

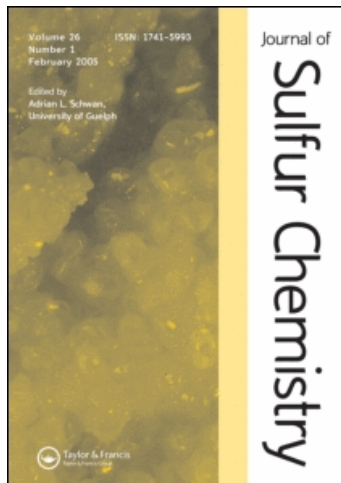
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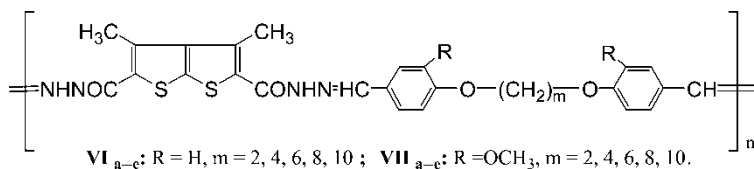
Liquid crystalline polymers VIII: thermotropic liquid crystalline poly(hydrazone–ether)s containing bis-thiophene linked to the main chain through spacers of various lengths

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A new series of poly(hydrazone–ether)s was synthesized from 3,4-dimethylthieno [2,3-b] thiophene-2,5-dicarbohydrazide, II and 4,4'-diformyl- α , ω -diphenoxyalkanes or 4,4'-diformyl-2,2'-dimethoxy- α , ω -diphenoxyalkanes. The inherent viscosities of the polymers were in the range 0.22 – 0.56 dI g⁻¹. Majority of the polymers were soluble in concentrated H₂SO₄. Their thermotropic liquid crystalline properties were examined by DSC, an optical polarizing microscopy using a hot stage and thermogravimetric analyses. The polymers exhibited almost thermotropic liquid crystalline properties. In most cases, the mesophases extended up to 430°C, where thermal decomposition prevented further observation.



Keywords: Thermotropic liquid crystals; Synthesis; Characterization; Poly(hydrazone-ether)s; Bis-thiophene

1. 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]. The anisotropy of the liquid crystalline mesophase offers the possibility of production of novel high-performance materials, exhibiting excellent properties in the field of film formation, production of fibers, and moldings due to a proper arrangement of macromolecules in the mesophase during processing. Moreover, polymers exhibiting liquid

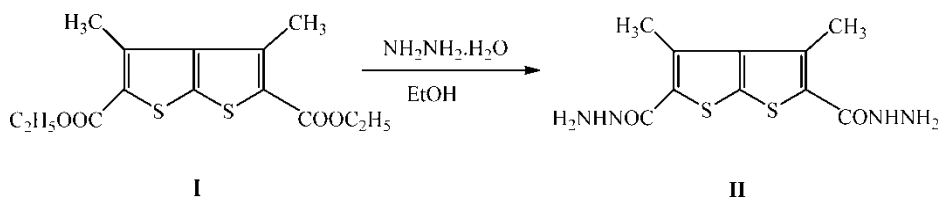
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crystallinity consist of macromolecules with rigid structure, characterized by high extension of backbones. This feature leads to the axial order that is typical of nematic fluids [5]. Furthermore, various classes of main chain liquid crystalline polymers have been reported, for example polyamides, polyesters, polyketones, poly(ether-sulfone)s and polycarbonates [6–11].

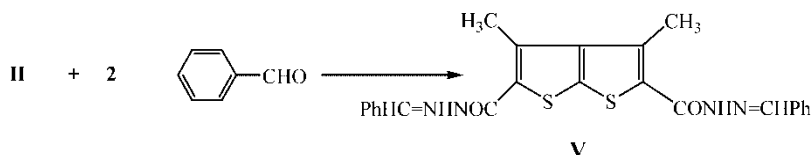
To our knowledge, no work has been reported in considering the synthesis of poly(hydrazone-ether)s containing bis-thiophene moiety in the main chain. The major aim of this work has been to investigate the effect of inclusion of flexible spacers as well as a thiophene ring in the moiety of poly(hydrazone-ether)s on liquid crystal properties. In addition, other characteristics of these polymers such as thermostability, solubility, and crystallinity are discussed.

2. Results and discussion

Fusion of diethyl-3,4-dimethylthieno[2,3-b]thiophene-2,5-diester I with hydrazine hydrate furnished 3,4-dimethylthieno[2,3-b]thiophene-2,5-dicarbohydrazide II (scheme 1). The model compound was synthesized, before attempting the polymerization, by interaction of monomer II with two moles of benzaldehyde (scheme 2). IR spectra of II and V are shown in figure 1.



SCHEME 1. Synthesis of monomer II.



SCHEME 2. Synthesis of model compound V.

2.1 Characterization of chemical properties of the polymers

The direct polycondensation easily affords high to moderate molecular mass polymers in quantitative yields.

The yields, inherent viscosities (η_{inh}), and elemental analyses of the poly(hydrazone-ether)s are listed in table 1.

Elemental analyses were performed on all the monomers (not shown) (as well as the new polymers). It should be noted that the results of the analysis of the polymers (c.f. table 1) deviated from 1.2% to 1.7% of the theoretical values. Especially polymers of high molecular weight and those containing polar groups capable of hydrogen bonding with solvent molecules that easily trap solvent molecules within the polymer matrix [12].

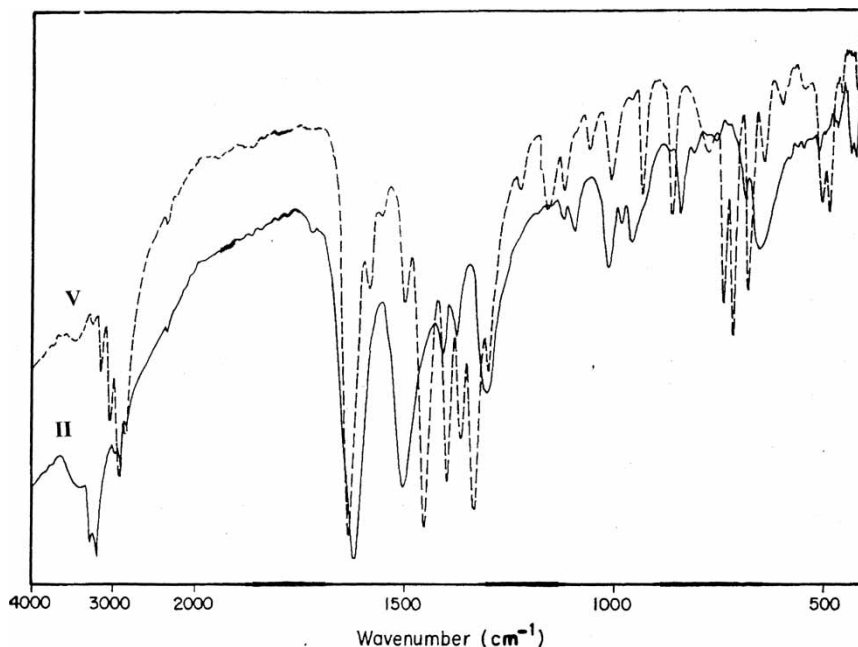


Figure 1. IR spectra of monomer II and model compound V.

