Synthesis and Properties of Side-Chain Liquid-Crystalline Polysiloxanes Containing Hemiphasmidic Mesogens

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ABSTRACT: The synthesis of hemiphasmidic monomers 4-[(3,4,5-triethoxy)benzoyloxy]-4'-[(*p*-allyloxy)benzoyloxy]-biphenyl (M$_1$), 4-[(3,5-diethoxy)benzoyloxy]-4'-[(*p*-allyloxy)-benzoyloxy]biphenyl (M$_2$), and of the corresponding side-chain liquid-crystalline polysiloxanes (P$_1$, P$_2$) was carried out. For comparison, rodlike monomer 4-[(*p*-ethoxy)-benzoyloxy]-4'-[(*p*-allyloxy)benzoyloxy]biphenyl (M$_3$) and its polysiloxanes (P$_3$) were also prepared. The chemical structures of the monomers and polymers obtained were confirmed by FTIR and ^{1}H-NMR spectra. Their mesomorphic properties and phase behavior were investigated by differential scanning calorimetry, polarizing optical microscopy, and X-ray diffraction measurements. The relationship between structures and properties was discussed. It was observed that M$_1$ and M$_3$ were enantiotropic nematic phase, M$_2$ was monotropic mesophase, and their poly(methylsiloxanes) (P$_1$–P$_3$) possessed a broad range enantiotropic nematic phases and high thermal stability. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 95: 946–952, 2005

Key words: hemiphasmidic monomers; liquid-crystalline polysiloxanes; phase behavior; synthesis; structure

INTRODUCTION

Conventional liquid-crystalline compounds consist of mesogens that are either rodlike or disclike molecular structures. With development of the science and technology of liquid crystals, an increasing number of new mesogens have been prepared and studied.[1–5] Hemiphasmidic liquid crystals, or hemiphasmids, are known as a kind of combination of a half-disclike and a rodlike moiety.[6] Because hemiphasmids and related structures can describe the borderline between rigid and flexible, rodlike and disclike, much attention has been paid to their synthesis, properties, and application.[7–10] Furthermore, polymers containing hemiphasmidic mesogens can bridge between these multiple mesogenic architectures and provide a series of supramolecular structures. Among these, side-chain liquid-crystalline polymers containing hemiphasmidic mesogens are of interest because they usually show mesogenic properties at moderate temperatures and have a broad enantiotropic mesophase and low viscosity.[11] However, to the best of our knowledge, research on hemiphasmids and their poly(methylsiloxanes) has been reported only rarely. It is necessary to synthesize various kinds of hemiphasmids and their side-chain liquid-crystalline poly(methylsiloxanes) to explore their properties and potential applications.

In a previous study, we reported the synthesis and properties of side-chain liquid-crystalline polysiloxanes containing sulfonic acid groups, quaternary ammonium salt groups, and crosslinking agents.[12–18] In this article, we report the synthesis of the hemiphasmidic monomers 4-[(3,4,5-triethoxy)benzoyloxy]-4'-[(*p*-allyloxy)benzoyloxy]biphenyl (M$_1$), 4-[(3,5-diethoxy)benzoyloxy]-4'-[(*p*-allyloxy)benzoyloxy]biphenyl (M$_2$), and rodlike monomer 4-[(*p*-ethoxy) benzoyloxy]-4'-[(*p*-allyloxy)benzoyloxy]biphenyl (M$_3$), and of the side-chain liquid-crystalline polysiloxanes (P$_1$–P$_3$) derived from them. Their liquid-crystalline (LC) properties were characterized by DSC, polarizing optical microscopy (POM), and X-ray diffraction (XRD) measurements. The influence of the monomer structures on the phase behavior of the monomers and their polysiloxanes is discussed.

