

SYNTHESIS AND CHARACTERIZATION OF LIQUID CRYSTAL POLYESTERS WITH T-SHAPED TWO-DIMENSIONAL MESOGENIC UNITS (III)*

Zi-fa Li, Lei Li, Shu-yuan Zhang, Shi-jun Zheng and Shao-kui Cao
Department of Materials Engineering, Zhengzhou University, Zhengzhou 450052, China

Qi-feng Zhou**

*Department of Polymer Science and Engineering, the College of Chemistry,
Peking University, Beijing 100871, China*

Abstract A new series of liquid crystal polyesters with T-shaped two-dimensional mesogenic units were synthesized by melt polycondensation of the diacetates of 2-(4'-alkoxy-phenyl)-hydroquinones with 4,4'-alkylenedioxydibenzoic acid. The polymers were characterized by using polarized microscopy, DSC and X-ray diffraction. It was realized that all the polymers have nematic thermotropic liquid crystalline characteristics. The melting temperature (T_m) and isotropization temperature (T_i) of the polymers change regularly with varying lengths of the alkoxy side group and the length of the alkylene group in the main chain in company with an even-odd effect. The mesophase temperature range also varies regularly with the polymer structure. It is shown that the mesophase range has been widened.

Keywords T-shaped two-dimensional mesogenic units, Liquid crystal polyester, Synthesis and characterization

INTRODUCTION

In recent years, we have made efforts to design and construct liquid crystal polymers (LCPs) with two-dimensional mesogenic units by using monomers having an X-shaped (or cross-shaped) geometry^[1-5]. Later on, some new polymers having T-shaped two-dimensional mesogenic units were also prepared and characterized in a similar manner for comparing the contributions of different mesogenic structure to the properties of LCPs^[6, 7]. The basic consideration for designing and preparing such polymers having two-dimensional mesogenic units is that the LCPs constructed in this way would be expected to show good mechanical properties both in the molecular chain direction and also in the lateral directions. This speculation arises from the fact that the polymer chains would have the shape of a tube-brush corresponding to a backbone wearing stiff hairs or stings. When these molecules come together their hairs would interlock with each other to form strong interactions. In this way the molecules are more tightly held together than otherwise. The present paper describes a new series of LCPs with T-shaped two-dimensional mesogenic units prepared from melt polycondensation of the diacetates of 2-(4'-alkoxy-phenyl)-hydroquinones with 4,4'-alkylenedioxydibenzoic acid.

* This work was supported by the National Natural Science Foundation of China.

** Corresponding author: Qi-feng Zhou (周其凤), E-mail: qfzhou@pku.edu.cn

Received September 8, 1998

EXPERIMENTAL

Measurements

Melting point measurement was conducted on a WRS-1 apparatus (Shanghai Physical and Optical Factory) with a programmed heating rate of 1 °C/min.

Elemental analysis was performed with a MOD 1106 apparatus.

IR spectrum was recorded on a Shimadzu-435 IR spectrophotometer with KBr pellets.

¹H-NMR was conducted on an AC-80 spectrometer using CDCl₃ or DMSO-d₆ as solvent.

DSC curves were measured on a Shimadzu DSC-50 apparatus with a heating /cooling rate of 10 °C/min.

TG analysis was carried out through a Rigaku TG-DAT-DSC thermal analyzer with a heating rate of 20 °C/min under N₂ atmosphere.

