

SYNTHESIS AND CHARACTERIZATION OF NOVEL CHIRAL SMECTIC C(Sc*) PHASE SHISH-KEBAB TYPE LIQUID CRYSTALLINE BLOCK COPOLYMERS*

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Abstract A new series of chiral shish-kebab type liquid crystal block copolymers that form the smectic C(Sc*) phase was synthesized by solution polycondensation. The copolymers were characterized by GPC, DSC, TG, POM, X-ray diffraction and polarimeter. The copolymers **7** entered into liquid crystal phase when they were heated to their melting temperatures (T_m) and the copolymers **8** were in liquid crystal phase at room temperature with low viscosities. The smectic sanded texture or focal-conic texture were observed on POM. All the chiral block copolymers showed high optical activity. No racemization has happened. Temperature-variable X-ray diffraction study together with POM and polarimetric analysis realized that they are chiral smectic C(Sc*) phase. Thus we offer in this report the first example of shish-kebab type liquid crystal block copolymers that form a chiral smectic C(Sc*) phase. The variation of melting and isotropization temperatures with molecular structure was also discussed.

Keywords Shish-kebab type liquid crystal, Block copolymers, Chiral smectic C phase, Synthesis and characterization

INTRODUCTION

The incorporation of chirality in liquid crystalline polymers has attracted much attention in recent years because of its scientific and technical potentiality for application in nonlinear optics, information storage and display devices^[1-3]. Since the discovery of the first polymer having a chiral smectic C(Sc*) in 1984 by Shibaev *et al.*^[4], many theoretical and experimental studies have been carried out extensively. In comparison with low-molar-mass liquid crystals, polymeric materials have the disadvantages of higher rotational viscosity, longer switching time to an applied electric field and poor reproducibility of the polymerization methods used to obtain these materials. For Sc* phase molecules an explanation was given in 1993 by Sekiya *et al.*^[5]. According to their view, the switch of molecular orientation from one tilted direction to the other can be achieved without translation of gravity center for low-molar-mass molecules. On the other hand, this translocation would occur for polymers because the end of the mesogenic unit is bound to the polymer

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backbone. Otherwise motions of main-chain segments are implicated.

Being interested in this model, we came to the idea of studying other types of liquid crystalline polymers. In these polymers the bonding of the mesogenic units to the main chain backbone is not at the end but at the gravity center of the mesogenic units. Thus, the reorientation of the titled direction may be achieved without translocation of the gravity center. Two classes of polymers are possible: the side-group type liquid crystalline polymers with mesogenic units laterally attached to the main chain (the "side-on polymer") and the shish-kebab type polymer, in which the mesogenic units are incorporated in the polymers as the "kebabs" with the main chain as the "shish" or "skewer" (the "shish-kebab polymer"). These two classes of polymers are relatively new and much less studied than the conventional main-chain type and side-group type ("end-on") polymers. The shish-kebab polymers have received little attention^[6-9].

In this paper, we report the design and synthesis of some new shish-kebab type liquid crystalline block copolymers with optical activity, as well as their properties. The presence of a non-liquid crystalline chain in the copolymers would reduce their viscosity.