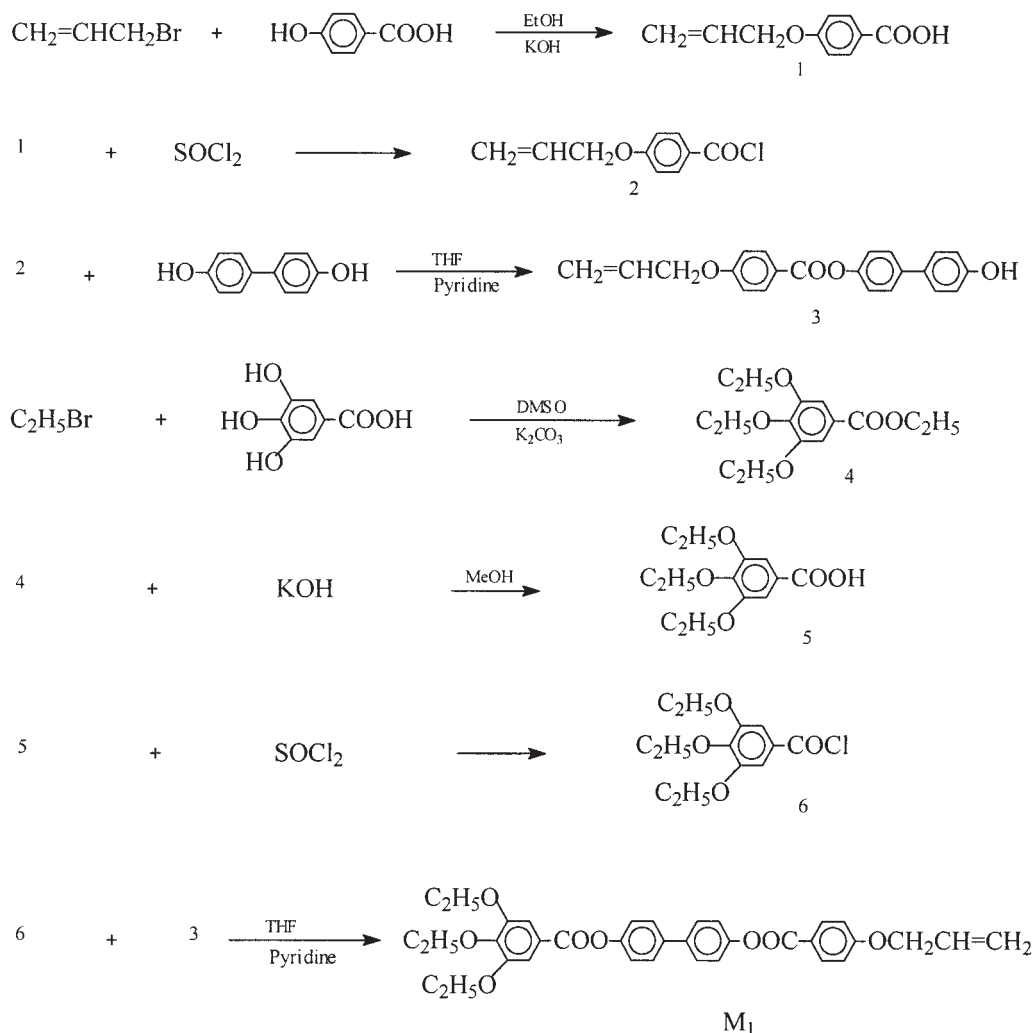## EXPERIMENTAL

Materials

Bromoethane, 3-bromopropene, *p*-hydroxybenzoic acid, 3,5-dihydroxybenzoic acid, 3,4,5-trihydroxybenzoic acid, 4,4'-biphenyldiol, and poly(methylhydrogeno)siloxane (PMHS, M_n = 700–800) were obtained from Beijing Chemical Co. (China) and used without

Scheme 1 Synthetic routes and structure of M_1.

any further purification. Pyridine, thionyl chloride, toluene, ethanol, dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), and methanol were purchased from Shenyang Xinxi Chemical Reagent Co. (China). Toluene, used in the hydrosilication reaction, was first refluxed over sodium and then distilled. All other solvents and reagents were purified by standard methods.