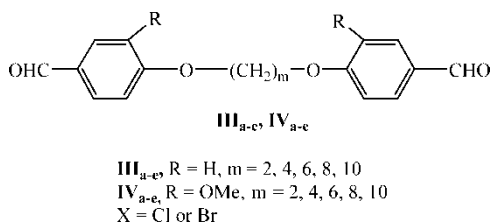
Table 1. Elemental analyses, yields, and inherent viscosity of poly(hydrazone-ether)s VI_{a-e} and VII_{a-e}.

Polymer number	Yield (%)	η^*_{inh} (dl/g)	Elemental formula	Elemental analyses				
				Calcd	Found	C%	H%	N%
VI _a	76	0.57	(C ₂₆ H ₂₂ N ₄ O ₄ S ₂) _n	Calcd	60.23	4.27	10.8	12.36
				Found	61.01	4.26	11.1	13.07
VI _b	89	0.45	(C ₂₈ H ₂₆ N ₄ O ₄ S ₂) _n	Calcd	61.53	4.79	10.25	11.73
				Found	61.84	4.88	10.3	12.13
VI _c	73	0.39	(C ₃₀ H ₃₀ N ₄ O ₄ S ₂) _n	Calcd	62.71	5.26	9.75	11.16
				Found	63.02	5.32	9.69	12.40
VI _d	96	0.22	(C ₃₂ H ₃₄ N ₄ O ₄ S ₂) _n	Calcd	63.78	5.68	9.29	10.64
				Found	63.66	5.78	9.43	10.48
VI _e	66	0.47	(C ₃₄ H ₃₈ N ₄ O ₄ S ₂) _n	Calcd	64.75	6.06	8.88	10.14
				Found	65.02	6.26	8.69	9.60
VII _a	88	0.32	(C ₂₈ H ₂₆ N ₄ O ₆ S ₂) _n	Calcd	58.13	4.52	9.68	11.06
				Found	56.9	4.8	9.17	11.17
VII _b	81	0.49	(C ₃₀ H ₃₀ N ₄ O ₆ S ₂) _n	Calcd	59.4	4.98	9.23	10.55
				Found	59.18	5.11	9.25	10.78
VII _c	91	0.35	(C ₃₂ H ₃₄ N ₄ O ₆ S ₂) _n	Calcd	60.56	5.39	8.82	10.08
				Found	60.43	5.23	8.97	11.69
VII _d	90	0.37	(C ₃₄ H ₃₈ N ₄ O ₆ S ₂) _n	Calcd	61.62	5.77	8.45	9.65
				Found	61.45	5.99	8.32	10.88
VII _e	92	0.41	(C ₃₆ H ₄₂ N ₄ O ₆ S ₂) _n	Calcd	62.59	6.12	8.11	9.26
				Found	63.3	6.52	7.98	9.62

*Measured in H₂SO₄, with C = 0.5 g/100 mL at 30°C.

The expected structures of the poly(hydrazone-ether)s VI_{a-e} and VII_{a-e} were also confirmed by elemental analyses and IR spectroscopy.

Spectral data support the structural assignment of the poly(hydrazone-ether)s. IR spectra recorded from pellets of KBr mixed with the respective polymer showed characteristic absorption bands due to NH stretching at 3400–3200 cm⁻¹; CH stretching of CH₂ groups (aliphatic

Figure 2. Diformyl diphenoxy alkanes III_{a-e}, IV_{a-e}.Table 2. Solubility characteristics of polymers VI_{a-e}, VII_{a-e}.

Polymer number	DMF	DMSO	NMP	DMA	CHCl ₃ +acetone (1 : 1)	HCOOH	Conc H ₂ SO ₄
VI _a	+	+	+	+	-	-	++
VI _b	+	+	+	+	-	-	++
VI _c	-	-	-	-	-	-	++
VI _d	+	+	+	-	-	-	++
VI _e	-	-	-	-	-	-	++
VII _a	-	-	-	-	-	-	++
VII _b	-	-	-	-	-	-	++
VII _c	-	-	-	-	-	-	++
VII _d	-	-	-	-	-	-	++
VII _e	-	-	-	-	-	-	++

++: Soluble at room temperature (RT).

+: Partially soluble at (RT).