EXPERIMENTAL

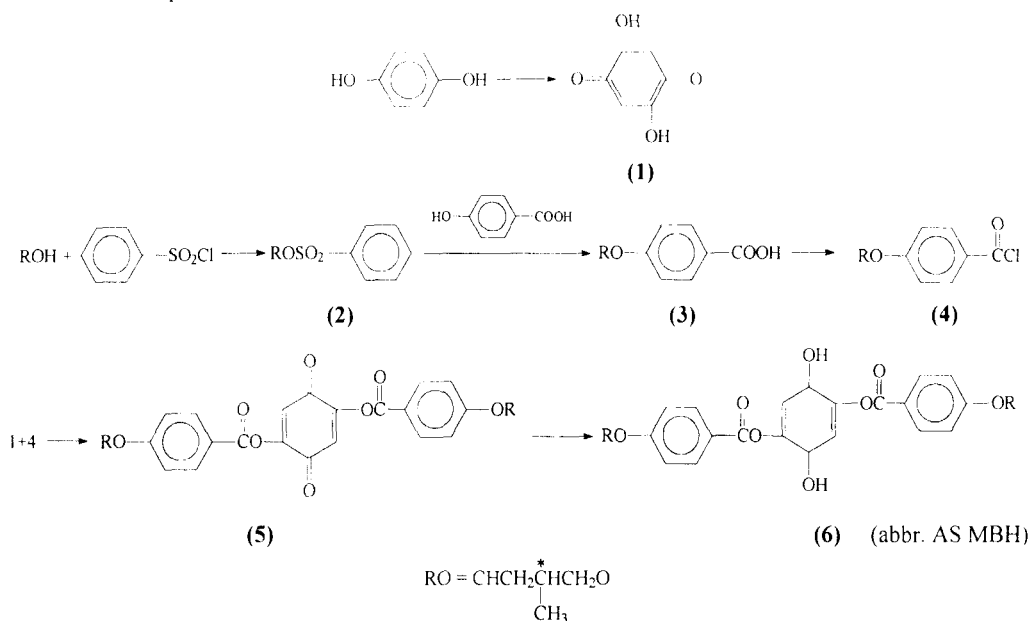
Characterization

The monomers and copolymers were characterized by the following techniques.

Melting point measurement: WRS-1 apparatus (Shanghai Physical and Optical Instrument Factory) with a heating rate of 1°C/min; Elemental analysis: MOD 1106 (Italy); IR: Shimadzu-435 IR spectrometer with KBr pellets; ¹H-NMR: DPX-400, with CDCl₃ as solvent based on TMS; MS: VG-ZAB-HS, EI source; DSC: MDSC TA Inst 2100, with a heating rate of 10°C/min; TG: Rigaku TG-DTA-DSC, with a heating rate of 20°C/min under N₂ atmosphere; X-ray diffraction: Phillip PW-1700, with Cu target, voltage 40 KV, electric current 30 mA, a scanning rate 5°/min, scanning scope 1.5~40°; GPC: Waters 515-410-2010, polystyrene standard; Optical activity study: a WZZ-1 automatic polarimeter at 20°C and 589.0 nm, the length of the sample cell is 200 mm; Liquid crystalline texture study: a Leitz 12 Pol type polarizing microscope with a Leitz 350 heating stage.

Monomer Synthesis

The reaction sequence is shown in Scheme 1.



Scheme 1

Preparation of compound 1

Compound **1** was prepared according to the procedure in literature^[10].

Preparation of compound 2

In a flask, 15 mL (0.14 mol) *s*-(*-*)-2-methyl-1-butanol was dissolved in 50 mL pyridine. 27 mL (0.21 mol) sulfophenyl chloride was added into the flask dropwise at 4~6°C under stirring. After reacting for 5 h, 100 mL water and 2 mL hydrochloric acid were added into the flask. The organic layer was separated, washed successively with water, sodium carbonate, dilute sulfuric acid and water, dried over sodium sulfate and evaporated under vacuum to yield 31.3 g (98.3%) of yellow product.

Preparation of compound 3

A mixture of 29.7 g (0.13 mol) compound **2**, 27.09 g (0.20 mol) 4-hydroxy benzoic acid, 27.09 g (0.40 mol) KOH, 90 mL alcohol and 90 mL water was refluxed for 36 h. After it was cooled, hydrochloric acid was added until the pH of the mixture equals to 1~2. Then a white precipitate (18.7 g) was obtained, yield 69.0%. The raw product was purified through recrystallization from ethanol. The product was identified as compound **3** through the following characterizations, melting point: 109~110.4°C; elemental analysis found (calc.)%: C 69.39 (69.21) and H 7.66 (7.74); ¹H-NMR (δ): 0.91~1.04 (*m*, 6H, 2×CH₃—), 1.27~1.58 (*m*, 2H, CH₃CH₂—), 1.88 (*m*, 1H, —C*H—), 3.78~3.90 (*m*, 2H, —CH₂O—), 6.74, 8.05 (*d*, each 2H, aromatic protons) and 10.08~12.55 (*w*, 1H, —COOH).

