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Synthesis of side-chain liquid crystalline polyoxetanes containing 4-dodecanyloxyphenyl *trans*-4-alkylcyclohexanoate side groups

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SUMMARY

The synthesis and characterization of side-chain liquid crystalline polyoxetanes containing 4-dodecanyloxyphenyl trans-4-alkylcyclohexanoate side groups are presented. All the obtained monomers exhibit smectic B mesomorphism, while all the obtained polymers present smectic A, smectic B and smectic G mesophases. A longer terminal alkyl group is leading to the formation of a more stable mesophase.

INTRODUCTION

In recent years considerable efforts has been directed to the synthesis of novel side-chain liquid crystalline polymers (SCLCPs) with narrow polydispersities and well-defined molecular weights. Percec et al. reported the synthesis of SCLCPs by living cationic polymerization(1). Schrock et al. reported the synthesis of SCLCPs by living ring-opening methathesis polymerization(2-6).

In 1991, Kawakami reported the first example of side-chain liquid crystalline polyoxetanes by cationic ring opening polymerization(7-9). The goal of this study is to present the synthesis of side-chain liquid crystalline polyoxetanes containing 4-dodecanyloxyphenyl trans-4-alkylcyclohexanoate side groups. The synthesized monomers and polymers were characterized by differential scanning calorimetry, optical polarizing microscopy and X-ray diffraction. The effect of terminal alkyl length on the mosomorphic properties of the obtained polyoxetanes is discussed.

EXPERIMENTAL

Materials

Trans-4-n-propylcyclohexanoic acid, trans-4-n-butylcyclohexanoic acid and trans-4-n-pentylcyclohexanoic acid were obtained from Tokyo Kaisei Inc. and were used as received. Boron trifluoride ether complex was also purchased from Tokyo Kaisei Inc. and was distilled before use. 3-(Hydroxymethyl)-3-methyloxetane and all other reagents were obtained from Aldrich and were used as received. Dichloromethane used in the ring-opening polymerization was refluxed over calcium hydride and then distilled under nitrogen.

Techniques

Experimental techniques used in the characterization of intermediary compounds and of polymers are identical to those previously reported(10-12).

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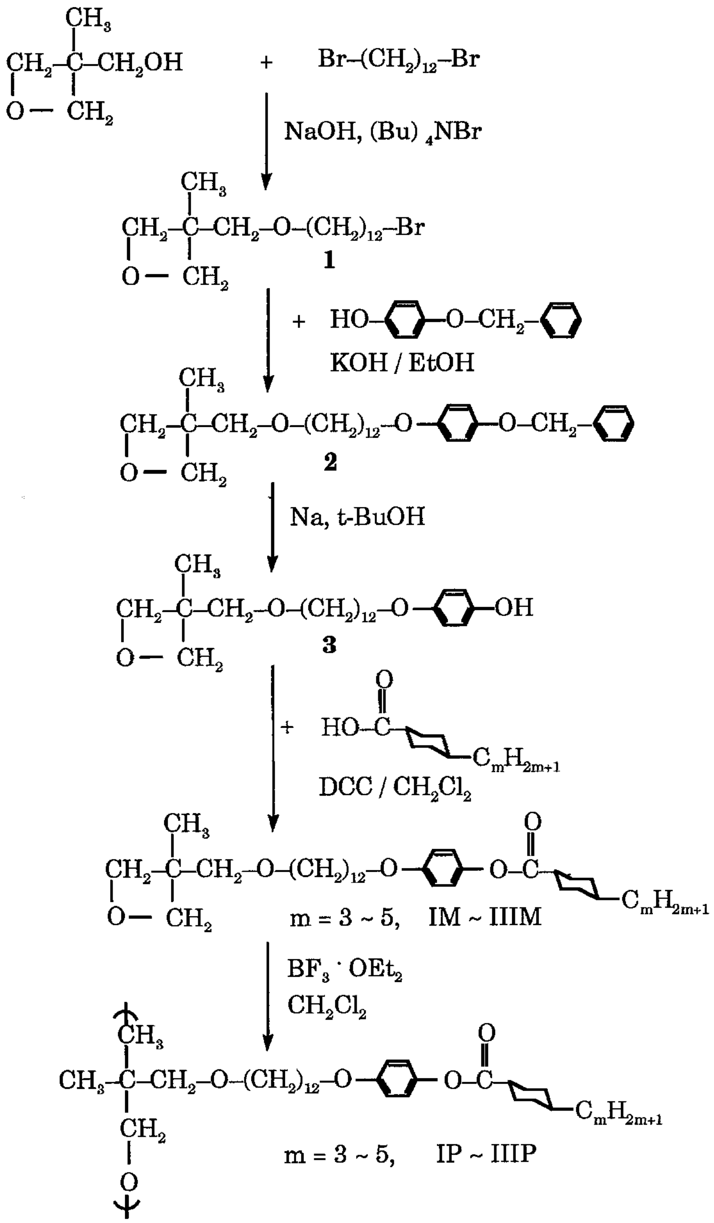
Synthesis of monomers