Characterization

FTIR spectra were measured on a Nicolet 510 FTIR spectrometer (Nicolet Analytical Instruments, Madison, WI). ^{1}H-NMR spectra (300 MHz) were recorded on a Varian WH-90PFT spectrometer (Varian Associates, Palo Alto, CA). Phase-transition temperatures and thermodynamic parameters were determined by using a Netzsch DSC 204 (Netzsch-Gerätebau GmbH, Bavaria, Germany), equipped with a liquid nitrogen cooling system. The heating and cooling rates were both 10°C min^{-1}. Phase-transition temperatures were

collected during the second heating and the first cooling scans. The thermal stability of the polymers under ambient atmosphere was measured with a Netzsch TG 209C thermogravimetric analyzer. A Leica DMRX (Wetzlar, Germany) polarizing optical microscope equipped with a Linkam THMSE-600 (Poole, UK) hot stage was used to observe phase-transition temperatures and analyze LC properties for the monomers and polymers through observation of optical textures. XRD measurements were performed with a nickel-filtered Cu–K$_\alpha$ radiation with a DMAX-3A Rigaku (Tokyo, Japan) powder diffractometer.

Synthesis of monomers

The synthetic routes of monomers M_1–M_3 were identical. Scheme 1 shows the synthesis and structure of M_1.

4-Hydroxy-4′-[(p-allyloxy)benzoyloxy]biphenyl (3)

4-(Allyloxy)benzoic acid (**1**) was synthesized according to a reported procedure.[19] 4-(Allyloxy)benzoyl
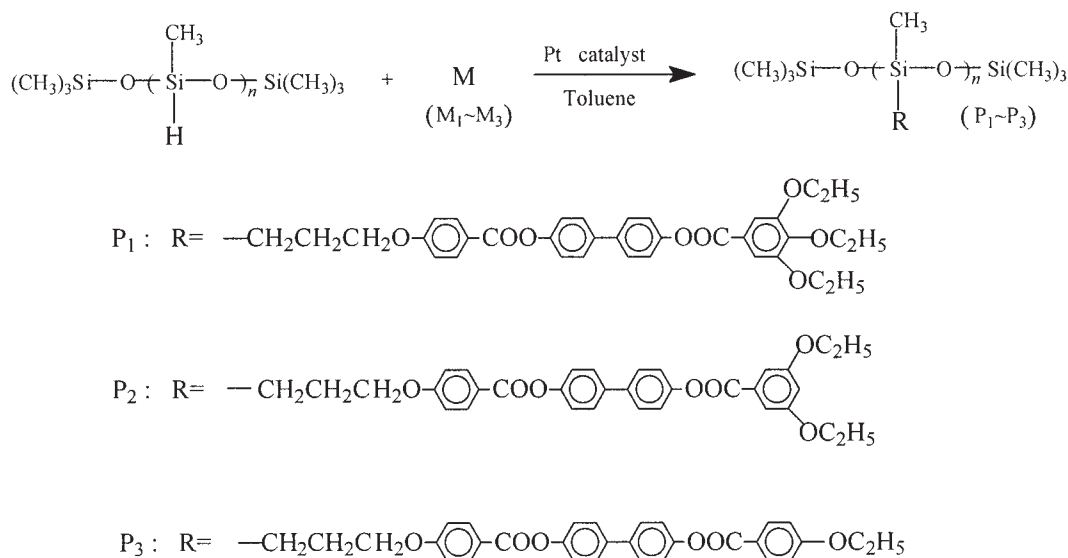
Scheme 2 Synthetic routes and structure of polymers.

chloride (**2**) was obtained from compound **1** with thionyl chloride. Compound **3** was synthesized from excess 4,4'-biphenyldiol with compound **2**.