Preparation of compound 5

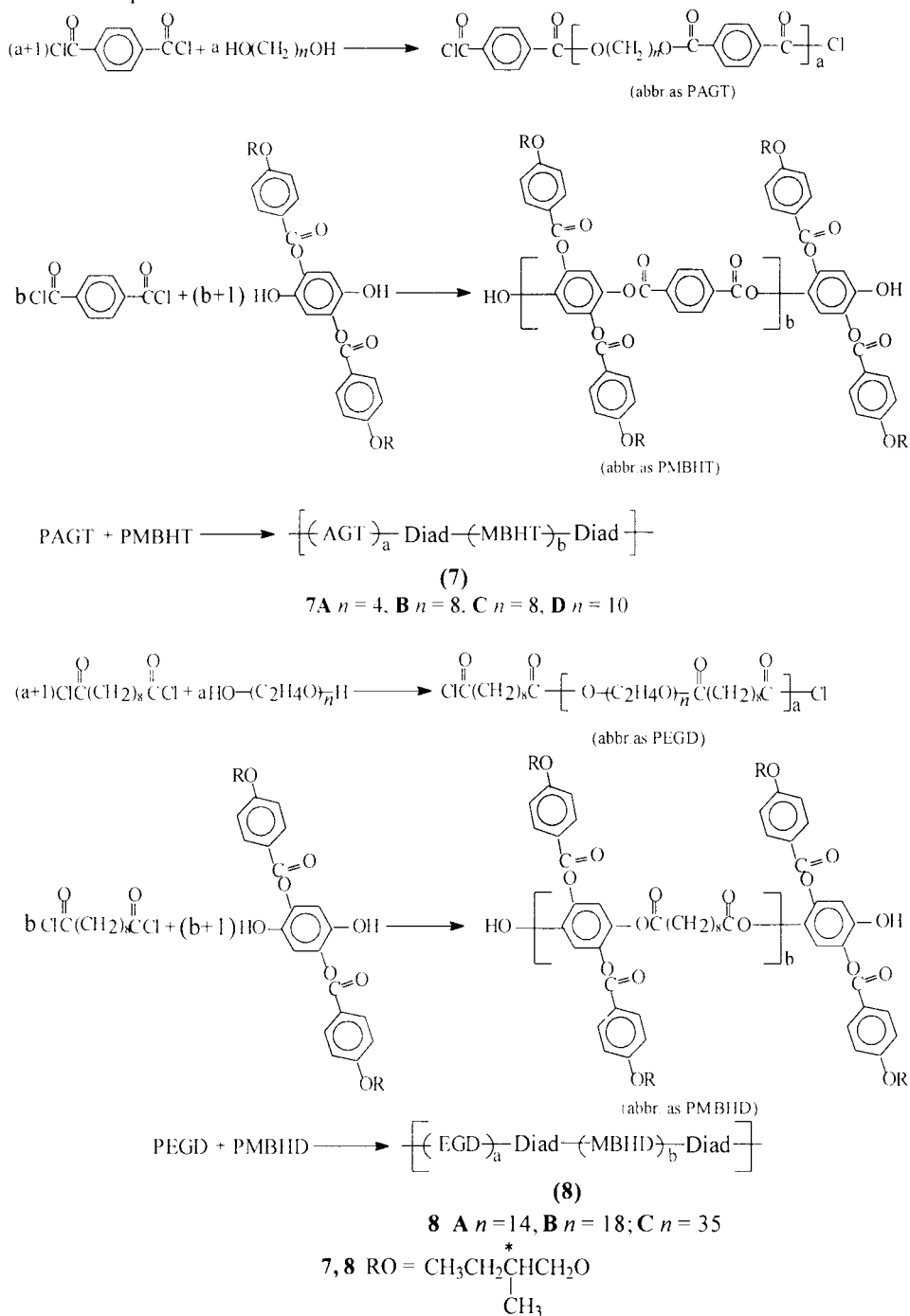
7.5 g (0.036 mol) compound **3** with an excess amount of thionyl chloride was heated to reflux for 1 h. The excess thionyl chloride was removed with a rotary evaporator. The acid chloride was washed with petroleum ether. THF (20 mL) and pyridine (2.6 mL) were added into the acyl chloride to make a solution, into which 2.3 g (0.016 mol) 2,5-dihydroxybenzoquinone dissolved in THF was added slowly, then stirred for 3 h. Compound **5** was isolated by removing THF, filtrated and dried in vacuum. Further purification was conducted by recrystallization from 1,4-dioxane. In the end a light yellow precipitate was obtained in 77.1% yield. The product was identified as compound **5** through the following characterizations, melting point: 115.9~116.1°C; elemental analysis found (calc.)%: C 69.44 (69.22) and H 6.29(6.20); IR (KBr, cm⁻¹): 1743 (C=O, ester), 1684 (C=O, quinone), 1600, 1508 (aromatic ring C=C), 1252~1038 (C—O—C, ether), 1122 (C—O—C, ester) and 840 (1,4-Ar); ¹H-NMR(δ): 0.95~1.05 (*m*, 12H, 2×CH₃CH₂C*(CH₃)H—), 1.28~1.59(*m*, 4H, 2×CH₃CH₂—), 1.90~1.92(*m*, 2H, 2×—C*H—), 3.81~3.93(*m*, 4H, 2×—CH₂O—), 6.84 (*s*, 2H, quinone ring protons) and 7.08, 8.11 (*d*, each 4H,aromatic protons); MS (*m/e*): M⁺(%) 520 (10), base 191 (100).