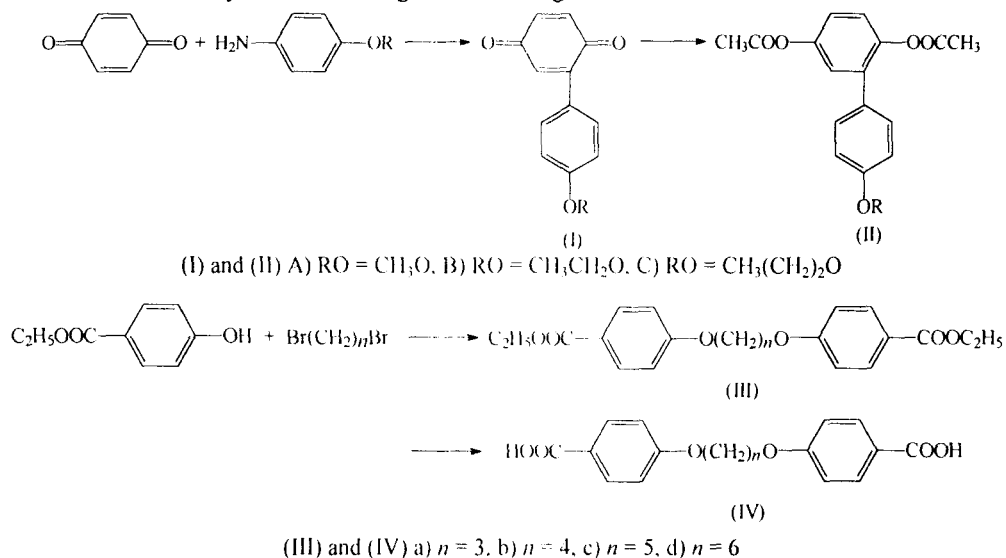
Wide-angle X-ray diffraction (WAXD) analysis was performed by using a Rigaku D/MAX-3B apparatus with a Ni-filtered Cu-Kα radiation, 35 kV voltage, 30 mA electric current, a scanning rate of 5 °/min and a scanning scope of 5–35 °.

Gel permeation chromatography (GPC) was measured on a Waters 201 apparatus with standard polystyrene calibration.

A Leitz polarizing microscope with a heating stage was used to study the liquid crystalline texture.

Monomer Synthesis

The monomers were synthesized through the following reaction route:



Preparation of compound I

Taking IB as an example for the synthesis of the substituted quinone compounds, into a 500 mL beaker containing 27.4 g (200 mmol) of *p*-ethoxy-aniline, 100 g of crashed ice and 53 mL of concentrated hydrochloric acid, 75 mL water solution of 13.8 g (200 mmol) of sodium nitrate was added dropwise under stirring. The mixture was allowed to react at a temperature lower than –2 °C till a Congo test paper turned light blue and a KI-starch test paper turned gray-blue. The diazo salt solution prepared above was then added slowly into a separated 2000 mL beaker containing 21.6 g (200 mmol) of quinone and 67.0 g (800 mmol) of NaHCO₃ with 50 g of crashed ice and 500 mL of cold water under stirring. During the addition, the temperature of the reaction mixture was kept lower than –10 °C. After the addition was completed, the reaction mixture was stirred for a further 4 h. A solid product was formed, which was then filtered, washed with water and dried in vacuo,

and then purified through recrystallization from *n*-butanol. The product was tested to be compound IB. Product IA and IC were prepared in a similar manner. The characterization results are listed in Table 1.

Table 1 The characterization of compounds I

Compound	IA	IB	IC
Yield (%)	87.5	89.0	86.8
Melting Point (°C)	112.0~112.6	120.1~120.9	90.7~91.6
Elementary analysis (%)			
Found (calcd.): C	72.83 (72.89)	73.71 (73.67)	74.32 (74.36)
Found (calcd.): H	4.65 (4.70)	5.34 (5.30)	5.89 (5.82)
IR (KBr, cm ⁻¹)	1680 (C=O, str.) 1225. 1100 (C—O—C, methoxy phenyl, str.) 2830 (methoxy, M-ST)	1660 (C=O, str.) 1230. 1100 (C—O—C, ethoxy phenyl, str.)	1660 (C=O, str.) 1230, 1100 (C—O—C, propoxy phenyl, str.)

Preparation of compound II

Compound IIB is used as an example for the synthesis of the diacetates of the substituted hydroquinone compounds. Using a three-necked flask equipped with a mechanical stirrer, a thermometer and a reflux condenser, 35.0 g (150 mmol) of compound IB dissolved in 75 mL of chloroform and a saturated water solution of 250 mmol of Na₂S₂O₄ were added and stirred for 30 min at room temperature. Hydroquinone compound of IIB was formed, which was filtered, washed with water and dried in vacuo at 94.3% yield (33.5 g). 23.0 g (10 mmol) of the hydroquinone was then dissolved in 30.6 g (300 mmol) of acetic anhydride and several drops of concentrated sulfuric acid were then added. When the reaction became milder, the reaction mixture was refluxed for 3 h, and then placed at room temperature overnight. The product, compound IIB was isolated through precipitation from 500 mL of cold water, then filtered and recrystallized from *n*-butanol.