4,4'-Biphenyldiol (46.5 g, 0.25mol) was dissolved in 25 mL of pyridine and 100 mL of THF. Compound **2** (9.8 g, 0.05mol), dissolved in 20 mL of THF, was slowly added dropwise to the solution at room temperature. Then the reaction mixture was stirred and boiled for10 h in a dry atmosphere. After cooling to room temperature, the mixture was poured into 300 mL cool water and acidified with hydrochloric acid. The precipitates were isolated by filtration and dried in a vacuum oven. Recrystallization in acetone resulted in white solid of compound **3**. The yield was 10.2 g (58.1%); mp: 205–206°C.
IR (KBr, plate) cm^{-1}: 3421 (–OH); 3030 (=CH); 2933, 2868 (–CH$_2$); 1710 (C=O); 1645 (C=C); 1605, 1510 (Ar).

4-[(3,4,5-Triethoxy)benzoyloxy]-4'-[(p-allyloxy)-benzoyloxy]biphenyl (M$_1$)

The synthesis of 3,4,5-triethoxybenzoic acid (**5**) was described in a previous publication.[20] 3,4,5-Triethoxybenzoyl chloride (**6**) was synthesized from compound **5** with thionyl chloride. Compound **6** (2.7 g, 0.01 mol), dissolved in 15 mL of THF, was slowly added to a solution containing 3.4 g (0.01 mol) of compound **3**, 10 mL of pyridine, and 50 mL of THF. The reaction mixture was refluxed for 6 h after stirring for 2 h at room temperature. Then it was poured into excess water, precipitated, filtered, and washed with water. The crude product was purified by recrystallization from ethanol. A white solid power was obtained. Yield of M$_1$: 2.5 g (43.3%); mp: 136–137°C.
IR (KBr, plate) cm^{-1}: 3040 (=CH); 2940, 2860 (CH$_3$, CH$_2$); 1731 (C=O); 1640 (C=C); 1604, 1510 (Ar). ^{1}H-NMR (CDCl$_3$):

δ (ppm) 1.33 (t, 9H, –OCH$_2$CH$_3$), 4.01 (q, 6H, –OCH$_2$CH$_3$), 4.60 (d, 2H, CH$_2$=CHCH$_2$O–), 5.3–5.8 (m, 3H, CH$_2$=CHCH$_2$O–), 7.02–8.03 (m, 18H, ArH).

4-[(3,5-Diethoxy)benzoyloxy]-4'-[(p-allyloxy)-benzoyloxy]biphenyl (M$_2$)

M$_2$ was synthesized and purified according to the same procedure as that used for the preparation of M$_1$. 3,5-Diethoxybenzoyl chloride (2.3 g, 0.01 mol) and compound **3** (3.4 g, 0.01 mol) were used to obtain a white solid. Yield M$_2$: 2.6 g (49.2%); mp: 152–153°C.
IR (KBr, plate) cm^{-1}: 3032 (=CH); 2940, 2860 (CH$_3$, CH$_2$); 1726 (C=O); 1643 (C=C); 1604, 1510 (Ar). ^{1}H-NMR (CDCl$_3$): δ (ppm) 1.31 (t, 6H, –OCH$_2$CH$_3$), 4.03 (q, 4H, –OCH$_2$CH$_3$), 4.62 (d, 2H, CH$_2$=CHCH$_2$O–), 5.3–5.8 (m, 3H, CH$_2$=CHCH$_2$O–), 7.02–8.03 (m, 18H, ArH).

4-[(p-Ethoxy)benzoyloxy]-4'-[(p-allyloxy)-benzoyloxy]biphenyl (M$_3$)

M$_3$ was synthesized and purified according to the same procedure as that used for the preparation of M$_1$. p-Ethoxybenzoyl chloride (1.9 g, 0.01 mol) and compound **3** (3.4 g, 0.01 mol) were used to obtain a white solid. Yield M$_3$: 3.5 g (70.8%); mp: 173–174°C.
IR (KBr, plate) cm^{-1}: 3044 (=CH); 2946, 2868 (CH$_3$, CH$_2$); 1728 (C=O); 1648 (C=C); 1604, 1510 (Ar). ^{1}H-NMR (CDCl$_3$): δ (ppm) 1.29 (t, 3H, –OCH$_2$CH$_3$), 3.98 (q, 2H, –OCH$_2$CH$_3$), 4.62 (d, 2H, CH$_2$=CHCH$_2$O–), 5.3–5.8 (m, 3H, CH$_2$=CHCH$_2$O–), 7.02–8.03 (m, 18H, ArH).