The synthesis of the oxetane monomers IM~IIIM is outlined in Scheme 1.



Scheme 1 : Synthesis of monomers IM ~ IIIM and polymers IP ~ IIIP

3-[(12-Bromododecoxy)methyl]-3-methyloxetane (1)

A two-phase system composed of dibromododecane (32 g, 0.098 mol) in hexane (100 ml) and 3-(hydroxymethyl)-3-methyloxetane (5 g, 0.049 mol), sodium hydroxide (32.5 g, 0.813 mol) and tetrabutylammonium bromide (0.5 g) in water (100 ml) was stirred for 24 h at room temperature and heated to reflux under stirring for 2 h. After the reaction system was cooled to room temperature, water (100 ml) was added, and the organic layer was extracted three times with hexane. Product was isolated by evaporating the solvent after drying the solution with anhydrous magnesium sulfate. The crude product was purified by column chromatography (silica gel, ethyl acetate : n-hexane = 1 : 6 as eluent) to yield 12.0 g (70.3%) of a colorless liquid. ^{1}H NMR chemical shifts of compound **1** are reported in Table I.

3-[[12-(4'-benzyloxyphenyloxy)dodecoxy]methyl]-3-methyl oxetane (2)

p-Benzyloxyphenol (7.60 g, 0.038 mol) was added to a solution of 2.32 g (0.041 mol) of potassium hydroxide in 200 ml (90%) of ethanol. Potassium iodide (0.2 g) was added and the solution was heated to reflux temperature for 1 h. 3-[(12-Bromododecoxy)methyl]-3-methyl oxetane (1) (12 g, 0.034 mol) was added slowly and the solution was heated to reflux temperature and stirred overnight. The solution was cooled and the solid salts were removed by filtration and ethanol was removed in a rotovap. The remaining solid was extracted with ethyl acetate, washed three times with 10% KOH. The collected ethyl acetate solution was dried over anhydrous magnesium sulfate and evaporated to dryness. The obtained crude product was purified by column chromatography (silica gel, ethyl acetate : n-hexane = 1 : 6 as eluent) to yield 13.9 g (86.1%) of white crystals. ^{1}H NMR chemical shifts of compound **2** are reported in Table I.

3-[[12-(4'-hydroxyphenyloxy)dodecoxy]methyl]-3-methyl oxetane (3)

Sodium (6.88 g, 0.299 mol) was added rapidly but in small pieces to a hot solution of compound **2** (14.0 g, 0.03 mol) in 250 ml of anhydrous t-BuOH. The solution was heated to reflux for 24 h. After the sodium had completely reacted, a small amount of cold water was added, followed by the addition of a cold, dilute hydrochloric acid solution. The t-BuOH was removed in a rotovap. and the residue was extracted with dichloromethane. The collected dichloromethane solution was washed with water, dried over anhydrous magnesium sulfate, and then evaporated to dryness. The obtained product was purified by column chromatography (silica gel, ethyl acetate : n-hexane = 1 : 5 as eluent) to yield 7.77 g (68.7%) of white crystals. ^{1}H NMR chemical shifts of compound **3** are reported in Table I.

