Syntheses and Characterization of Novel Siloxane Liquid Crystalline Polymers Containing Two Symmetric Mesogens

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Received July 11, 1996
Revised Manuscript Received January 13, 1997

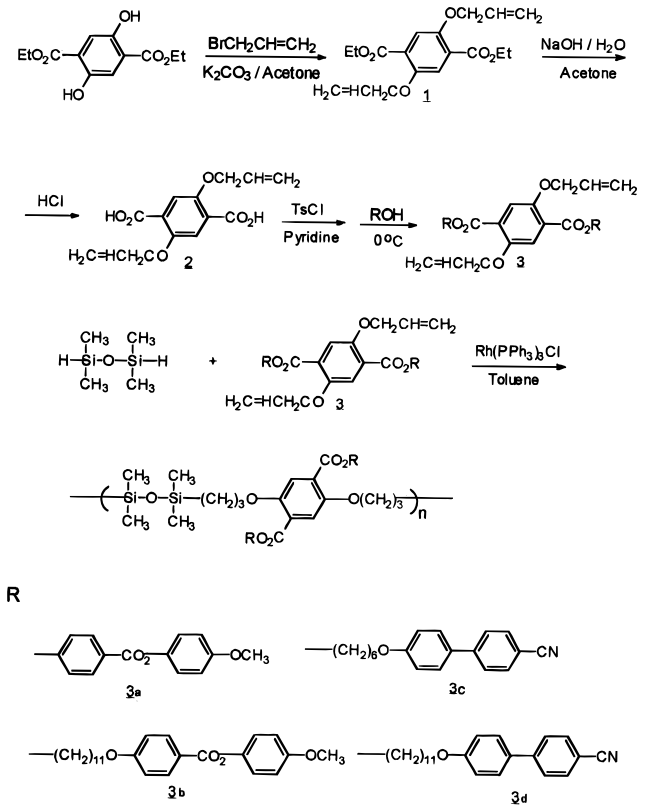
Introduction. Thermotropic liquid crystalline (LC) polymers have become an interesting research topic in the past decade[1−3] because of scientific applications such as information storage[4−6] in elements requiring nonlinear optical characteristics[7] and in piezo-, pyro-, and ferroelectric devices. Extensive studies concerning the morphology,[8] the dielectric relaxation, and the behavior in electric and magnetic fields[9] together with their optical properties revealed a number of additional applications of anisotropic glasses having liquid crystalline properties. Applications based on light modulation can lead to optical filters, reflectors, and linear polarizers.[10] Side-chain liquid crystalline polymers exhibit a lower transition temperature and tend to harden into a glassy state with the retention of LC order when cooled from the LC state. Furthermore, the side-chain LCPs have good solubility in common organic solvents, display a rich variety of LC phases, and exhibit a quick response to an external field due to their low melt viscosity. Interest in the polysiloxane backbone for LCPs comes from the low glass transition temperature and the high thermal stability exhibited by this class of polymers.[11,12] Although the Si−O bond is strong, the rotational energy of the Si−O bond is low. As a result of this, conformational changes in this backbone may easily occur. Hence, research attention shifted to their application as materials into which information could be written and then stored.

In this paper, we first report in detail the results on the preparation and properties of novel siloxane liquid crystalline polymers containing two symmetric mesogens. The synthetic routes and polymer structures are shown in Scheme 1.

Experimental Section. Monomer Synthesis. 2,5-Bis(allyloxy)terephthalic Acid Diethyl Ester (1). A mixture of diethyl 2,5-dihydroxyterephthalate (15 g, 59 mmol), allyl bromide (12.3 mL, 142 mmol), and anhydrous K_2CO_3 (16.3 g) in 80 mL of acetone was refluxed with stirring for 24 h. The mixture was poured into water and extracted with ethyl acetate. The extract was dried over anhydrous magnesium sulfate and evaporated to dryness. Yield: 95%. Mp: 54 °C. ^{1}H-NMR ($CDCl_3$): (ppm) 7.5 (s, 2H), 6.3−6.0 (m, 2H), 5.5−5.2 (m, 4H), 4.5 (d, 4H), 4.4−4.2 (q, 4H), 1.4−1.2 (t, 6H).

2,5-Bis(allyloxy)terephthalic Acid (2). A mixture of diethyl 2,5-bis(allyloxy)terephthalate (7.0 g, 20.9 mmol) and sodium hydroxide (3.5 g, 88 mmol) in acetone (50 mL) was stirred at 50 °C for 20 h. After acidification with HCl, the white solid was filtered. The crude solid product was purified by recrystallization from ethanol. Yield: 97%. Mp: 181 °C. ^{1}H-NMR ($CDCl_3$): (ppm) 13.0 (s, 2H), 7.4 (s, 2H), 6.3−6.0 (m, 2H), 5.5−5.2 (m, 4H), 4.5 (d, 4H).