Preparation of compound 6

4.7 g (9.0 mmol) compound **5** was dissolved in 100 mL THF in a flask placed in an ice/water bath. With stirring, a solution of 22 g ammonium chloride and 22 g sodium hydrosulfite in 130 mL deionized water was added dropwise into the flask. A white product was obtained. The product was collected, washed with water, dried and recrystallized from 1,4-dioxane. Yield: 97%. The product was identified as compound **6** through the following characterizations, melting point:185.1~185.7°C; elemental analysis found (calc.)%: C 68.77(68.95) and H 6.76(6.56); IR (KBr, cm⁻¹): 3400 (—OH), 1710 (C=O), 1604, 1504 (aromatic ring C=C), 840 (1,4-Ar); ¹H-NMR (δ): 0.92~0.96 (*t*, 6H, 2×CH₃—), 1.00~1.02 (*d*, 6H, 2×—C*(CH₃)H—), 1.25~1.57 (*m*, 4H, 2×CH₃CH₂—), 1.85~1.89 (*m*, 2H, 2×—C*H—), 3.88~4.00 (*m*, 4H, 2×—CH₂O—), 6.73 (*s*, 2H, phenolic ring protons), 7.13, 8.07 (*d*, each 4H,aromatic protons) and 9.29 (*s*, 2H, 2×—OH); MS (*m/e*): M⁺(%) 522(20), base 191 (100).

Block Copolymer Synthesis

The reaction sequence is shown in Scheme 2



Diad: the diad represents different connective segments

Scheme 2

Synthesis of prepolymers PAGT, PMBHT and block copolymers 7

Taking **7A** as an example. 0.2895 g (1.425 mmol) terephthaloyl chloride was dissolved in 5 mL 1,1,2,2-tetrachloroethane (TCE). To this solution 0.1028 g (1.1407 mmol) of butanediol was added

and the temperature was raised to 90~100 °C. The reaction was conducted under nitrogen atmosphere for 12 h. In another reaction vessel 0.1168 g (0.5730 mmol) terephthaloyl chloride was dissolved in 2 mL TCE and 0.4497 g (0.8605 mmol) compound **6** dissolved in a mixed solvent composed of 2 mL TCE and 0.5 mL pyridine was added. The temperature was raised to 90~120 °C and the reaction was carried out under nitrogen atmosphere for 12 h. The contents of the second flask were carefully transferred under nitrogen atmosphere to the first flask. The temperature was increased to 110~120 °C. After stirring for 24 h, the solution was cooled, and the block copolymer was precipitated in a large volume of methanol. After being filtered, washed and dried in vacuum, the product was recrystallized from THF/methanol.

The prepolymers PAGT ($n = 6, 8, 10$) and the block copolymers **7B**, **7C** and **7D** were prepared in a similar manner.

Synthesis of prepolymers PEGD, PMBHD and block copolymers 8

Taking **8C** as an example. 0.1234 g (0.6010 mmol) decanedioic acid and an excess amount of thionyl chloride were heated to reflux for 1 h. Excess thionyl chloride was removed with a rotary evaporator. The decanedioyl chloride was washed with petroleum ether. 1 mL TCE was added into the acyl chloride to make a solution, into which 0.7232 g (0.4696 mmol) polyethylene glycol dissolved in 8 mL TCE and 0.2 mL pyridine was added slowly. After stirring for 48 h at room temperature, in another reaction vessel 0.3329 g (0.6370 mmol) compound **6** dissolved in 2 mL TCE and 0.2 mL pyridine and 0.5014 mmol decanedioyl chloride dissolved in 1 mL TCE were added. The reaction solution was stirred for 48 h at room temperature. The contents of the second flask were carefully transferred to the first flask. The reaction continued for 72 h at room temperature, then the block copolymer was precipitated from a large volume of methanol. After being filtered and dried in vacuo, the product was recrystallized from THF/methanol.