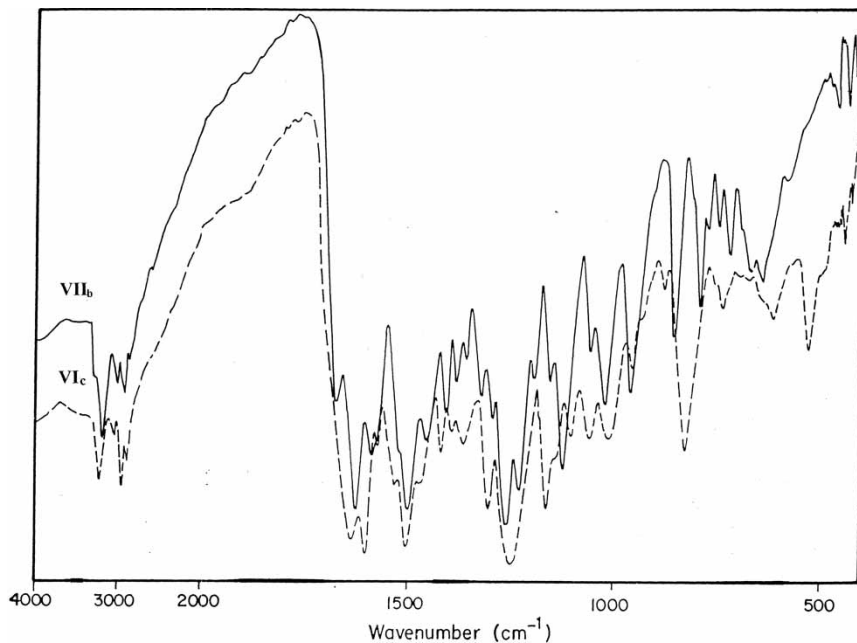
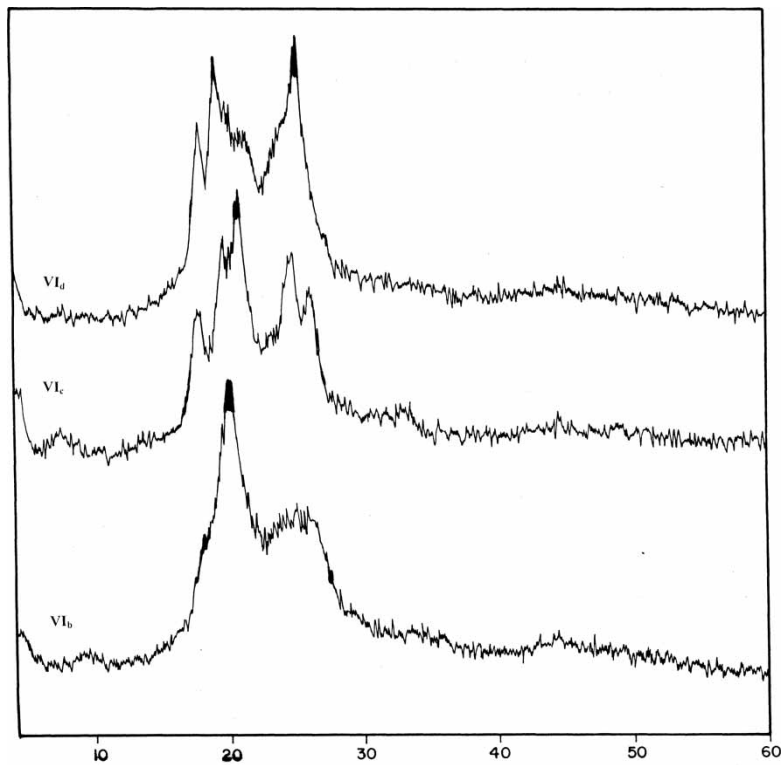
-: Insoluble.

spacers) at 2950–2860 cm⁻¹; C=O of hydrazone at 1640 cm⁻¹; CH=N–NH (hydrazone groups) at 1620–1600 cm⁻¹; phenylene rings at 1590–1510 cm⁻¹; C–O–C bonds (ether linkage) at 1275–1235 cm⁻¹, C=C at 1590–1610 cm⁻¹, and C=S at 690–710 cm⁻¹ of bis-thiophene moiety; as examples the IR spectra of VI_c and VII_d are shown in figure 3.

2.2 Characterization of physical properties of the polymers

2.2.1 Solubility. The solubility characteristics of the poly(hydrazone–ether)s VI_{a-e} and VII_{a-e} were tested using various solvents including (DMF) dimethylformamide, (DMSO) dimethylsulfoxide, (NMP) *N*-methylpyrrolidone, (DMA) dimethylacetamide, chloroform – acetone (1:1), formic acid and conc. H₂SO₄. A 5% (w/v) solution was taken as a criterion for solubility. The results are shown in table 2. All the poly(hydrazone–ether)s are freely soluble in H₂SO₄. In common organic solvents (CHCl₃, acetone, HCOOH) and halogenated hydrocarbons, all polymers are insoluble. In polar aprotic solvents, such as DMF, DMSO, NMP, and DMA, the majority of the polymers showed poor solubility (polymers VI_a, VI_b, and VI_d are partially soluble). When comparing the solubility of polymers derived from 4,4'-diformyl- α,ω -diphenoxyalkanes (polymers VI_{a-e}) with those derived from 4,4'-diformyl-2,2'-dimethoxy- α,ω -diphenoxyalkanes (polymers VII_{a-e}), we found that the former have better solubility than the latter, the presence of fused thiophene moiety in the polymer backbone leads to increasing chain packing distances and decreasing inter-chain interactions, such as hydrogen bonding, thereby increasing the solubility compared with other polyhydrazides [13].

2.2.2 X-ray measurements. X-ray diffractograms of selected examples of poly (hydrazone-ether)s VI_b, VI_c, VI_d, VII_a, and VII_c are shown in figures 4 and 5. Few reflection peaks intermediate between crystalline and amorphous interferences in the region

Figure 3. IR spectra of polymer VI_c and VII_b.Figure 4. X-ray diffraction patterns of polymers VI_{b,c,d}.

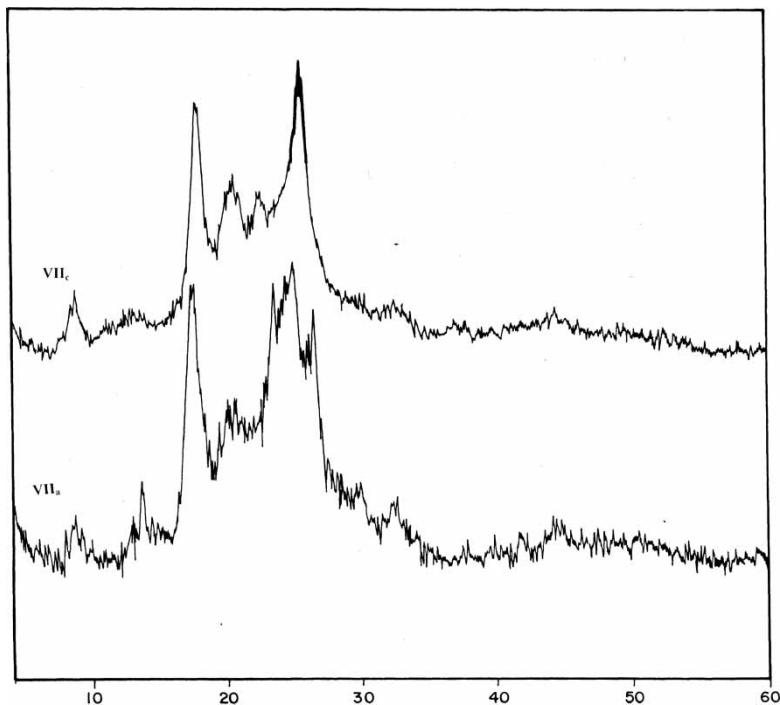


Figure 5. X-ray diffraction patterns of polymers VII_{a,c}.

$2\theta = 5^\circ\text{--}60^\circ$ can be seen. This indicates that there is a large class of structures that are intermediate in the order state. Moreover, the presence of C=O polar groups, in addition to high C=N bond levels induces some order between two adjacent chains of polymers, leading to some extended crystallinity [14].