Compounds IIA and IIC were synthesized in a similar manner, except the isolation of products was directly conducted by evaporating the volatiles under reduced pressure from the acetation mixture without precipitation using cold water. The residue was then purified through recrystallization from *n*-butanol. The characterization results are listed in Table 2.

Table 2 The characterization of compounds II

Compound	IIA	IIB	IIC
Yield (%)	70.7	85.0	69.5
Melting Point (°C)	77.8~78.1	100.5~101.2	79.6~80.9
Elementary analysis (%)			
Found (calcd.): C	67.96 (67.99)	68.81 (68.78)	69.55 (69.50)
Found (calcd.): H	5.34 (5.37)	5.74 (5.78)	6.19 (6.14)
IR (KBr, cm ⁻¹)	1760 (C=O, str.) 1248, 1040 (C—O—C, methoxy carbonyl, str.) 1260, 1105 (C—O—C, methoxy phenyl, str.) 2840 (methoxy, M-ST)	1745 (C=O, str.) 1242, 1040 (C—O—C, methoxy carbonyl, str.) 1280, 1105 (C—O—C, ethoxy phenyl, str.)	1745 (C=O, str.) 1240, 1040 (C—O—C, methoxy carbonyl, str.) 1280, 1105 (C—O—C, propoxy phenyl, str.)
¹ H-NMR (CDCl ₃ , δ)	2.09 (s, 3H, CH ₃) 2.29 (s, 3H, CH ₃) 3.83 (s, 3H, OCH ₃) 6.87~7.44 (m, 7H, Ar-H)	1.34~1.51 (t, 3H, CH ₃) 2.09 (s, 3H, CH ₃) 2.29 (s, 3H, CH ₃) 3.93~4.19 (q, 2H, OCH ₂) 6.86~7.39 (m, 7H, Ar-H)	0.96~1.26 (m, 5H, CH ₃ CH ₃) 2.07 (s, 3H, CH ₃) 2.30 (s, 3H, CH ₃) 3.94 (t, 2H, OCH ₂) 6.68~7.42 (m, 7H, Ar-H)
M (m/z)			
M ⁺ (%)	300.0 (20)	314.0 (25)	328.0 (20)
base	216.0 (100)	230.0 (100)	244.0 (100)

Preparation of compound III^[8]

Compounds III were prepared through the coupling reaction of ethyl *p*-hydroxy-benzoate with different α,ω -dibromoalkanes. In a 250 mL three-necked flask, 33.3 g (200 mmol) of ethyl *p*-hydroxy-benzoate was dissolved into 50 mL of DMF under stirring. 26.5 g (250 mmol) of sodium carbonate and 100 mmol of α,ω -dibromoalkane were then added. The mixture was allowed to reflux for 4 h, then cooled and poured into 2000 mL of water. After filtration, the product was washed thoroughly with water, dried in vacuo and then purified through recrystallization from ethanol. The characterization results are listed in Table 3.

