as substitute in the phenyl ring with tertiary butyl group in cyclohexanone moiety caused some hindering between the repeating units so decrease chain packing distances and increasing inter chain interactions such as hydrogen bonding so that making salvation of polymers containing methoxyl group more difficult than those which contain hydrogen atom instead, while increase length of the chain increase this solubility even for those which contain methoxyl group.

4.2. Inherent Viscosity

The inherent viscosity (η_{inh}) of some poly (arylidene-ether)s $\mathbf{V_{b-d}}$ and $\mathbf{VI_{c,d}}$ were determined in $CHCl_3$ at 23˚C with Ubbelohde Suspended Level Viscometer. The inherent viscosity value is defined as:

$$\eta_{inh} = \left[2.3\log\left(\eta/\eta_\circ\right)\right]/C$$

The solution concentration C is 0.5 g/100 ml, $\eta/\eta_\circ$ = relative viscosity (or viscosity ratio). The data are listed in **Table 2**. It can be clarified from this table that polymer $\mathbf{VI_{c,d}}$ have high viscosity value (0.92, 0.22 dL/g) and this may be attributed to high molecular weight of these polymers. On the other hand, polymers $\mathbf{V_{b-d}}$ have low viscosity (0.049, 0.26, 0.08, 0.18 dL/g) respectively, and this may be attributed to low molecular weight of these polymers.

4.3. U.V. Visible Spectra

The electronic spectra of selected examples of poly(arylidene-ether)s $\mathbf{V_b}$, $\mathbf{V_d}$ and $\mathbf{V_f}$ were obtained in chloroform $CHCl_3$ at a concentration 2×10^{-5} (w/v). The electronic spectra of $\mathbf{V_{b,d}}$ showed absorption band at 269 - 270 nm due to π-π^* transition within the benzenoid system for all polymers. For polymers $\mathbf{V_{b,d}}$ λ_{max} near 270 nm and at λ_{max} near 269 nm for polymer. All of these polymers showed absorption band at λ_{max} near 363 - 375 nm which was due to the π-π^* and n-π^* excitation of C=C and C=O groups. For polymer $\mathbf{V_b}$ λ_{max} near 364 nm, and at λ_{max} near 363 nm for polymer $\mathbf{V_d}$.

4.4. X-Ray Analysis

The X-ray diffractograms of selected examples of the poly(arylidene-ether)s $\mathbf{V_d}$, $\mathbf{VI_b}$ and are shown in **Figures 1** and **2** as example. The polymers show few reflection peaks that are ranging between crystalline and amorphous lying in region $2\theta = 5^\circ$ - 60°. This indicates that there is a large class of structures that are intermediate in the ordered states between crystalline and amorphous phases (with pronounced long-range order) in the arrangement of their atoms and molecules. Moreover, the presence of C=O as polar group in addition to high content of C=C bonds provides some order between the two extents of crystallinity[128]. More particularly, the diffractogram of polymer $\mathbf{V_e}$ which contains short spacer $-(CH_2)_3-$ in **Figure 1,** Shows some reflection sharpness peaks, when the length of spacer increase as in polymer $\mathbf{V_d}$ which contains ten methylene groups $-(CH_2)_{10}-$, in **Figure 2**, the reflection sharpness increased and the polymer became semicrystalline. This is explained by the fact that increasing the number of methylene groups in the spacers results in increasing polymer chain flexibility, and hence

Table 2. Transition behavior of selected copoly(arylidene-ether)s containing 4-tertiary butyl cyclohexanone moiety in the main chain V_{a-d} and VI_{a-d}.