Moreover, the XRD spectra show that polymer VI_b, which contains a short spacer, (CH₂)₄–, has only few reflection peaks (amorphous), polymer VI_c, which contains six methylene groups, –(CH₂)₆–, also having rather few reflection peaks (semicrystalline), and VI_d with a longer spacer, which contains eight methylene groups, –(CH₂)₈–, with an increasing reflection peaks (more semicrystalline). It is noted that the presence of eight methylene groups in the poly(hydrazone-ether) VI_d increases the polymer chain flexibility [15]. In polymer VII_a that contains two methylene groups, –(CH₂)₂–, and polymer VII_c that contains six methylene groups, –(CH₂)₆–, the number of reflection peaks increases and the polymers become more semicrystalline. It should be observed that the presence of methoxy groups as substituent in the phenyl rings causes hindering between the repeating units. This hindering forces the chains to an unsymmetrical orientation in the polymer chains and reduces the crystallinity [16].

2.2.3 Thermotropic liquid crystal properties of poly(hydrazone-ether)s VI_{a–e} and VII_{a–e}. The thermal behavior of the poly(hydrazone-ether)s VI_{a–e} and VII_{a–e} were characterized by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), differential thermal gravimetry (DTG), and by an optically polarized microscope (OPM) with hot stage. The microscopic observation allows detection in 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 endothermal maxima [17]. The isotropization temperatures of these polymers were observed using the OPM equipped with a heating stage in the

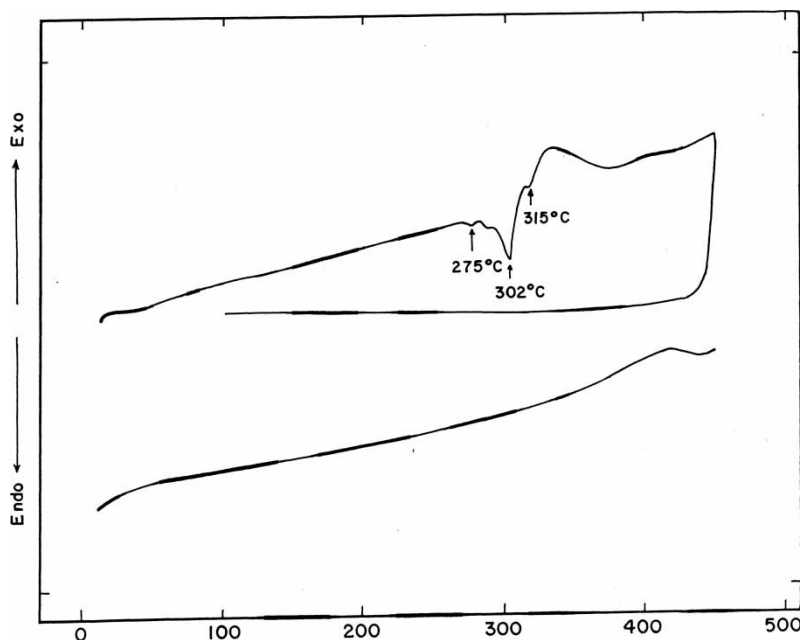
Table 3. Transition behavior of poly(hydrazone-ether)s VI_{a-e} and VII_{a-e}.

Polymer number	n	X	Stirred opalescence	Phase transition* temperatures (°C, microscope)			Phase transition temperatures (°C, DSC)			TGA**	
				T _m	T _i	ΔT	T _m	T _i	ΔT	10%	50%
VI _a	2	H	Yes	342	363	21	–	–	–	326	450
VI _b	4	H	–	329	347	18	–	–	–	–	–
VI _c	6	H	Yes	316	324	8	317	328	11	333	423
VI _d	8	H	–	–	–	–	–	–	–	330	440
VI _e	10	H	Yes	294	312	18	302	315	13	–	–
VII _a	2	OCH ₃	Yes	315	336	21	–	–	–	330	473
VII _b	4	OCH ₃	–	–	–	–	–	–	–	–	–
VII _c	6	OCH ₃	Yes	279	288	9	282.8	307	–	336	496
VII _d	8	OCH ₃	Yes	262	297	17	–	–	–	329	492
VII _e	10	OCH ₃	Yes	245	263	18	250	264	14	–	–

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

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

temperature range 263–363 °C of polymers VI_{a,b,c,e} and VII_{a,c,d,e}. The phase transition temperatures of the polymers are shown in table 3. In DSC studies, most of the polymers revealed multiple or more endothermic DSC thermograms, probably due to polymorphism [18, 19]. In some cases (especially in polymers VI_{c,e} and VII_c), the peaks in DSC are broad, which indicate 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. The heating traces of the polymers display a glass-transition (T_g), which is weak in the case of polymer VI_e. Figure 6 shows the DSC profiles of the melting process of sample VI_e, which revealed multiple endotherms at 275 °C (T_g), 302 °C (T_m), and 370 °C, (decomposition). When the sample was cooled after preheating to 440 °C, there were no endothermal

Figure 6. The DSC curve of polymer VI_e.

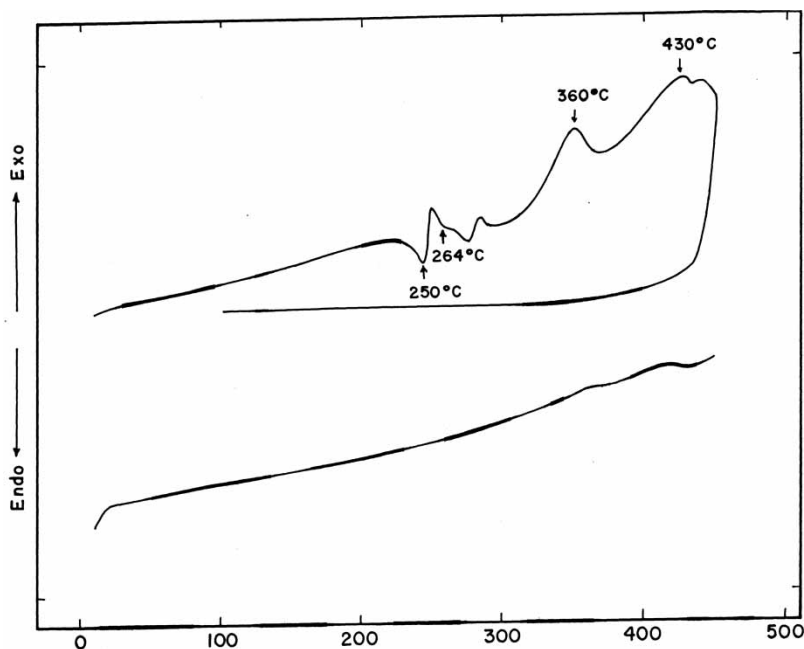


Figure 7. The DSC curve of polymer VII_e.

or exothermal peaks. On the second heating cycle, there was an exotherm at 420 °C. Figure 7 shows the DSC profiles of the melting process of sample VII_e, which also revealed multiple endotherms at 250 °C (T_m), 264 °C (T_i), and 375 °C, (decomposition). When the sample was cooled after preheating to 460 °C, there were no endothermal or exothermal peaks. On the second heating cycle there was an exotherm at 418 °C. This effect might be due to solid-to-solid (T_{ss}), solid-to-mesophase (T_m) and mesophase-to-solid (T_i) [20] transitions, which are observed with the optical microscope.