3-[[12-[4-(trans-4'-n-propylcyclohexylcarbonyloxy)phenyloxy] dodecoxy] methyl]-3-methyloxetane (IM)

3-[[12-[4-(trans-4'-n-butylcyclohexylcarbonyloxy)phenyloxy] dodecoxy] methyl]-3-methyloxetane (IIM)

3-[[12-[4-(trans-4'-n-pentylcyclohexylcarbonyloxy)phenyloxy] dodecoxy] methyl]-3-methyloxetane (IIIM)

The monomers IM - IIIM were synthesized by the same method. The preparation of monomer IM is described below.

A solution of trans-n-propylcyclohexane carboxylic acid (1.01 g, 5.95 mmol), N,N-dicyclohexylcarbodiimide (0.90 g, 4.36 mmol), compound 3 (1.50 g, 3.97 mmol) and 4-dimethylaminopyridine (0.048 g, 3.93 mmol) in dichloromethane (30 ml) was allowed to stirred at room temperature until esterification was complete. The N,N-dicyclohexyl urea was filtered. The obtained filtrate was washed three times with water, dried over anhydrous magnesium sulfate and the solvent evaporated in vacuum to give the crude product. The obtained product was purified by column chromatography (silica gel, ethyl acetate : n-hexane = 1 : 8 as eluent) to yield 1.59 g of white crystals. Table I summarized the yields and ^1H NMR chemical shifts for all synthesized monomers.

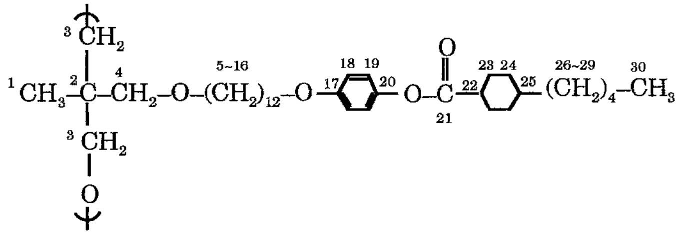
Table I : Characterization of Compounds 1 ~ 3 and monomers IM ~ IIIM.