Table 3 The characterization of compounds III

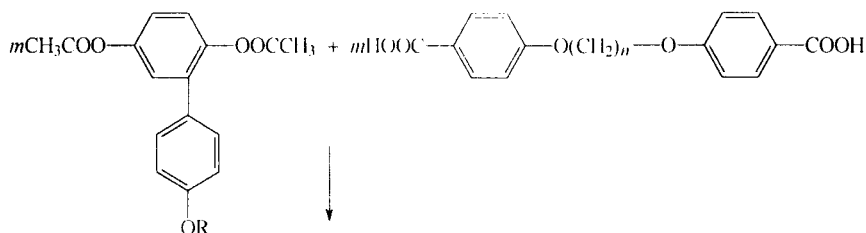
Compound	IIIa	IIIb	IIIc	IIId
Yield (%)	89.4	91.0	88.5	92.8
Melting point (°C)	107.3~108.0	98.8~99.2	93.2~93.6	130.6~131.2
Elementary analysis (%)				
Found (calcd.): C	67.70 (67.73)	68.33 (68.38)	69.03 (68.98)	69.52 (69.55)
Found (calcd.): H	6.45 (6.50)	6.75 (6.78)	7.01 (7.05)	7.35 (7.29)
IR (KBr, cm ⁻¹)	1720 (C=O, str.) 1320, 1120 (C—O—C, carbethoxy, str.)	1717 (C=O, str.) 1328, 1100 (C—O—C, carbethoxy, str.)	1720 (C=O, str.) 1322, 1100 (C—O—C, carbethoxy, str.)	1720 (C=O, str.) 1324, 1100 (C—O—C, carbethoxy, str.)
¹ H-NMR (DMSO-d ₆ , δ)	1.28 (t, 6H, CH ₃) 1.41 (m, 2H, CH ₂) 4.21 (t, 4H, OCH ₂) 4.36 (q, 4H, COOH ₂) 6.38~8.08 (m, 8H, Ar-H)	1.35 (t, 6H, CH ₃) 1.65~1.91 (m, 4H, CH ₂) 4.15 (t, 4H, OCH ₂) 4.31 (q, 4H, COOH ₂) 6.91~7.95 (m, 8H, Ar-H)	1.37 (t, 6H, CH ₃) 1.66~1.96 (m, 6H, CH ₂) 4.04 (t, 4H, OCH ₂) 4.34 (q, 4H, COOH ₂) 6.81~8.04 (m, 8H, Ar-H)	1.36 (t, 6H, CH ₃) 1.54~1.89 (m, 8H, CH ₂) 4.05 (t, 4H, OCH ₂) 4.28 (q, 4H, COOH ₂) 6.86~7.89 (m, 8H, Ar-H)

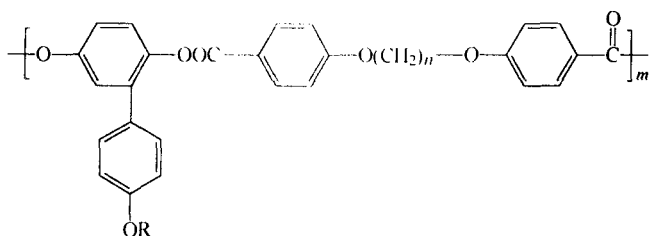
Preparation of compound IV

15 mmol of compound III was placed in a flask together with 150 mL of 10% (w/v) KOH ethanol solution, and refluxed for 4 h. 2000 mL of water was then added into the reaction mixture and warmed to 60 °C. The pH value of the mixture was adjusted to be acidic using concentrated hydrochloric acid. The reaction mixture was cooled, filtered, washed with water and dried. The purification of compound IV was carried out by recrystallization from the monomethyl ether of glycol. The characterization results are listed in Table 4.

Polymer Synthesis

The polymers were synthesized by the following reactions:





(V)

a) $n = 3$, b) $n = 4$, c) $n = 5$, d) $n = 6$ VA: RO = CH₃O, VB: RO = CH₃CH₂O.VC: RO = CH₃(CH₂)₂O**Table 4** The characterization of compounds IV

Compound	IVa	IVb	IVc	IVd
Yield (%)	81.5	83.8	88.9	85.7
Melting point (°C)	331.0~332.5 (lit.: 332~334)	339.0~341.0 (lit.: 338~341)	286.0~287.5 (lit.: 285~288)	291.0~292.5 (lit.: 290~292)
Elementary analysis (%)				
Found (calcd.): C	64.50 (64.55)	65.41 (65.35)	66.22 (66.26)	67.05 (67.03)
Found (calcd.): H	5.05 (5.10)	5.40 (5.48)	5.83 (5.85)	6.15 (6.19)
IR (KBr, cm ⁻¹)	3200~2400 (acid O—H, str.) 1684 (C=O, str.)	3300~2400 (acid O—H, str.) 1686 (C=O, str.)	3200~2400 (acid O—H, str.) 1680 (C=O, str.)	3100~2400 (acid O—H, str.) 1682 (C=O, str.)
¹ H-NMR (DMSO-d ₆ , δ)	2.52~2.32 (<i>m</i> , 2H, CH ₃) 4.23 (<i>t</i> , 4H, OCH ₂) 6.89~7.94 (<i>m</i> , 8H, Ar-H)	1.91~1.98 (<i>m</i> , 4H, CH ₃) 4.14 (<i>t</i> , 4H, OCH ₂) 6.89~7.94 (<i>m</i> , 8H, Ar-H)	1.72~1.87 (<i>m</i> , 6H, CH ₃) 4.05 (<i>t</i> , 4H, OCH ₂) 6.94~7.93 (<i>m</i> , 8H, Ar-H)	1.61~1.81 (<i>m</i> , 8H, CH ₃) 4.04 (<i>t</i> , 4H, OCH ₂) 6.83~7.93 (<i>m</i> , 8H, Ar-H)
MS(<i>m/z</i>)				
M ⁺ (%)	316.0 (20)	333.0 (22)	344.0 (25)	358.0 (40)
base	45 (100)	193 (100)	69 (100)	55 (100)