It should be noted that the phase transition temperatures of polymers VI_e and VII_e observed by DSC (figures 6 and 7, respectively), are very close to the phase transition temperatures observed by the microscope. The small variance between the temperature grades (not more than 9 °C) may be attributed to observation of the temperatures during heating in OPM [21, 22]. The effect of length of the spacer on the thermal properties of poly(hydrazone-ether)s, VI_{a-e} and VII_{a-e}, is also shown in table 3. Both melting points and isotropization temperatures decreased as the length of the flexible aliphatic spacer in the polymer chain increased. The effect of the substituents on the thermal properties of the polymers is also shown in table 3. Both the melting points and isotropization temperatures were decreased by the introduction of methoxy groups into the polymer main chain [23]. Similar observations were reported in a previous work [24]. 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 [25].

The thermographs of selected examples of polymers VI_d and VII_d are shown in figure 8, while table 3 gives the temperatures for various weight losses (%). TGA curves show a small weight loss in the range 2–4% starting at 160 °C until 200 °C, which may be attributed to the loss of observed moisture and entrapped solvents. The initial decomposition of these polymers (5% loss) started at 286 °C for series VI_{a-e} and at 319 °C for series VII_{a-e}. All the polymers showed similar decomposition patterns. The expected nature of decomposition

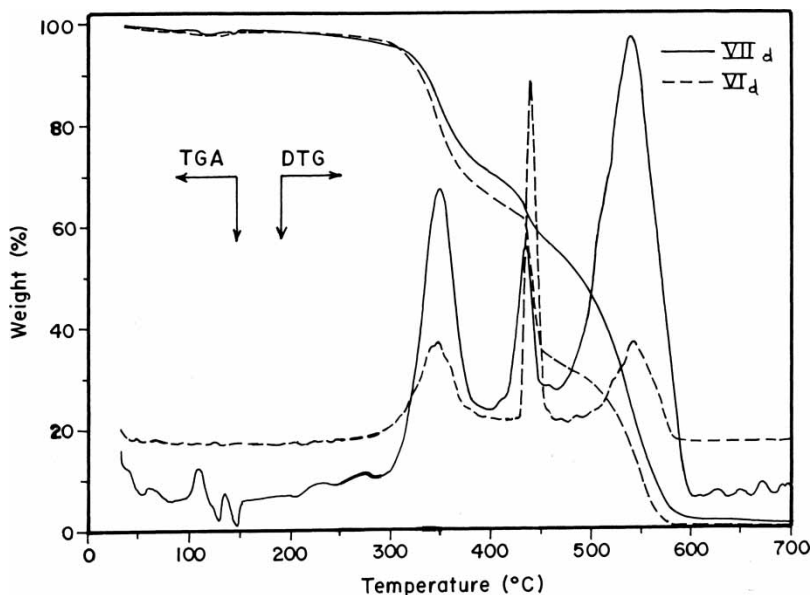


Figure 8. The TGA and DTG traces of polymers VI_d and VII_d in air at a heating rate of $10^\circ\text{C}/\text{min}$.

of these polymers is through pyrolytic oxidation of $\text{C}=\text{C}$ and rupture of many bonds. The temperature at 10% weight loss is considered to be the polymer decomposition temperature (PDT) [15]. It occurs in the range $330\text{--}333^\circ\text{C}$ for polymers $VI_{a\text{--}e}$ and $329\text{--}336^\circ\text{C}$ for polymers $VII_{a\text{--}e}$. The mass loss for polymer VI_a was observed to be rapid between $\sim 310\text{--}390^\circ\text{C}$ in the first region, and between $\sim 395\text{--}580^\circ\text{C}$ in the second region. For polymer VI_d , the mass loss in the first region was rapid between $\sim 300\text{--}375^\circ\text{C}$, in the second region between $\sim 380\text{--}450^\circ\text{C}$, and between $\sim 455\text{--}572^\circ\text{C}$ in the third region. For polymer VII_a , the mass loss was rapid between $\sim 255\text{--}370^\circ\text{C}$ in the first region and between $\sim 375\text{--}550^\circ\text{C}$ in the second region. For polymer VII_d , the mass loss was rapid between $\sim 305\text{--}403^\circ\text{C}$ in the first region and between $\sim 408\text{--}575^\circ\text{C}$ in the second region.

It should be noted that, the behavior of all the polymers in the first region was nearly identical. The expected nature of decomposition of this type of polymer is a pyrolytic oxidation of $\text{C}=\text{N}$, scission of many bonds, in addition to the formation of char as an end product [26].

The character of the texture of the polymers at a given temperature was fixed by quenching the samples in liquid nitrogen. Micrographs were then obtained by heating to room temperature (not shown). Observation of poly(hydrazone-ether) VI_e under a OPM revealed that this polymer exhibited a threaded-schlieren texture of nematic with a thick dark rim shown in figure 9a (before melting), and the mesophase extended up to the isotropic temperature at 324°C (T_i). After cooling to room temperature, a highly-spheroidal texture was noted (c.f. figure 9b).

Observation of poly(hydrazone-ether) VII_e under the OPM revealed that this polymer exhibited a good spheroid structure with a thick dark rim shown in figure 10a (before melting), and the mesophase extended up to the isotropic temperature at 288°C (T_i) figure 10b. After cooling to room temperature, a highly spheroidal texture was noted (c.f. figure 10b).