Synthesis of polymers

The synthetic routes of polymers P$_1$–P$_3$ are outlined in Scheme 2. The hydrosilation of monomers M$_1$–M$_3$
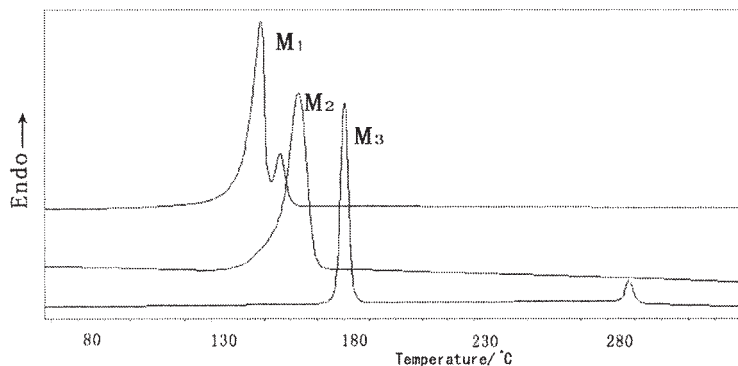
Figure 1 DSC thermograms of the monomers.

with a poly(hydrogenmethylsiloxane) was used to obtain polymers P_1–P_3. A general method for their preparation and purification is described as follows: a 3.5 mmol sample of one of the monomers was dissolved in 30 mL of dry toluene. PMHS (0.5 mmol) and 1 mL of H_2PtCl_6/THF (0.5 g hexachloroplatinic acid hydrate dissolved in 100 mL of THF) were added to the stirred solution and heated to 70°C under nitrogen and anhydrous conditions for 48 h. The polymers were obtained by precipitation in methanol and then dried under vacuum.

IR (KBr, plate) cm^{-1}: 2980–2850 (CH_3, CH_2); 1730 (C=O); 1605, 1508 (Ar); 1020–1150 (Si—O—Si).

RESULTS AND DISCUSSION

Syntheses

Monomers M_1–M_3 were synthesized as outlined in Scheme 1. The molecular structures of the monomers obtained substantially agreed with the prediction. They were confirmed by spectroscopic analysis (see experimental section). Here, we focused on the esterification of terminal benzoyl chloride having different number of ethoxy groups with 4-hydroxy-4'-[(p-allyloxy)benzoyloxy]biphenyl (**3**), which was prepared in three steps from p-hydroxybenzoic acid. Terminal benzoic acid, having different number of ethoxy groups, was synthesized as previously reported,[20] and the acyl chloride was obtained from thionyl chloride.

Polymers P_1–P_3 were prepared by a one-step hydrosilication reaction between Si—H groups of PMHS and olefinic C=C of M_1, M_2, and M_3 in toluene, with hexachloroplatinate hydrate used as catalyst at 70°C. The synthetic routes are described in Scheme 2. IR spectra of the polymers showed the complete disappearance of the Si—H stretching band at 2166 cm^{-1} and olefinic C=C stretching band at 1648–1638 cm^{-1}. Characteristic Si—O—Si stretching bands appeared at 1200–1000 cm^{-1}. In addition, the absorption bands of ester C=O and aromatic appeared.