compounds	yield	^1H NMR chemical shifts (δ, $CDCl_3$, ppm)
1	70.3%	1.20~2.00 (m, 23H, $-C\underline{H}_3$ and $-O-CH_2-(C\underline{H}_2)_{10}-$), 3.35~3.60 (m, 6H, $-C\underline{H}_2-O-C\underline{H}_2-$ and $-C\underline{H}_2-Br$), 4.33 and 4.51 (two d, 4H, two $-CH_2-$ in oxetane ring).
2	86.1%	1.20~2.00 (m, 23H, $-C\underline{H}_3$ and $-O-CH_2-(C\underline{H}_2)_{10}-$), 3.40~3.53 (m, 4H, $-C\underline{H}_2-O-C\underline{H}_2-$),3.90 (t, 2H, $-C\underline{H}_2-O-Ph-$), 4.33 and 4.50 (two d, 4H, two $-CH_2-$ in oxetane ring), 5.01 (s, 2H, $-O-C\underline{H}_2-Ph$), 6.83~7.46 (m, 9 aromatic protons).
3	68.7%	1.15~2.00 (m, 23H, $-C\underline{H}_3$ and $-O-CH_2-(C\underline{H}_2)_{10}-$), 3.40~3.53 (m, 4H, $-C\underline{H}_2-O-C\underline{H}_2-$), 3.90 (t, 2H, $-C\underline{H}_2O-Ph-$), 4.33 and 4.50 (two d, 4H, two $-CH_2-$ in oxetane ring), 6.76 (two d, 4 aromatic protons).
IM	75.8%	0.80~2.20 (m, 39H, $-C\underline{H}_3$ and $-O-CH_2-(C\underline{H}_2)_{10}-$and $\begin{matrix}-C\underline{H}_2-C\underline{H}_2\\-C\underline{H}_2-C\underline{H}_2\end{matrix}> C\underline{H}-C_3\underline{H}_7$), 2.43 (tt, 1H, $-O-\overset{O}{\overset{\Vert}{C}}-C\underline{H}\langle$), 3.46 (m, 4H, $-C\underline{H}_2-O-C\underline{H}_2-$), 3.92 (t, 2H, $-C\underline{H}_2-O-Ph-$), 4.33 and 4.50 (two d, 4H, two $-CH_2-$ in oxetane ring), 6.87 and 6.93 (two d, 4 aromatic protons).
IIM	77.4%	0.80~2.20 (m, 41H, $-C\underline{H}_3$ and $-O-CH_2-(C\underline{H}_2)_{10}-$and $\begin{matrix}-C\underline{H}_2-C\underline{H}_2\\-C\underline{H}_2-C\underline{H}_2\end{matrix}> C\underline{H}-C_4\underline{H}_9$), 2.43 (tt, 1H, $-O-\overset{O}{\overset{\Vert}{C}}-C\underline{H}\langle$), 3.46 (m, 4H, $-C\underline{H}_2-O-C\underline{H}_2-$), 3.92 (t, 2H, $-C\underline{H}_2-O-Ph-$), 4.33 and 4.50 (two d, 4H, two $-CH_2-$ in oxetane ring), 6.87 and 6.93 (two d, 4 aromatic protons).
IIIM	81.2%	0.80~2.20 (m, 43H, $-C\underline{H}_3$ and $-O-CH_2-(C\underline{H}_2)_{10}-$and $\begin{matrix}-C\underline{H}_2-C\underline{H}_2\\-C\underline{H}_2-C\underline{H}_2\end{matrix}> C\underline{H}-C_5\underline{H}_{11}$), 2.43 (tt, 1H, $-O-\overset{O}{\overset{\Vert}{C}}-C\underline{H}\langle$), 3.46 (m, 4H, $-C\underline{H}_2-O-C\underline{H}_2-$), 3.92 (t, 2H, $-C\underline{H}_2-O-Ph-$), 4.33 and 4.50 (two d, 4H, two $-CH_2-$ in oxetane ring), 6.87 and 6.93 (two d, 4 aromatic protons).

Synthesis of polyoxetanes IP - IIIP

The synthesis of liquid crystalline polyoxetanes is also outlined in Scheme I. All the polymers were synthesized by the same method. The preparation of polymer IIIP is described below.

Dichloromethane was dried over calcium hydride and was distilled under nitrogen just prior to use. Freshly distilled boron trifluoride ether complex was used as an initiator. A solution of monomer IIIM (1 mmole) and dichloromethane (1 ml) was cooled to 0°C under nitrogen and the initiator (2% mole) was then injected with a syringe. The reaction mixture was stirred at 0°C for 24 h. After the reaction time, the polymers were separated and purified by several reprecipitations from dichloromethane solution into n-hexane. The absence of monomer in polymer was checked by ^{1}H NMR and GPC.



^{1}H NMR (CDCl$_3$, TMS, ppm) δ : 0.80 - 2.20 (m, 43H, $-C\underline{H}_3$, $-(-C\underline{H}_2)_{10}-$ and $\left.\begin{matrix}-C\underline{H}_2-C\underline{H}_2\\ -C\underline{H}_2-C\underline{H}_2\end{matrix}\right\rangle C\underline{H}-C_5\underline{H}_{11}$), 2.43 (broad triplet, 1H, $-O-\overset{\overset{O}{\|}}{C}-C\underline{H}\langle$), 3.22 (broad doublet, 6H, $CH_3-\underset{C\underline{H}_2-}{\overset{C\underline{H}_2-}{C}}-C\underline{H}_2-O-$), 3.34 (t, 2H, $-O-C\underline{H}_2-(-CH_2)_{10}-$), 3.89 (t, 2H, $-C\underline{H}_2-$O-Ph-), 6.85 and 6.92 (two d, 4 aromatic protons).