Cpolymer number	m	*X*	Stirred Opalescence	Phase transition temperature (˚C, microscope)[a]		
				T_m	T_i	ΔT
IV_a	2	H	Strong	118	135	17
IV_b	6	H	Strong	108	112	4
IV_c	8	H	Strong	81	90	9
IV_d	10	H	Strong	79	92	13
V_a	2	OCH_3	Strong	151	160	11
V_b	6	OCH_3	Strong	197	210	13
V_c	8	OCH_3	Strong	100	121	11
V_d	10	OCH_3	Strong	81	87	6

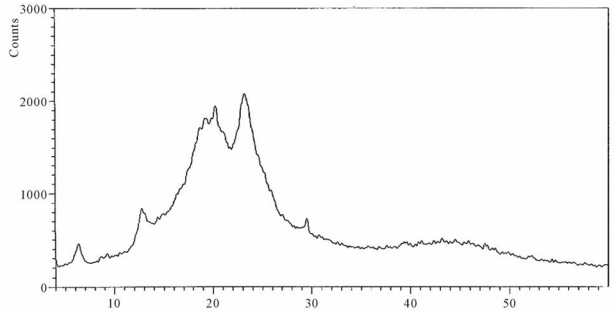


Figure 1. X-ray diffraction pattern of polymer IV_d.

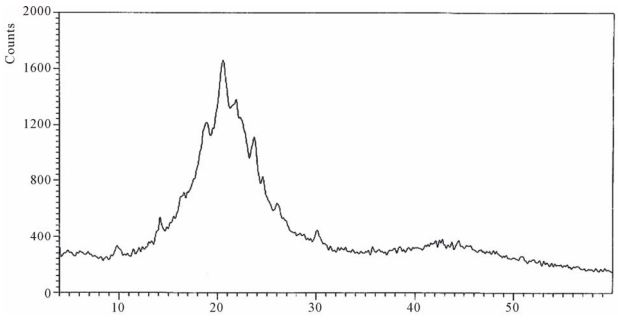


Figure 2. X-ray diffraction pattern of polymer IV_d.

increases crystallinity. This can be explained by the trans molecular conformation of polymer when the number of methylene units is even, molecules can be fitted easily into the crystal lattice and the rate of crystalization is faster as it cools down from the liquid crystal states.

4.5. Scanning Electron Microscope (SEM) Measurement

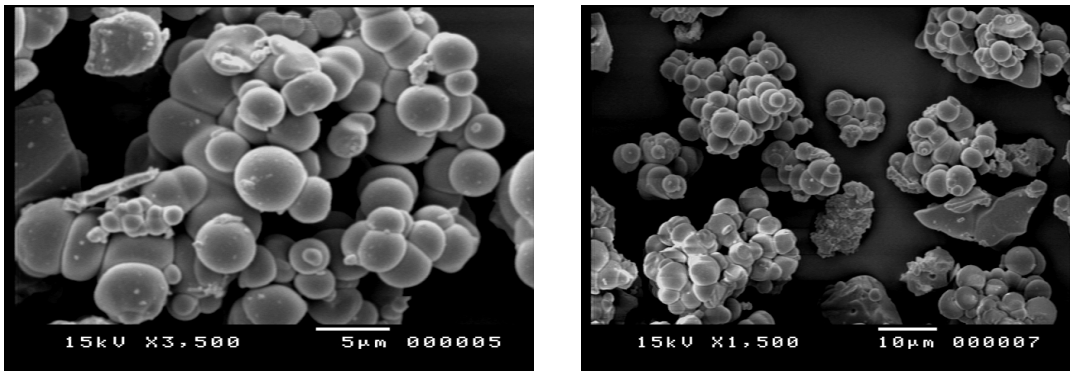
The morphology of selected examples of copoly(arylidene-ether)s $\mathbf{V_d}$, $\mathbf{VI_d}$ were examined as example by SEM using a low dose technique. **Figure 3(a)** (*X* = 1000) shows that polymer $\mathbf{V_d}$ has aggregates of layer structure. The higher magnification (*X* = 3500, 1500) in **Figure 3(b)** show that the aggregates show cavity shape. After dissolving of $\mathbf{V_d}$ in (DCM) and evaporation of solvent. **Figures 4(a)** and **(b)** (*X* = 500, 1000) show that polymer $\mathbf{V_d}$ has sponge structure.