Table 5 Polymer yields, molecular weights and elemental analysis

Polymer	Yield (%)	<i>M_n</i>	<i>M_w</i>	Elemental analysis(%)	
				C	H
VA _a	90	5900	20000	71.71 (72.57)	4.81 (4.87)
VB _a	87	8600	25000	72.85 (72.93)	5.18 (5.13)
VC _a	91	6400	21000	73.21 (73.27)	5.31 (5.38)
VA _b	84	5400	19000	73.01 (72.93)	5.19 (5.13)
VB _b	89	6700	21000	73.17 (73.27)	5.45 (5.38)
VC _b	94	6100	18000	73.51 (73.59)	5.69 (5.61)
VA _c	91	6400	22000	73.38 (73.27)	5.31 (5.38)
VB _c	93	7400	21000	73.69 (73.59)	5.71 (5.61)
VC _c	90	7100	24000	73.81 (73.90)	5.89 (5.84)
VA _d	92	5500	17000	73.51 (73.59)	5.70 (5.61)
VB _d	93	7100	21000	73.81 (73.90)	5.75 (5.84)
VC _d	95	6400	20000	74.10 (74.19)	6.12 (6.05)

* The values in parentheses are those calculated from the chemical formulae of repeating units.

3 mmol of the diacetate of 2-(4'-alkoxyphenyl)-hydroquinone and an equimolar amount of 4,4'-alkylene-dioxydibenzoic acid together with 3 mg of *p*-tolyl sulfuric acid were heated to 260°C

within 1 h under N_2 atmosphere. The mixture was allowed to react at this temperature for a further 2h under stirring, then at reduced pressure (60 Pa) for 4 h. After cooling, the reaction mixture was dissolved with 1,1,2,2-tetrachloroethane, followed by precipitation from acetone. The precipitate was filtered and dried in vacuo. Further purification was conducted by reprecipitation of a THF solution of the polymer in methanol and drying in vacuo. Finally, the polymer was obtained as white powders. The polymerization results are summarized in Tables 5 and 6.

Table 6 Thermal behavior and liquid crystallinity of polymers

Polymer	$T_m(^{\circ}C)$	$T_i(^{\circ}C)$	$\Delta T(^{\circ}C)$	$T_d(^{\circ}C)^*$	Liquid crystallinity
VA _a	140	214	74	319	nematic
VB _a	137	207	70	301	nematic
VC _a	125	194	69	310	nematic
VA _b	210	295	85	315	nematic
VB _b	203	282	79	331	nematic
VC _b	196	275	79	308	nematic
VA _c	125	200	75	307	nematic
VB _c	123	194	71	309	nematic
VC _c	119	184	65	305	nematic
VA _d	197	280	83	301	nematic
VB _d	191	269	78	327	nematic
VC _d	185	261	76	302	nematic

* Decomposition temperature (3% weight loss in N_2)

RESULTS AND DISCUSSION

The structures of low molecular weight compounds I, II, III and IV were identified by using elemental analysis, IR, NMR and MS etc. Their characterization results are shown in Tables 1, 2, 3 and 4, respectively.

A series of new LCPs with T-shaped two-dimensional mesogenic units were prepared by melt polycondensation of the substituted hydroquinones II and the dicarboxylic acids IV. All the polyesters are white powders soluble in organic solvents, such as THF etc. The polymerization yield, the molecular weight and elemental analysis results of the polymers are summarized in Table 5, while the thermal behavior and the mesogenic properties of the polymers are listed in Table 6.