^{13}C NMR (CDCl$_3$, ppm) δ : 14.09 (C30), 17.50 (C1), 36.91 (C25), 43.55 (C22), 114.91 (C18), 122.16 (C19), 144.13 (C20), 156.66 (C17), 175.02 (C21), 22.70 - 37.10 and 68.30 - 74.30 (other CH$_2$ carbons).

^{1}H NMR and ^{13}C NMR signals of the other two polymers appeared at the similar positions to those of polyoxetane IIIP.

Results and Discussion

The synthetic routes used for the preparation of monomers IM ~ IIIM are outlined in Scheme 1. The thermal behavior of three monomers is reported in Table III. Both monomers IM and IIM show monotropic smectic B phase, while monomer IIIM reveals enantiotropic smectic B phase.The phase assignment has been conducted by optical polarizing microscopic observation and X-ray diffraction measurements. Figure 1 presents the typical smectic B texture exhibited by monomer IIIM. The powder X-ray diffraction pattern of monomer IIIM (Figure 2) shows two sharp diffraction rings with d-spacing of 40.38 A° and 4.49 A°, also verifies the formation of a smectic B phase.

The results of ring-opening polymerization of oxetane monomers by BF$_3$·OEt$_2$ as initiator are summarized in Table II. All monomers gave reasonable yields in the polymerization. The obtained polymers show very narrow molecular weight distribution. The molecular weights of these polymers were determined by GPC using a calibration based on polystyrene standards and therefore have only a relative meaning. The calculated degrees of polymerization based on GPC results are higher than 67 for all polymers.

Table II : Ring opening polymerization of monomers IM ~ IIIM.

monomer	m	concn. mol/L	$BF_3.OEt_2$ mol%	yield %	$\overline{Mw}$	$\overline{Mn}$	$\overline{Mw}/\overline{Mn}$	$\overline{DP}$
IM	3	1.0	2.0	74.3	48.9	39.0	1.25	74
IIM	4	1.0	2.0	68.2	54.8	42.4	1.29	78
IIIM	5	1.0	2.0	78.7	39.0	37.4	1.04	67

solvent : dichloromethane; reaction temperature : 0°C; reaction time : 24 h.

$\overline{DP}$: degree of polymerization.

Table III : Phase Transitions and Phase Transition Enthalpies of Monomers IM ~ IIIM and Polymers IP ~ IIIP

Monomer or Polymer	m[a]	Phase Transition, °C (corresponding enthalpy changes, Kcal/mol or Kcal/mru[b]) heating / cooling
IM	3	K 42.5 (9.77) I
		I 31.4 (2.84) S_B -7.5 (3.41) K
IIM	4	K 42.8 (9.39) I
		I 35.1 (3.01) S_B -5.9 (3.87) K
IIIM	5	K 40.9 (–)[C] S_B48.1 (9.22) I
		I 44.7 (3.21) S_B - 10.1 (2.14) K
IP	3	G 34.1 S_G 67.9 (0.11) S_B 73.9 (0.90) S_A 112.2 (1.32) I
		I 107.3 (1.42) S_A 70.3 (–) S_B 64.2 (1.09) S_G
IIP	4	G 36.6 S_G 75.6 (0.22) S_B 83.2 (0.99) S_A 118.2 (1.39) I
		I 112.9 (1.47) S_A 79.5 (0.92) S_B 71.5 (0.20) S_G
IIIP	5	G 43.0 S_G 74.7 (0.21) S_B 93.3 (1.04) S_A 126.3 (1.50) I
		I 120.6 (1.59) S_A 89.6 (1.06) S_B 70.7 (0.23) S_G

a) According to Scheme 1. b) mru = mole repeating unit (for polymers).
c) Overlapped transition. d) G = glassy, K = crystalline, S = smectic, I = isotropic.