4.6. Thermotropic Liquid Crystalline Properties of Poly(Arylidene-Ether)s V_{a-d} and VI_{a-d}

The thermal properties of the selected poly(arylidene-ether)s $\mathbf{V_{b,d}}$ and $\mathbf{VI_{b,d}}$ were characterized by TGA and optical polarized microscope (OPM) with heating stage. The copoly(arylidene-ether)s $\mathbf{V_{b,d}}$ and $\mathbf{VI_{b,d}}$ did not exhibit liquid crystalline properties while observed under optical polarized microscope with heating rate (6˚/min). The mesophase could be observed when the microscopic observation was made by placing the sample on a preheated hot stage. The liquid crystalline states of polymers $\mathbf{V_{b,d}}$, and, $\mathbf{VI_{b,d}}$ measured on a preheated hot stage of polarizing microscope at temperature 109˚C, 89˚C, 102˚C, 170˚C, 197˚C, 80˚C, 160˚C and 110˚C for the eight respective polymers; upon continued heating or heating at higher temperatures the liquid crystalline properties appeared at 112˚C, 92˚C, 114˚C, 182˚C, 210˚C, 87˚C, 162.7˚C and 119˚C for these polymers (**Figures 5** and **6**).

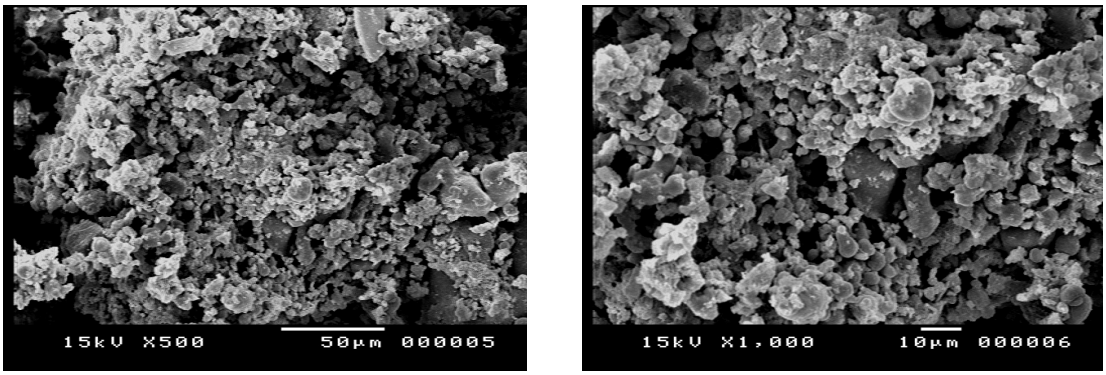
4.6.1. TGA Studies

The thermal behavior of the selected copoly(arylidene-ether)s $\mathbf{V_{b-f}}$ and $\mathbf{VI_{b-f}}$ was evaluated by TGA and DTG under nitrogen atmosphere at heating rate of $10^{\circ}C \cdot min^{-1}$. The thermographs of these polymers samples are given in **Figures 5** and **6** while **Table 3** gives the temperature for various% weight loss. TGA curves show initial decomposition of these polymers (10% loss) is considered to be the polymer decomposition temperature (PDT), which occurred in the range 503˚C to 694˚C for the samples.



(a) (b)

Figure 3. SEM images of polymer V_e surface at different magnification; (a): *X* = 3500; (b): *X* = 1500.



(a) (b)

Figure 4. SEM images of polymer V_e surface at different magnification; (a): *X* = 500; (b): *X* = 1000.

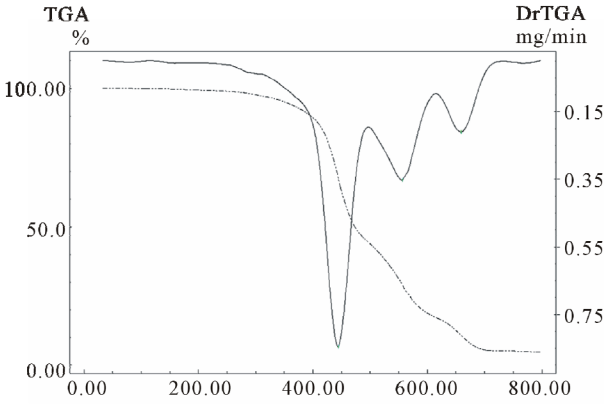


Figure 5. The TGA and Dr TGA traces of polymer IV_b in nitrogen at a heating rate of 10˚C/m.