Scheme 1



2,5-Bis(allyloxy)terephthalic Acid Bis[(((4-methoxyphenyl)oxy)carbonyl)phenyl] Ester (3a). 2,5-Bis(allyloxy)terephthalic acid (1.5 g, 5.4 mmol) was dissolved in 10 mL of anhydrous pyridine, and *p*-toluenesulfonyl chloride (4.1 g, 22 mmol) was added to the solution. After the reaction mixture was stirred for 2 h at room temperature, 4-hydroxybenzoic acid 4′-methoxyphenyl ester (3.2 g, 13 mmol) was added. The solution was kept cold in an ice bath for 10 h and then poured into water. A crude product was washed in methanol. The white solid was filtered and purified by column chromatography on silica gel using a 1:1 mixture of ethyl acetate and hexane as an eluent. Yield: 45%. Mp: 112 °C. ^{1}H-NMR ($CDCl_3$): (ppm) 8.4−6.9 (d, 18H), 6.3−6.0 (m, 2H), 5.5−5.3 (m, 4H), 4.6 (d, 4H), 3.7 (s, 6H).

2,5-Bis(allyloxy)terephthalic acid esters 3b, 3c, and 3d were prepared according to the same procedure described above.

2,5-Bis(allyloxy)terephthalic Acid Bis[((((((4-methoxyphenyl)oxy)carbonyl)phenyl)oxy)undecyl] Ester (3b). Yield: 48%. Mp: 69 °C. ^{1}H-NMR ($CDCl_3$): (ppm) 8.2−6.9 (m, 18H), 6.3−6.0 (m, 2H), 5.5−5.2 (m, 4H), 4.7 (d, 4H), 4.3 (t, 4H), 4.0 (t, 4H), 3.7 (s, 6H), 1.8−1.2 (m, 36H).

2,5-Bis(allyloxy)terephthalic Acid Bis[((4-cyanobiphenylyl)oxy)hexyl] Ester (3c). Yield: 45%. Mp: 116 °C. ^{1}H-NMR ($CDCl_3$): (ppm) 7.7−6.9 (m, 18H), 6.3−6.0 (m, 2H), 5.5−5.2 (m, 4H), 4.6 (d, 4H), 4.3 (t, 4H), 4.0 (t, 4H), 1.8−1.4 (m, 16H).

2,5-Bis(allyloxy)terephthalic Acid Bis[((4-cyanobiphenylyl)oxy)undecyl] Ester (3d). Yield: 50%. Mp: 94 °C. ^{1}H-NMR ($CDCl_3$): (ppm) 7.7−6.9 (m, 18H),

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S0024-9297(96)01004-2 CCC: $14.00

Table 1. Elemental Analyses of the 2,5-Bis(allyloxy)terephthalic Acid Esters

monomers	empirical formula (mol weight)	C cal, found	H cal, found	N cal, found
3a	$C_{42}H_{34}O_{12}$ (729.2)	69.17, 69.01	4.66, 4.44	
3b	$C_{64}H_{78}O_{14}$ (1069.2)	71.88, 71.32	7.29, 7.68	
3c	$C_{52}H_{52}N_2O_8$ (831.7)	75.08, 75.38	6.25, 6.29	3.37, 3.01
3d	$C_{62}H_{72}N_2O_8$ (971.2)	76.67, 76.47	7.41, 7.47	2.28, 2.88

Table 2. Molecular Weights and Polydispersities of the Polymers

polymers	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
Pa	1380	2220	1.61
Pb	3120	6100	1.96
Pc	2290	2730	1.19
Pd	2030	2280	1.12

6.3−6.0 (m, 2H), 5.5−5.3 (m, 4H), 4.7(d, 4H), 4.4 (t, 4H), 4.0 (t, 4H), 1.8−1.2 (m, 36H).

Elemental analyses of the ester monomers are shown in Table 1. All of the LC mesogenic units (**a**, **b**, **c**, and **d** in scheme) were also synthesized by us.

Polymerization. Monomer **3a** (1.0 g, 3.6 mmol) was dissolved in 5 mL of dry distilled toluene with 1 equiv of 1,1,3,3-tetramethyldisiloxane. The reaction mixture was heated to 85 °C under a nitrogen atmosphere and 1 mg of $Rh(PPh_3)_3Cl$ was then added. The reaction mixture was stirred for 2 days. The polymers were separated and purified by several precipitations from tetrahydrofuran solution into methanol and further purified by acetone and then dried under vacuum. Other polymers were prepared according to the same procedure for monomers **3b**, **3c**, and **3d**, respectively.

Analysis. The synthesized compounds were identified by ^{1}H-NMR spectra that were obtained using a Bruker AM 200 spectrometer. Melting points were determined using an Electrothermal Model 1307 digital analyzer. FT-IR spectra were measured by Bomem Michelson Series FT-IR spectrophotometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of polymers were performed under a nitrogen atmosphere at a heating rate of 20 °C/min with a DuPont 910 analyzer. Elemental analyses were performed by the Analytical Department of the Korea Research Institute of Chemical Technology.