The prepolymers PEGD ($n = 14, 18$) and block copolymers **8A** and **8B** were prepared in a similar manner.

RESULTS AND DISCUSSION

Characterization of the Monomers, Prepolymers and Block Copolymers

The synthetic routes for the monomers and block copolymers were shown in Scheme 1 and 2. The structure of the low molecular weight compounds **3**, **5** and **6** were identified by using elemental analysis, ¹H-NMR, IR and MS etc. A polarized optical microscope with a heating stage and DSC were used to measure the T_m (melting temperature) and T_i (isotropization temperature) of the compounds. Both methods gave the same results. Upon heating, compounds **3**, **5**, prepolymers PMBHT and PMBHD will melt to form a liquid crystal phase and show a typical smectic phase texture.

All the polymers are in the form of powder and soluble in THF at room temperature. The prepolymers PAGT, PMBHT, PEGD, PMBHD and the block copolymers were characterized by using GPC, MDSC, X-ray diffraction, TG and polarizing optical microscopy. Their molecular weight polydispersities and thermal properties were collected in Table 1 and Table 2. The number average molecular weight (M_n) of the prepolymers is controlled by molar ratio of the monomers and does not increase with further increase of the time. So their M_n is low. From Table 1 and 2, we can see that M_n of the block copolymers is higher than that of the prepolymers and increases with a further increase of the time. This suggested the formation of the block copolymers. The T_m of prepolymers PAGT and PEGD decreased when the flexible spacer unit in the polymers gets longer. Both T_m and T_i of the block copolymers decreased when the flexible spacer unit in the polymers gets longer.

Table 1 Molecular weights and phase transition temperatures of the prepolymers

Prepolymers	Mol. wt. ^a		Phase tr. temp.(°C) ^b	
	M_n	M_w	T_m	T_i
PAGT ($n = 4$)	1400	2400	67	—
PAGT ($n = 6$)	1500	2500	64	—
PAGT ($n = 8$)	1500	2600	62	—
PAGT ($n = 10$)	1600	2500	61	—
PMBHT	2600	4100	132	240
PEGD ($n = 14$)	3100	5100	45	—
PEGD ($n = 18$)	3800	6500	41	—
PEGD ($n = 35$)	5400	8200	39	—
PMBHD	2400	4000	75	123

a) Determined by GPC, b) Phase transition temperature were determined by combining the data from optical polarized microscopy and DSC studies

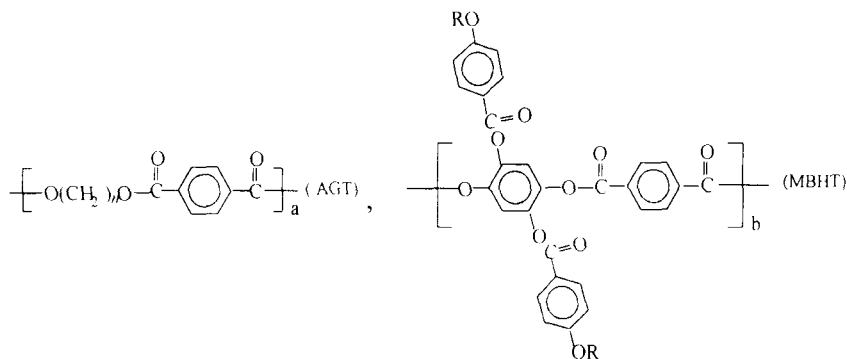
Table 2 Molecular weights and thermal properties of the copolymers

Copolymers	Mol. wt. ^a		Phase tr. temp.(°C) ^b		T_d (°C) ^c
	M_n	M_w	T_m	T_i	
7A	8500	12000	97	163	325
7B	8600	13000	75	118	321
7C	8600	14000	70	112	324
7D	8700	14000	67	105	311
8A	13000	20000	30	102	305
8B	14000	21000	28	98	300
8C	17000	26000	25	95	298

a) Determined by GPC, b) phase transition temperature were determined by combining the data from optical polarized microscopy and DSC studies.