Thermal analysis

Phase behaviors of the monomers and the obtained polymers were characterized by DSC. Figure 1 shows the DSC thermograms and the results are included in

TABLE I
Phase Transition Temperatures of Monomers

Monomer	Transition temperature (°C) [corresponding enthalpy changes (J g^{-1})]^a _Heating_ / _Cooling_	ΔT_1[b]	ΔT_2[c]
M_1	K137.3(57.8)N145.6(4.1)I		
	1138.7(4.6)N112.8(52.9)K	8.3	25.9
M_2	K152.5(63.0)I		
	1146.9(4.6)N127.7(59.9)K	—	19.2
M_3	K 173.1(55.4)N278.9(3.7)I		
	1266.8(3.0)N135.5(51.8)K	105.8	131.3

[a] K, solid; N, nematic; I, isotropic.
[b] Mesophase temperature ranges on heating cycle;
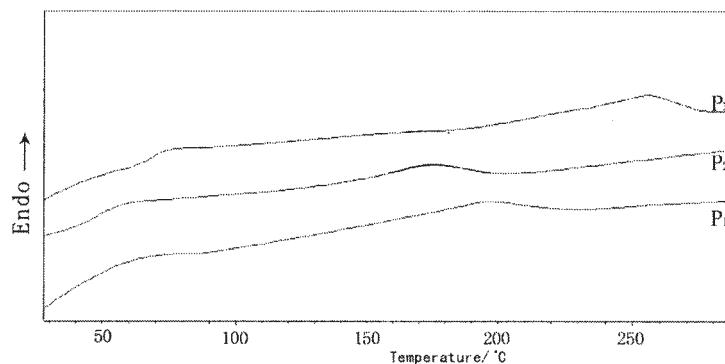[c] Mesophase temperature ranges on cooling cycle.

Figure 2 DSC thermograms of the polymers.

Table I. According to the data listed in Table I, hemiphasmidic monomer M_1 shows enantiotropic liquid-crystalline behavior. In the heating trace, the mesomorphic temperature range (ΔT) of M_1 was 8.3°C, whereas it was extended to 25.9°C in the subsequent cooling cycle. However, hemiphasmidic monomer M_2 was monotropic: its mesogenic phase could be observed only on supercooling. When M_2 was heated from room temperature, the DSC trace showed only one sharp endothermic peak at 152.5°C, which indicated a melting point. On cooling from the melt, the thermogram showed two exothermic peaks: one at a higher temperature (146.9°C) was attributed to isotropic phase to liquid-crystal phase transition and the other, at a lower temperature (127.7°C), was attributed to liquid-crystal phase to crystal transition; the region of mesogenic phase was 19.2°C. In contrast, rodlike monomer M_3 was a typical enantiotropic liquid crystal, and it showed a wide mesomorphic temperature range. As seen from these data, the width of the mesogen structure significantly affected the phase behavior of the monomers.

Hemiphasmidic monomers M_1 and M_2, which had two ethoxy groups situated at two sides of the ring of mesogen, were characterized by a much broader molecular width than that of rodlike monomer M_3. Because swallow tail–like terminal branches caused an increase in the distance between the two molecules, the interaction between neighboring molecules was weakened and the general plane of the whole molecule was destroyed. Thus compared to rodlike monomer M_3, the melting point, the isotropic point, and the extent of liquid-crystal phase region (ΔT) of hemiphasmidic monomers M_1 and M_2 obviously decreased, particularly in ΔT, which was less than about 95°C in the heating cycle and 105°C in the cooling cycle. As we know, sometimes when side groups are too bulky, their monomers do not show liquid-crystal properties at all. This effect has been observed in other hemiphasmidic compounds.[10] In addition, the terminal polarity groups played quite an important role during the liquid-crystal phase formation, which maintained the molecular orientation through the acting forces of molecular induction and polarization. Compared to M_2, M_1 with a terminal ethoxy group substituent at the end of the molecule displayed better mesogenic properties. M_1 was an enantiotropic liquid crystal, whereas M_2 was monotropic, and the mesomorphic temperature range of M_1 was wider than that of M_2.