2.2.4 Scanning electron microscope measurements. Morphology of selected examples of poly(hydrazone-ether)s, VII_a and VI_d , were examined by scanning electron microscopy (SEM). The SEM sample was prepared by putting a smooth part of polymer on a copper

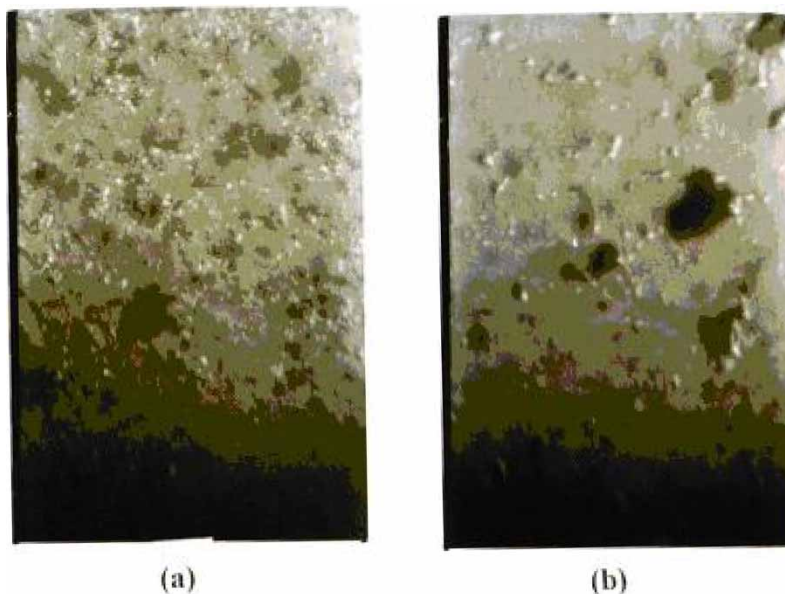


Figure 9. Photomicrographs of polymer VI_c in the heating cycle at (a) 316 °C (b) 324 °C (magnification X 217).

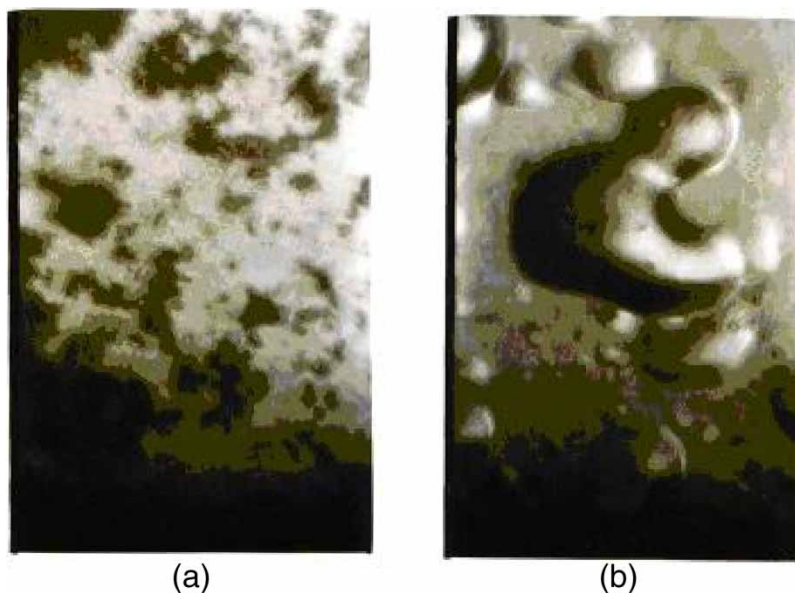
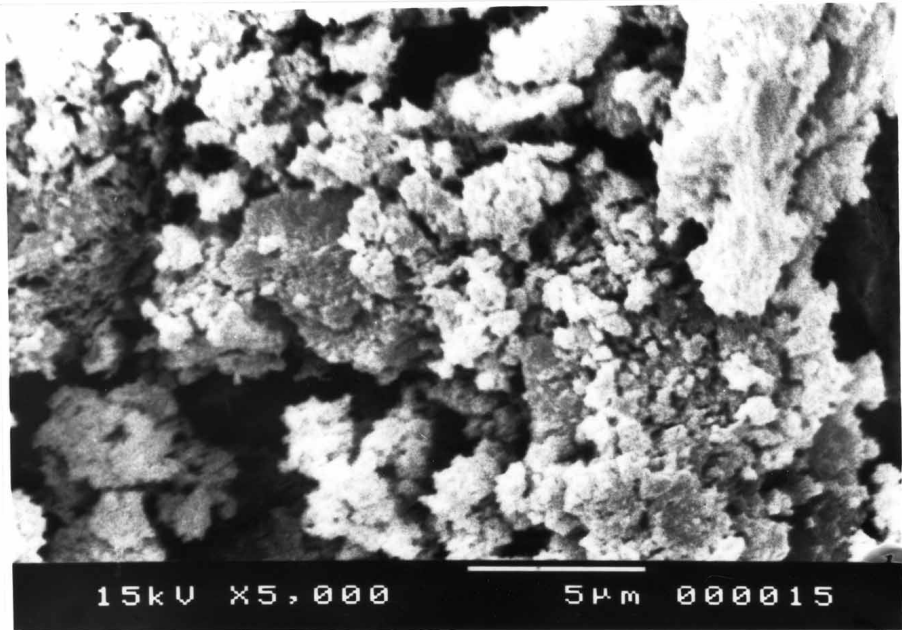
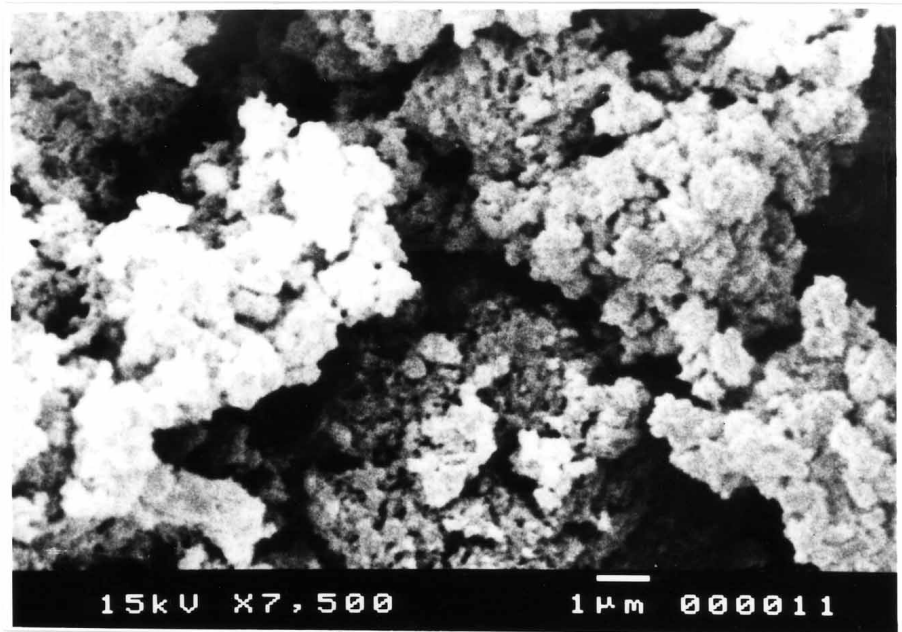


Figure 10. Photomicrographs of polymer VII_c in the heating cycle at (a) 279 °C, (b) 288 °C (magnification X 217).

holder and subsequently coating it with gold palladium alloy. Figure 11a ($X = 5000$) shows that polymer VI_d has polymorph-aggregated like particles structure. The higher magnification ($X = 7500$) in figure 11b shows cavity shape. Figure 12a ($X = 500$) shows that polymer VII_a has sponge shape. A higher magnification ($X = 1500$) in figure 12b shows cavity shape. These shapes are common in previous polyhydrazones [27].