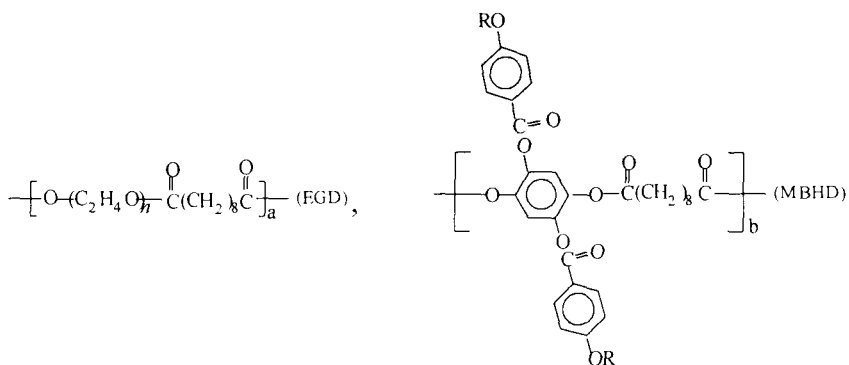
c) decomposition temperature (5 wt% loss in N₂)

The structure of the copolymers was characterized by using infrared spectroscopic analysis. The block copolymers **7** were found to be composed of four different structural units: AGT, MBHT and two different diads. The structures of AGT and MBHT are shown in Scheme 3.

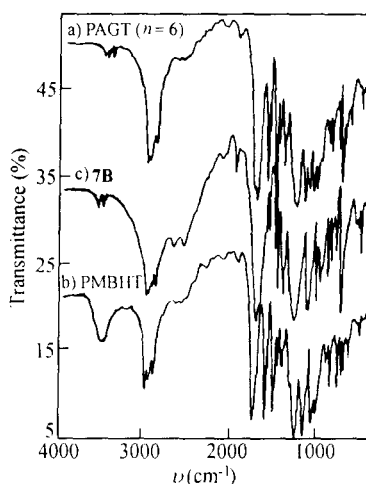
**Scheme 3**

The block copolymers **8** are composed of four different structural units: EGD, MBHD and two different diads. The structures of EGD and MBHD are shown in Scheme 4.

Take **7B** as an example. The IR spectra of PMBHT, PAGT ($n = 6$) and copolymer **7B** are shown in Fig. 1. There is a strong absorption peak of hydroxy group ($O-H$) at 3415 cm^{-1} in the IR spectrum of PMBHT. PAGT shows a strong absorption peak at 1747 cm^{-1} due to the chloroformyl group ($Cl-C=O$). In the IR spectrum of copolymer **7B**, the peaks assigned to the $O-H$ group (3415 cm^{-1}) and the $Cl-C=O$ group (1747 cm^{-1}) disappear. The disappearance of these characteristic peaks indicates that the polymerization proceeds to completion.



Scheme 4

Fig. 1 IR spectra of PAGT ($n = 6$), PMBHT and 7B

The other copolymers were verified in a similar way.

Optical Activity Studies

Optical activity of the dilute block copolymers solutions was determined at 20°C and 589.0 nm. The length of the sample cell is 200 mm. The results obtained are shown in Table 3.

Table 3 Optical activity of the block copolymers

Chiral compounds	No. of chiral C*/compounds ^a	Solution concentration (10 ⁻² g/mL)	Optical rotation (deg ^a)	Specific rotation (deg dm ⁻¹ g ⁻¹ cm ³)	Molar rotation (10 ⁻² deg dm ⁻¹ mol ⁻¹ cm ³) ^b
7A	2	1.543	0.200	6.48	551
7B	2	1.615	0.220	6.81	586
7C	2	1.612	0.187	5.83	501
7D	2	1.721	0.196	5.68	494
8A	2	1.548	0.156	5.04	655
8B	2	1.650	0.219	4.64	650
8C	2	1.704	0.105	3.08	524

a) Number of chiral C* of repeating unit of copolymers, b) molar rotations were calculated from molecular weight of low mass molecular and number average molecular weight of polymers

It can be seen that all the block copolymers listed in Table 3 have high optical activity. No racemization has happened during the synthesis process.

Liquid Crystallinity

The results from DSC and polarizing microscopic studies illustrated that all the copolymers show thermotropic liquid crystalline behavior. From the DSC curves of copolymers **7A~7D** and **8A~8C** in Fig. 2 it can be found that all the polymers show two endo thermal peaks in the process of heating. The first peak designates the melting of the copolymers from solid phase to mesomorphic phase while the second peak designates the transition from the mesomorphic phase to the isotropic liquid phase.