As a rule, the phase behavior of side-chain liquid-crystalline polymers mainly depends on the nature of the polymer backbone, the rigidity of the mesogenic unit, and the length of the flexible spacer. To obtain mesomorphic properties at moderate temperatures, we used polysiloxanes as backbone to synthesize side-chain liquid-crystalline polymers containing hemiphasmidic mesogens. Figure 2 shows the DSC thermograms of polymers P_1–P_3. The phase-transition temperatures and corresponding enthalpy changes of polymers P_1–P_3, derived from DSC curves, are summarized in Table II. According to Table II, P_1 and P_2, which are side-chain liquid-crystalline polysiloxanes containing hemiphasmidic mesogens, both exhibited enantiotropic mesophases. On the DSC heating scan polymers P_1 and P_2 presented glass transitions at a low temperature, near 60°C, followed by isotropization transitions at temperatures > 170°C. The region of the liquid-crystal phase exceeded 110°C. Compared to hemiphasmidic monomers M_1 and M_2, the mesomorphic temperature ranges of P_1 and P_2 were much broader than those of the corresponding monomers,

TABLE II
Polymerization and Thermal Properties of Polymers

Polymer	Feed (mmol) PMHS	Feed (mmol) M	T_g (°C)	T_i (°C)	ΔH (J/g)	ΔT^a (°C)	$T_d{}^b$ (°C)
P_1	1	7	61.3	201.9	2.07	140.6	349.6
P_2	1	7	62.8	175.4	2.49	112.6	347.5
P_3	1	7	74.6	261.5	3.11	186.9	358.3

[a] Mesophase temperature ranges (T_i–T_g).
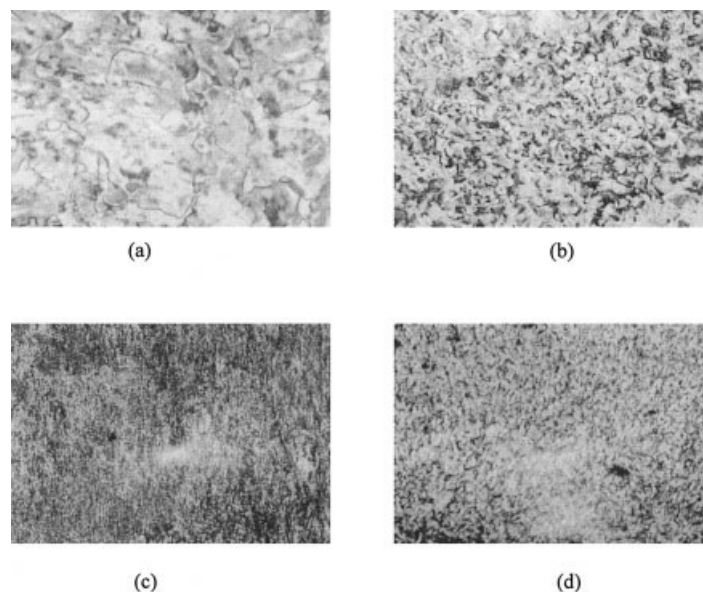[b] Temperature at which 5% weight loss occurred.

Figure 3 Optical textures of monomers and polymers (×200): (a) threadlike texture of M_1 on heating to 138°C; (b) threadlike texture of M_2 on cooling to 135°C; (c) threadlike texture of P_1 on heating to 166°C; (d) threadlike texture of P_2 on heating to 153°C.

which indicated that polymerization could result in the stabilization of the mesomorphic phase. This was also the case for P_3, which is a side-chain liquid-crystalline polysiloxane that contains rodlike monomer M_3. In particular, as predicted on the basis of thermodynamic assumptions,[21] monotropic monomer M_2 became enantiotropic when side-chain liquid-crystalline polysiloxanes containing hemiphasmidic mesogen M_2 were synthesized. DSC curves obtained from polymers $P_1–P_3$ also revealed that the glass-transition temperature (T_g) was not significantly affected by the structure of the monomers. It could be seen that T_g of P_1 and P_2 decreased by 11.8 and 13.3°C, respectively, compared with P_3. However, the isotropization temperatures (T_i) of $P_1–P_3$ clearly decreased concomitantly with the weakening of the mesogenic properties of monomers from 261.5 to 175.4°C, which resulted in the narrowing of mesophase ranges. The reason was that T_g involved movement of segments in the polymers, whereas T_i involved whole-chain movement of the polymers. With increasing width of the monomer molecules and disappearance of the terminal polar group, the motion and orientation of the polymers were prevented, so T_i decreased.