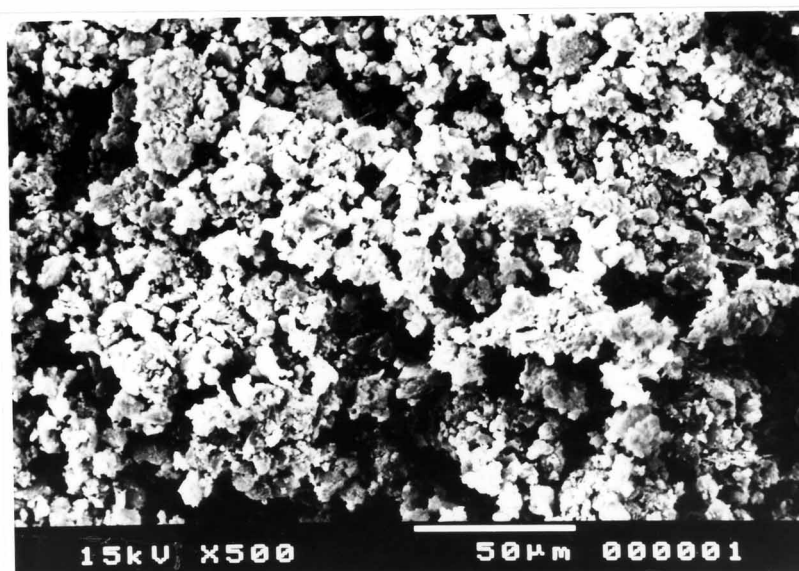


A

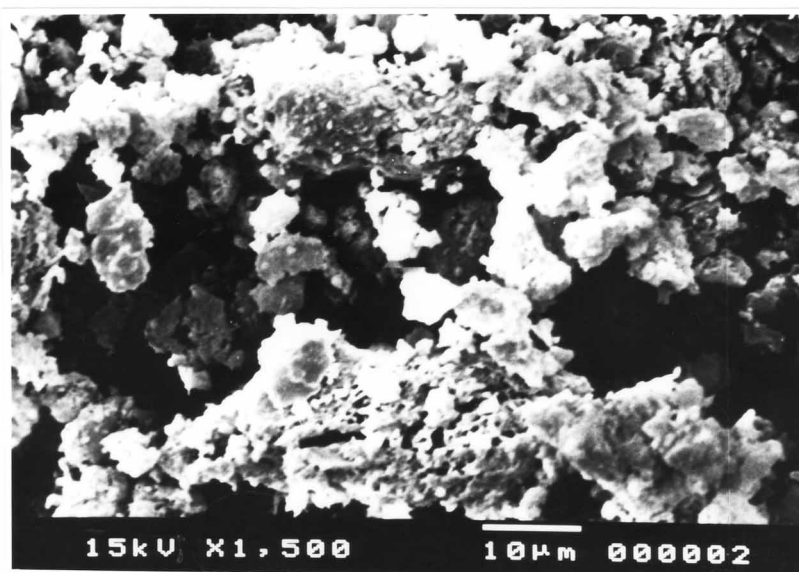


B

Figure 11. (a, b). SEM images of polymer VI_d surface at different magnifications (A: X = 5000) (B: X = 7500).



A



B

Figure 12. SEM images of polymer VII_a surface at different magnifications (A: X = 500) (B: X = 1500).

3. Experimental

3.1 Measurements

Solid samples were characterized by IR spectroscopy in the wavelength range 4000–600 cm⁻¹. The synthesized monomers and polymers were mixed with KBr and pressed into pellets.

A Shimadzu 2110 PC Scanning Spectrophotometer was used. Nuclear magnetic resonance spectra (NMR) were recorded on an EM-390-NMR, 90 MHz spectrometer at room temperature in dimethylsulfoxide (DMSO), using TMS as an internal reference. The inherent viscosities were measured with an Ubbelohde Viscometer in conc. H_2SO_4 at 30 °C (0.5 g/L). Mass spectra (MS) were recorded on a Jeol JMS₆₀₀ mass spectrometer. X-ray diffractographs (WAXD) were obtained at room temperature with a Phillips X-ray PW1710 diffractometer, using Ni-filtered $\text{Cu K}\alpha$ radiation. Thermal gravimetric analyses (TGA) of the polymers were examined in air atmosphere using a thermal analyser DuPont 2000 at a heating rate of 10 °C min^{-1} . Differential Scanning Calorimetry (DSC) was examined in nitrogen atmosphere using a Shimadzu 501 TA (Thermal-analyser). Most of the poly(hydrazone-ether)s VI_{a,b,c,e} and VII_{a,c,d,e} were characterized by DSC (VI_{c,e} and VII_{c,e}) and conducted at a heating and cooling rate of 10 °C min^{-1} . 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 followed to determine the nature of their mesophases.

3.2 Reagents and solvents

p-Hydroxybenzaldehyde (Aldrich) was used without crystallization. 4-Hydroxy-3-methoxybenzaldehyde (vanillin) (EL-Nassr Chemical Company Egypt), dihaloalkanes and hydrazine hydrate (Aldrich) were used without further purification. All solvents and other reagents were of high purity and were further purified by standard methods [28].

3.3 Synthesis of the monomers

3.3.1 3,4-Dimethylthieno[2,3-b]thiophene-2,5-diester I. Monomer I, was synthesized according to reference [29]. A mixture of acetyl acetone (10.26 mL, 10 mmol) and anhydrous potassium carbonate (~3 g) dissolved in dimethylformamide (DMF) (20 mL) was added to a solution of carbon disulfide (9.06 mL, 10.5 mmol) in DMF (20 mL) and stirred at 40 °C for half an hour. Ethyl chloroacetate (24.5 mL, 20 mmol) was then added dropwise and stirred at 60 °C for three hours. Then, the reaction mixture was cooled down to 40 °C, and poured into cold water including a few drops of concentrated HCl. The solid material was filtered off, washed well with water, dried, and recrystallized twice from ethanol; colorless needles were obtained; yield: 80%; m.p.: 140 °C. Anal. Calcd. for $\text{C}_{14}\text{H}_{16}\text{O}_4\text{S}_2$: C, 53.82; H, 5.15; S, 20.52%. Found: C, 53.61; H, 5.23; S, 20.30%.