As shown in Table 5, the M_n of the polymers ranges from 5400–8600, and the polydispersity index (M_w/M_n) is broad. The reason for the low molecular weight is probably because of the steric hindrance of the bulky substituent on the substituted hydroquinone monomers II.

All the polymers show thermotropic liquid crystal properties through measurement by DSC and observation by polarizing microscope, which is different from the results of Rötze *et al.* They found that there were no mesogenic properties for polymers similar to the present polymers VA_b and VA_c^[9]. Figure 1 shows the DSC thermograms of polymers VB_a–VB_d. It can be seen that all of them exhibit two endothermal peaks in the first process of heating. The first one designates the melting of the polymers from solid phase to mesogenic phase, and the second one designates the transition from mesogenic phase to isotropic liquid phase. In the process of cooling, the exothermal peaks from isotropic liquid phase to mesogenic phase appeared at 200, 278, 188 and 264 °C, respectively and those from mesogenic phase to solid phase appeared at 70, 154, 60 and 140 °C, respectively. It also can be found that the melting peaks of polymers VB_b ($n = 4$) and VB_d ($n = 6$) are narrower and stronger than those of polymers VB_a ($n = 3$) and VB_c ($n = 5$), which implies that the former have higher crystallinity than the latter.

The transition temperatures of the polymers observed from polarizing microscope with a heating stage were the same as those obtained from DSC. At room temperature, the powder polymer samples show weak birefringence, illustrating that the present series of polymers have crystallinity to some extent. Upon heating the sample to above their T_m , birefringence became

much more obvious and clear nematic threaded texture can be observed for all the polymers studied. It was also observed that different samples present different viscosity in their mesophase state. Along with the increase of the carbon atoms in the side alkoxy group or in the main chain alkylene group, the mobility of the polymer was apparently improved. On heating the polymer samples to above their T_i , birefringence vanished, and the polymers turned to their isotropic liquid phase. When the polymers were gradually cooled down from the isotropic liquid phase, birefringence appeared again. Figure 2 shows the liquid crystal phase textures of polymers VA_b and VA_c .

The influence of the side alkoxy group on the mesogenic properties of polymers is shown in Table 6. The polymers with even number of carbon atoms in the side alkoxy group have higher T_m and T_i than those with odd number of carbon atoms. Along with the increase of the carbon atoms in the side alkoxy group, the T_m and T_i of the polymers became lower and is accompanied by an even-odd effect.

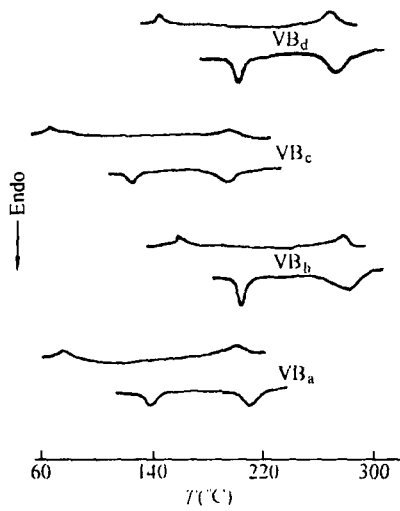


Fig. 1 DSC thermograms of heating/cooling scan of $VB_a \sim VB_d$ obtained under N_2 atmosphere at a heating/cooling rate of $10^\circ C/min$

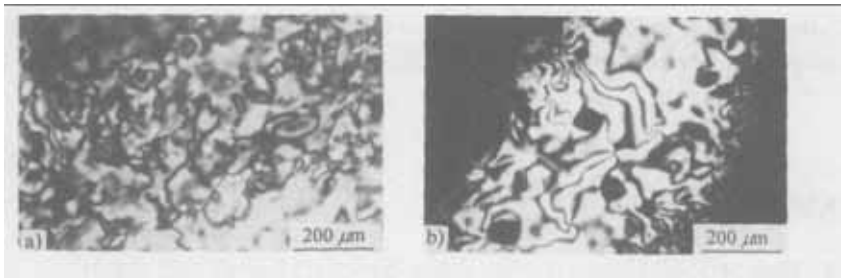


Fig. 2 Photomicrographs of a) VA_b and b) VA_c taken at $255^\circ C$ and $175^\circ C$, respectively

The length of the flexible chain segment in the main chain also has an influence on the T_m and T_i of the polymers. Both T_m and T_i decrease with increasing carbon atoms in the alkylene group. An even-odd effect also accompanies this variation, and the polymers with even numbers of carbon atoms have higher T_m and T_i than those with odd numbers of carbon atoms.