TGA results showed that the temperatures, when 5% weight loss occurred (T_d), were higher than 340°C for $P_1–P_3$, which revealed that the synthesized polymers had a high thermal stability.

Analysis of textures

The optical textures of the monomers and polymers were investigated by POM analysis with a hot stage

under nitrogen atmosphere. POM observation results showed hemiphasmidic monomer M_1 was similar to the rodlike monomer M_3, which exhibited an enantiotropic nematic phase, and M_2 revealed monotropic nematic phases on cooling cycles. When M_1 was heated to 137°C, the sample began to melt, a typical nematic threadlike texture gradually appeared, and the texture disappeared at 145°C. When the isotropic state was cooled to 139°C, the threadlike texture appeared again and did not change until 113°C when the sample began to crystallize. No mesophase was observed for M_2, which melted at 152°C and came into isotropic liquid phase directly. During the cooling cycle, however, a nematic threadlike texture occurred at 147°C, and mesomorphic properties did not disappear until 128°C, when the sample began to crystallize. Photomicrographs of M_1 and M_2 are shown in Figure 3(a) and (b), respectively.

Polymers $P_1–P_3$ exhibited a nematic threadlike texture during both heating and cooling cycles. Transition temperatures obtained from POM analysis were consistent with the results obtained by DSC. Photomicrographs of P_1 and P_2 are shown in Figure 3(c) and (d) as examples, indicating that the formation of side-chain liquid-crystalline polysiloxanes did not change their mesogenic types. XRD measurements could provide more detailed information on the liquid-crystalline phase structures. The quenched samples of polymers $P_1–P_3$, studied by wide-angle X-ray diffraction and small-angle X-ray scattering, showed amorphous diffuse peaks at about 2θ of 20°, and no sharp peak in the lower Bragg angle region was observed. This result suggested that the liquid-crystalline polymers

P_1–P_3 exhibited only nematic mesophases,[22] which was consistent with the optical textures. In contrast, in the previous report,[10] polysiloxane containing 4-[3,4,5-tris(*n*-dodecan-1-yloxy)benzoyloxy]-4′-[(*p*-allyloxy)-benzoyloxy]biphenyl displayed a hexagonal columnar mesophase. Results indicated that the length of the alkyl tails of the hemiphasmidic monomers had an important contribution to the mesogenic behavior of polymers. Short alkyl tail–ethoxy groups in hemiphasmidic mesogen of this type favored the formation of nematic mesophase, attributed to short alkyl tails permitting a rod-like conformation, whereas long alkyl tails favored the formation of columnar hexagonal mesophases.

CONCLUSION

Two hemiphasmidic monomers (M_1, M_2) and their corresponding polymers (P_1, P_2) were synthesized and characterized. For comparison, rodlike monomer (M_3) and its polysiloxanes (P_3) were also prepared. The monomers and polymers obtained were all thermotrophic liquid crystals and all phase transitions were reversible on repeated heating and cooling cycles. M_2 exhibited monotropic nematic threadlike texture on cooling course, whereas M_1 displayed an enantiotropic nematic phase just like that of rodlike monomer M_3. Polymers P_1–P_3 revealed a broad enantiotropic nematic phase and high thermal stability. The glass-transition temperatures undulated slightly with the structure of the monomers compared with the changes of isotropization temperatures and the mesomorphic temperature ranges, which decreased with increasing molecular width of the monomers.

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