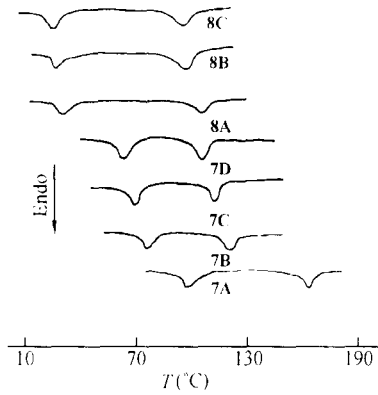


Fig. 2 DSC thermograms (first scan) of block copolymers **7A~7D** and **8A~8C**

The results obtained from polarizing microscope with a heating stage were in a good agreement with those from DSC. Heating the copolymer samples to above their melting temperature, the copolymers turned into liquid crystal phase, and showed strong birefringence. The birefringence disappeared with further heating, the copolymer transformed from liquid crystal phase to isotropic liquid phase. Conversely, by cooling the isotropic liquid phase slowly, the birefringence appeared again.

Temperature-Variable X-Ray Diffraction

Temperature-variable X-ray diffraction measurements confirm the existence of the chiral smectic C phase by calculating the tilted angle of the mesogens with respect to the normal of the Sc layer plane. The tilted angles (α) were calculated from the equation $\alpha = \cos^{-1}(d/L)$. The layer thickness

Table 4. The results of X-ray diffraction measurements

Copolymers	$T(^{\circ}\text{C})$	$2\theta(^{\circ})$	$d(\text{nm})$	$L(\text{nm})$	$\alpha(^{\circ})$
7A	125	4.56	1.934	2.686	43.92
	145	4.45	1.985	2.686	42.35
7B	85	4.50	1.962	2.686	43.07
	100	4.42	2.002	2.686	41.81
7C	75	4.49	1.967	2.686	42.92
	90	4.36	2.024	2.686	41.10
7D	75	4.52	1.953	2.686	43.39
	85	4.43	1.992	2.686	42.13
8A	45	4.35	2.029	2.686	40.94
	80	4.26	2.073	2.686	39.50
8B	-	-	-	2.686	-
	-	-	-	2.686	-
8C	40	4.32	20.43	2.686	40.48
	80	4.20	21.01	2.686	38.53

Note: The copolymer **8B** has not been measured

(d) of the chiral smectic C phase was compared with the length (L) of the monomer 6. L was calculated for monomer's most extended conformation by molecular simulation. The results were presented in Table 4. As an example, Fig. 3 was the temperature-variable X-ray diffraction powder patterns for copolymer 7D.

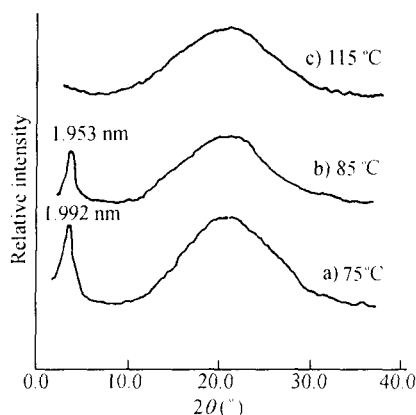


Fig. 3 Temperature-variable X-ray diffraction patterns of block copolymer 7D

In all the cases, the tilted angle is over 38° . This suggests that the copolymers have the chiral smectic C phase. The formation of the chiral smectic C phase was further verified by the fact that the tilted angle is decreased when the measurement temperature is increased^[11]. Using the same method we have proved that all the copolymers synthesized have the chiral smectic C phase. In addition, a phase transition at T_i is also observed from this WAXD study.

CONCLUSION

A successful synthesis of a series of novel chiral shish-kebab type liquid crystalline polymers was presented. The polymers were characterized by GPC, DSC, TG, X-ray diffraction, polarimeter and polarizing microscope with heating stage. It was found that all the polymers turned into liquid crystal phase above their T_m . The sanded or focal-conic texture can be observed. The block copolymers are optically active, and no racemization has happened. Both T_m and T_i of all the polymers are decreased when the flexible spacer unit in the polymer becomes longer. Temperature-variable X-ray diffraction study demonstrates that they belong to the chiral smectic C phase.

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