The thermal transitions and thermodynamic parameters of polymers IP ~ IIIP are reported in Table III. All three polymers present polymorphism of smectic phases. They show respectively enantiotropic smectic A, smectic B and smectic G phases. Figure 3 reveals the temperature-dependent X-ray diffraction diagrams obtained from powder sample of IIIP at 110, 85 and 55°C. Curve A shows a diffuse reflection at 4.78A°, which corresponds to lateral spacing of two mesogenic side groups, and a sharp first-order reflection at 37.76 A° and a second-order reflection at 18.90 A°, which correspond to smectic layers. The optical polarizing micrograph (Figure 4A) reveals a focal-conic fan texture for polymer IIIP at this temperature range. Both results are consistent with a smectic A structure. When the measuring temperature has been lower from 110°C to 85°C, the wide-angle reflection becomes very sharp (curve B) and the first-order reflection increases to 38.67A°. Optical polarizing micrograph (Figure 4B) reveals some arc lines across the back of fan at transition temperature region

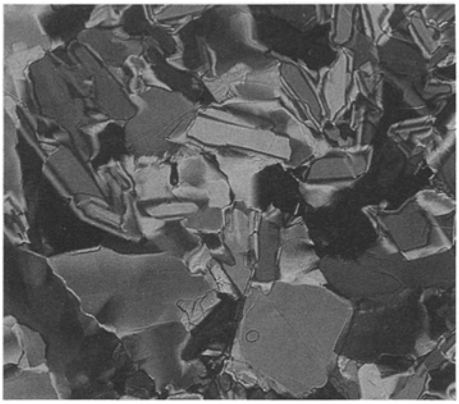


Figure 1 : Optical polarizing micrograph displayed by IIIM : S_B texture obtained after cooling from isotropic phase to 30°C.

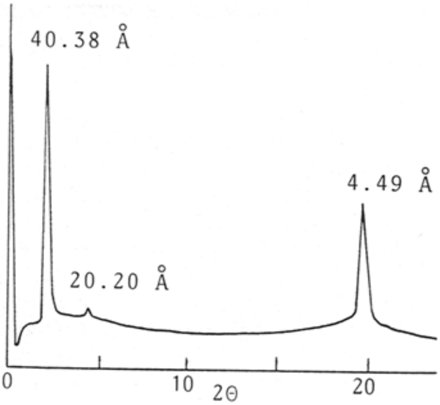


Figure 2 : X-ray measurement for monomer IIIM after cooling from isotropic phase to 30°C.

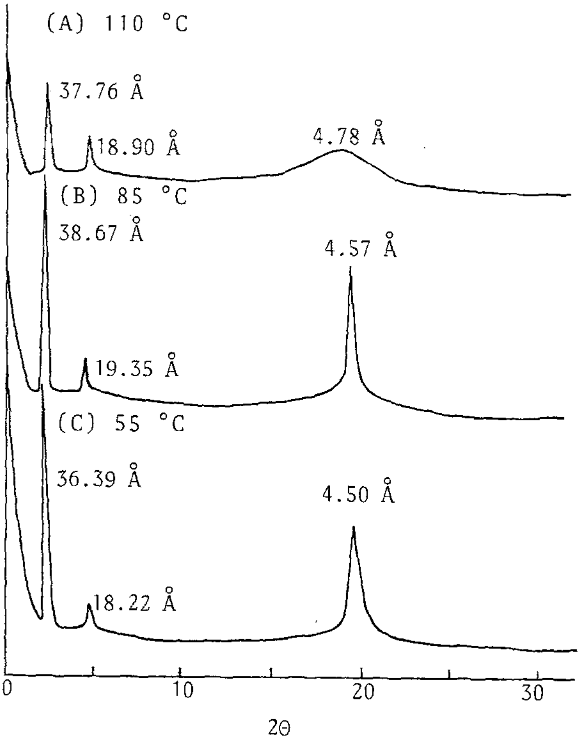


Figure 3 : Temperature-dependent X-ray measurements for polymer IIIP after cooling from isotropic phase to (A) 110, (B) 85, and (C) 55°C.