3.3.2 3,4-Dimethylthieno[2,3-b]thiophene-2,5-dicarbohydrazide, II. Synthesis of monomer II is shown in scheme 1. A mixture of 3,4-dimethylthieno[2,3-b]thiophene-2,5-diester, I (3.12 g, 10 mmol) and hydrazine hydrate (50 mmol) was stirred under heat for two hours and then refluxed in ethanol (50 mL) for another two hours. The reaction mixture was cooled down and the resulting precipitate was collected by filtration and washed with alcohol. The white precipitate was crystallized from DMSO [30] to give yellow crystals of II in 92% yield, m.p. >350 °C. IR (KBr) cm^{-1} = 3300 s and 3200 s (NH); 2950 m (C-H aliphatic) and 1625 s (C=O) (c.f. figure 1). The mass spectrum exhibited a molecular ion peak at m/z = 284.0 (20.4%), which is in agreement with its molecular formula $\text{C}_{10}\text{H}_{12}\text{N}_4\text{O}_2\text{S}_2$. Furthermore, the mass spectral data was in accordance with the proposed structure. Anal. Calcd. for $\text{C}_{10}\text{H}_{12}\text{N}_4\text{O}_2\text{S}_2$: C, 42.24; H, 4.25; S, 22.50%. Found: C, 41.96; H, 4.1; S, 22.3%.

3.3.3 4,4'-Diformyl- α , ω -diphenoxyalkanes, III_{a-e} and 4,4'-diformyl-2,2'-dimethoxy- α , ω -diphenoxyalkanes, IV_{a-e}. III_{a-e} and VI_{a-e} were prepared as in [31–33]. The molecular structures of III_{a-e} VI_{a-e} are shown in figure 2.

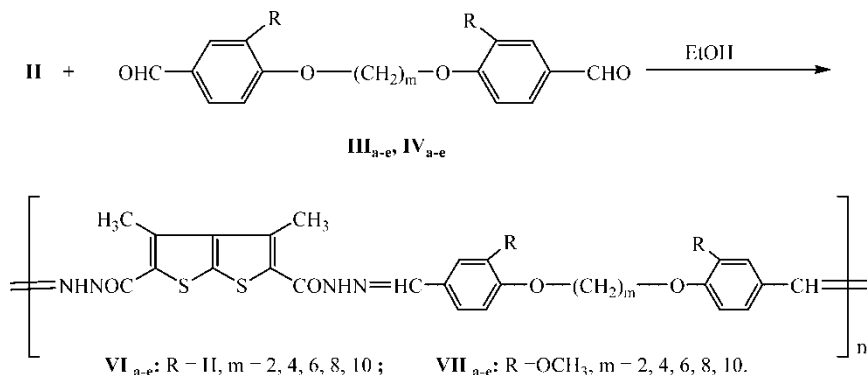
3.4 Synthesis of model compound, V

Synthesis of V is shown in scheme 2. A mixture of II (0.284 g, 1 mmol) and benzaldehyde (0.212 g, 2 mmol) suspended in 20 mL absolute ethanol containing a few drops of piperidine as a catalyst was stirred at room temperature for 30 min under dry nitrogen. Then, the temperature was increased to $\sim 80^\circ\text{C}$ and stirring was continued for six hours. During stirring, at an early state of reaction, a highly yellowish white precipitate appeared. The precipitated compound was isolated by filtration, washed with water, and the product was purified by exhaustive extraction with benzene leaving cream-yellow crystals, which were dried and analysed; m.p. 327°C , yield 87%. In the IR spectrum of this model compound V, IR (KBr) $\nu\text{cm}^{-1} = 3150\text{ s (NH)}$; $2950\text{ m (C-H aliphatic)}$; 1625 s (C=O) ; 1595 s (CH=N-NH) and $1595\text{ s, }1560\text{ s, }1500\text{ s, }1450\text{ s (C-H of phenylene rings)}$ can be found (c.f. figure 1). $^1\text{H-NMR}$ (DMSO, 90 MHz) $\delta = 2.9\text{ (s, 6H, 2CH}_3\text{)}$, $\delta = 7.4\text{--}8.3\text{ (m, 12H, 2C}_6\text{H}_5\text{ and 2CH)}$ and $\delta = 11.4\text{ (s, 2H, 2NH)}$. The mass spectrum of compound V exhibited a molecular ion peak at: $m/z = 460.24$ (12.2%), which is in agreement with its molecular formula $\text{C}_{24}\text{H}_{20}\text{N}_4\text{O}_2\text{S}_2$. Furthermore, the mass spectral data was in accordance with the proposed structure. Anal. Calcd. For $\text{C}_{24}\text{H}_{20}\text{N}_4\text{O}_2\text{S}_2$: C, 62.59; H, 4.37; N, 12.16; S, 13.93%. Found: C, 62.96; H, 4.30; N, 12.0; S, 13.63%.

3.5 Synthesis of poly(hydrazone-ether)s, VI_{a-e} and VII_{a-e}

All thermotropic poly(hydrazone-ether)s, VI_{a-e}, VII_{a-e}, were synthesized using a similar procedure of solution polycondensation. An example of it is given below.

A mixture of II (0.284 g, 1 mmol) and dialdehyde III_a (0.270 g, 1 mmol) suspended in 20 mL absolute ethanol containing a few drops of piperidine as catalyst was stirred at 25°C for 20 min under dry nitrogen. Then, the temperature was increased to $\sim 80^\circ\text{C}$ and stirring continued for 18–20 h. During the stirring, at an early state, the viscosity of the solution increased rapidly and the polymer began to precipitate. The polymer precipitate was isolated by filtration, washed with hot methanol and acetone, and dried under reduced pressure (1 mm/Hg) at 80°C for 24 h. The synthesized polymers are depicted in scheme 3.



SCHEME 3. Synthesis of poly(hydrazone-ether)s VI_{a-e} and VII_{a-e}.

4. Conclusions

A new series of liquid crystalline poly(hydrazone-ether)s containing bis-thiophene moiety have been synthesized. A solution polycondensation technique at $\sim 80^\circ\text{C}$ was used. The majority of the polymers were insoluble in common organic solvents and halogenated hydrocarbons. Most of them exhibited melt birefringence and stirred opalescence during polarized microscope observation. X-ray diffraction analyses showed that polymer VI_b has lower degree of crystallinity in comparison with other polymers. SEM examination of polymer VI_d showed cavity shape, while polymer VII_a showed sponge shape.

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