Figure 3 shows the WAXD patterns of the powder samples of polymers $VB_a \sim VB_d$. Diffraction peaks with different strengths can be observed at $2\theta = 19.3 \sim 28.8^\circ$, illustrating the influence of the carbon atoms in the flexible chain segment on the crystallinity of the polymers. Polymers VB_b and

VB_d have higher diffracted intensities than polymers VB_a and VB_c, which implies that the former two have higher crystallinity. These results are in good agreement with those obtained from DSC measurement.

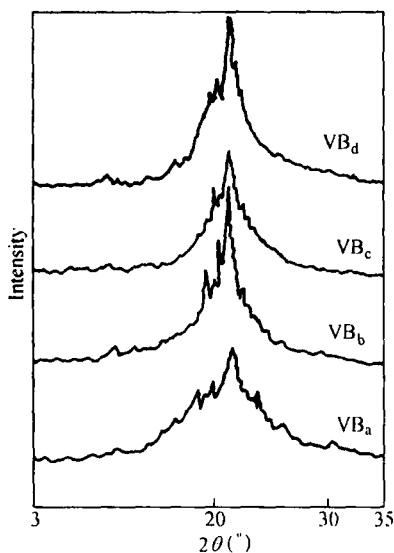


Fig. 3 WAXD powder patterns of VB_a~VB_d, measured at room temperature

CONCLUSIONS

By using the melt polycondensation method, a new series of polyesters containing different alkoxy-phenyl side groups and different lengths of alkylene flexible spacer were prepared and their relationship between structure and properties was examined. All the polymers were found to have nematic mesogenic properties upon heating to above their melting temperatures, and clear threaded textures was observed. The mesogenic texture of all the polymers can be maintained for a long period upon cooling down from the mesogenic phase to room temperature. Polymers with even numbers of carbon atoms in the side alkoxy group have higher T_m and T_i than those with odd numbers of carbon atoms. Both T_m and T_i of the polymers decrease with increasing carbon atoms in the side alkoxy group accompanied by an even-odd effect. The influence of the length of the flexible alkylene spacer on the transition temperatures of the polymers also varies in a similar manner.

REFERENCES

- 1 Li, Z.F., Zhou, Q.F. and Zhang, Z.Y., *Acta Polym. Sinica* (in Chinese), 1990, (1): 51
- 2 Li, Z.F., Zhang, Z.Y. and Li, T.H., *Acta Polym. Sinica* (in Chinese), 1991, (2): 162
- 3 Li, Z.F., Zhou, Q.F. and Zhang, Z.Y., *Acta Polym. Sinica* (in Chinese), 1991, (6): 694
- 4 Li, Z.F., Zhang, Z.Y. and Fu, X.Y., *Acta Polym. Sinica* (in Chinese), 1992, (5): 611
- 5 Li, Z.F., Li, L., Zhang, S.Y., Cao, S.K. and Zhou, Q.F., *Polym. Adv. Technol.*, 1997, 8: 647
- 6 Li, Z.F., Chen, Z.J., Zhang, S.Y., Cao, S.K. and Zhou, Q.F., *Ch. J. Polym. Sci.*, 1996, 14: 71
- 7 Li, Z.F., Zheng, S.J., Zhang, S.Y., Cao, S.K., Li, L., Liu, G.S. and Zhou, Q.F., *Ch. J. Polym. Sci.*, 1997, 15: 66
- 8 Donahoe, H.B., Benjamin, L.E., Fennoy, L.V. and Greiff, O., *J. Org. Chem.*, 1961, 26: 474
- 9 Rötz, U., Lindau, J., Fischer, H. and Kuschel, F., *Mol. Cryst. Liq. Cryst.*, 1993, 225: 167