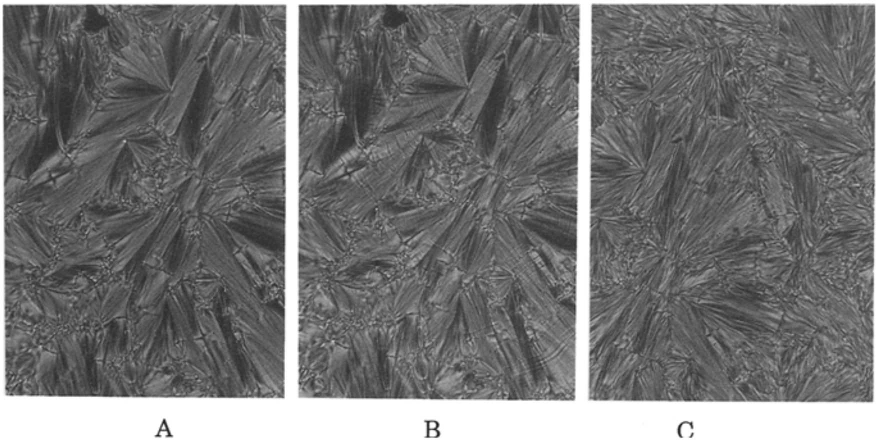


Figure 4 : Optical polarizing micrographs displayed by IIIP : A) S_A texture obtained at 95°C; B) S_B texture obtained at 89.6°C; C) S_G texture obtained at 52°C.

(near 89.6°C). The arc lines will disappear when the temperature is further cooled. These results indicate the formation of a smectic B phase. When the measuring temperature has been further cooled to 55°C, the d-spacing of first-order reflection deceases from 38.67 to 36.39. This gives strong evidence for the formation of a tilted smectic G phase. This result is also in agreement with the optical microscopic observation which reveals a typical smectic G texture (Figure 4C).

Some conclusions can be obtained from the data reported in Table III. All the polymers show only liquid crystalline mesophases and do not undergo side chain crystallization even if twelve methylene units are used as the flexible spacers. The difference among three polymers is due to the length of the terminal alkyl groups. As the length of a terminal alkyl group increases from propyl to pentyl, it does not affect the type of mesophase formed, but does affect the isotropization temperature (Ti). The polymer with a pentyl terminal group has a highest Ti value. The results demonstrate that a longer terminal alkyl group is leading to the formation a more stable mesophase.

REFERENCES

1. Percec V, Tomazos D (1992) Adv. Mater., 4 : 548.
2. Komiya Z, Pugh C, Schrock R-R (1992) Macromolecules, 25 : 3609.
3. Komiya Z, Pugh C, Schrock R-R (1992) Macromolecules, 25 : 6586.
4. Pugh C, Schrock R-R (1992) Macromolecules, 25 : 6593.
5. Komiya Z, Schrock R-R (1993) Macromolecules, 26 : 1387.
6. Komiya Z, Schrock R-R (1993) Macromolecules, 26 : 1393.
7. Kawakami Y, Takahashi K, Hibino H (1991) Macromolecules, 24 : 4531.
8. Kawakami Y, Takahashi K (1991) Polym. Bull., 25 : 439.
9. Kawakami Y, Takahashi K, Nishiguchi S, Toida K (1993) Polym. Int. 31 : 35.
10. Hsu C-S, Lu Y-H (1991) J. Polym. Sci., Polym. Chem., 29 : 977.
11. Hsu C-S, Lu Y-H (1991) Polym. Bull. 25 : 169.
12. Hsu C-S, Lin J-H, Chou L-R, (1992) Macromolecules, 25 : 7126.

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