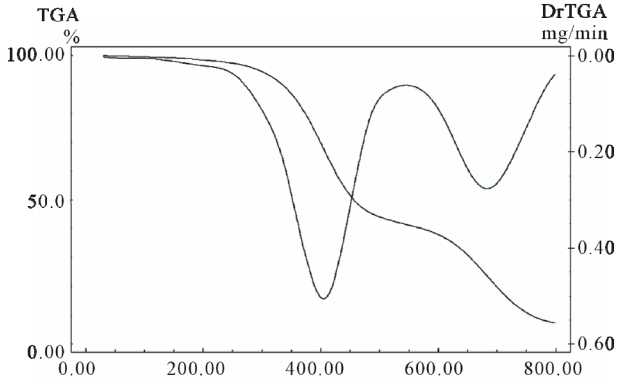
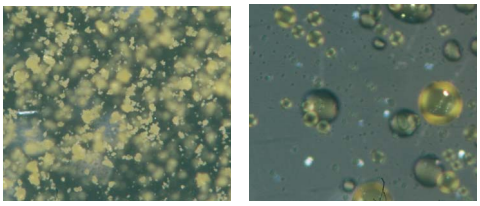


Figure 6. The TGA and Dr TGA traces of polymer IV_b in nitrogen at a heating rate of 10˚C/m.

In **Figure 5**, for polymer $\mathbf{V_b}$ the mass loss is seen to be rapid loss between ~282.02˚C - 557.46˚C (−81.95%). For polymer $\mathbf{V_d}$ in **Figure 6**, the mass loss was rapid between ~310.22˚C - 574.38˚C (−85.38%). From these data, it appears that the polymers containing methoxyl groups instead of hydrogen atoms with tertiary butyl group tend to exist in separated rather than more packed chains, appeared to be readily susceptible to easier thermal decomposition [24,25].

4.6.2. Texture Observations

The phase behavior of the selected copoly(arylidene-ether)s $\mathbf{V_a}$ as example according to optical polarizing microscope is summarized in **Table 3**. The examples ofpoly(arylidene-ether)s $\mathbf{V_a}$ is shown in **Figure 7**. Observation of polymer $\mathbf{IV_a}$ under polarizing microscope revealed that this polymer exhibited a good spheroid structure **Figure 7(a)** (before melting), in polarized light show that polymer has yellow color **Figure 7(b)**. The meso-



(a) (b)

Figure 7. Photomicrographs of polymer 119_f in the heating cycle at (a) < 81˚C (Magnification ×500), (Magnification ×200); (b) > 87˚C, in polarized light (Magnification ×200).

Table 3. Thermal properties of selected copoly(arylidene-ether)s containing 4-tertiary butyl cyclohexanone moiety in the main chain $V_{b,d}$ and $VI_{b,d}$.

Copolymer number	Temperature (˚C) for various decomposition levels*				
	10% Wt. loss	20% Wt. loss	30% Wt. loss	40% Wt. loss	50% Wt. loss
$\mathbf{V_b}$	361	407	427	442	454
$\mathbf{V_d}$	370	417	429	439	440
$\mathbf{VI_b}$	350	393	410	426	460
$\mathbf{VI_d}$	372	400	415	426	438

*Heating rate: 10˚C·min^{-1}.

phase extended up to the isotropic temperature at > 81˚C (T_i). After cooling to room temperature a highly spheroid structure with coalescence appeared as shown in **Figure 7(b)** in polarized light. Observation of polymer $\mathbf{V_a}$ under polarizing microscope revealed that this polymer exhibited good spheroid structure with thick dark rim **Figure 7(a)** (before melting), and the mesophase to the isotropic temperature at 87˚C (T_i). After cooling to room temperature a spheroid structure appeared as shown in **Figure 7(b)**.

5. Conclusion

A novel series of liquid crystalline copoly(arylidene-ether)s containing 4-teriary butyl cyclohexanone moiety have been synthesized. A solution polycondensation technique at ~80˚C was used. All the copoly(arylidene-ether)s were insoluble in common organic solvents but dissolved completely in concentrated H_2SO_4 and formic acid. The majority of the polymers are insoluble in common organic solvents and halogenated hydrocarbons. Most of them exhibited melt birefringence and stirred opalscence during polarized microscope observation. Both (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 polymers main chain.

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