Results and Discussion. Melting temperatures of the monomers (**3a**, **3b**, **3c**, **3d**) were 112, 69, 116, and 94 °C, respectively. Melting temperatures of the monomers decreased with increasing flexible methylene spacers of the monomers. Here, **3c** and **3d** monomers showed the higher melting points because of the strong molecular interactions due to the highly polar −CN groups compared to those of the methoxy-substituted **3a** and **3b** monomers. The side-chain liquid crystalline polymers with siloxane spacers were prepared by addition of the monomers to tetramethyldisiloxane catalyzed by $Rh(PPh_3)_3Cl$. The structures of monomers and polymers were characterized by ^{1}H-NMR and IR spectra. As shown in ^{1}H-NMR data in the Experimental Section, as the hydrosilation reaction proceeded, allyl proton peaks at about 4.5−6.3 ppm disappeared and a new strong peak due to the methyl protons of the siloxane backbone of the polymer appeared at 0 ppm. Molecular weights and polydispersities of the polymers which were determined by GPC are shown in Table 2. The average number of the repeating units of the polymers ranged from 1.6 to 2.6, which indicates that synthesized polymers mainly consist of low molecular weight dimer or trimer. From the NMR study, allyl proton peaks of the monomers absolutely disappeared after polymerization, which means that most of the polymer chain ends were blocked with siloxane monomers. All the polymers are highly soluble in various organic solvents such as chloroform, THF, and 1,4-dioxane due to their low molecular weights. However, polymer **Pa** which has no methylene spacer group, was partially soluble due to its rigidity.

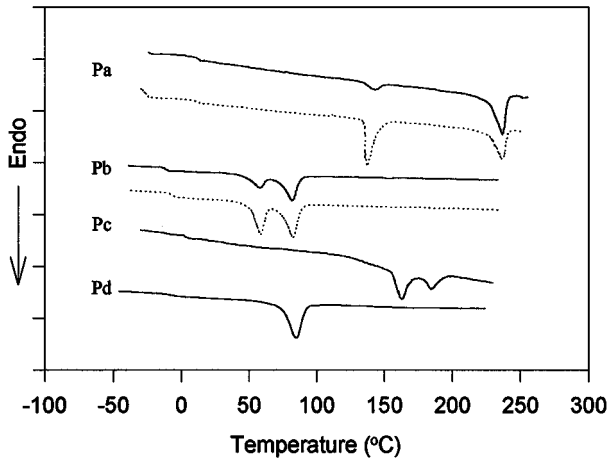


Figure 1. First heating DSC curves of polymers (scanning rate = 20 °C/min) and second heating curves of the annealed samples (broken lines).

The glass transition temperatures (T_g) of the polymers could be precisely determined from heating curves of their DSC analyses (Figure 1). The T_g's of **Pb** and **Pd** are especially lower than those of the rest, which can be ascribed to their longer flexible methylene units. As expected, the flexible siloxane backbone significantly affects the lowering[13] of T_g than those of corresponding polyacrylate and polymethacrylate.

As shown in the first heating of Figure 1, the enthalpy the of crystalline−nematic transition is smaller than that of the nematic−isotropic transition in **Pa** and **Pb**. This result can be explained by the kinetic effect that the crystallization rates of **Pa** and **Pb** are very slow because of the bulky methyl groups and the less polar mesogenic groups as well as the odd-numbered long methylene spacer, especially in **Pb**. On the other hand, the crystallization rate of **Pc** should be fast due to the highly polar −CN groups and the even-numbered methylene spacer, resulting in a larger ΔH_m. Therefore, we measured the phase transition with well-annealed samples several times (broken lines). Interestingly, the enthalpy of the crystalline−nematic transition of **Pa** became larger than that of the nematic−isotropic transition. But the enthalpy of the crystalline−nematic transition of **Pb**, even though quite increased, was still smaller than that of the nematic−isotropic transition. We believe that the methoxy-substituted mesogenic units and the odd-numbered long methylene spacer groups hardly contribute to the crystallization in **Pb**.

Table 3 shows general properties of the polymers. T_m and T_i of the polymers also decreased with the increasing flexible spacer length of the liquid crystalline mesogen. Polymers **Pa**, **Pb**, and **Pc** showed the nematic phases, but polymer **Pd** had no mesophase. It is interesting to observe that monomers did not show liquid crystalline phases; otherwise, the low molecular weight liquid crystalline polymers exhibited nematic phases, except for **Pd**.

Figure 2 shows the dramatic change of the nematic liquid crystalline phases of polymer **Pa** on cooling. Figure 2a exhibits the nematic schlieren texture at 220 °C. As the temperature cooled, the nematic phase which shows the four and two brushes' droplet (Figure 2b) was

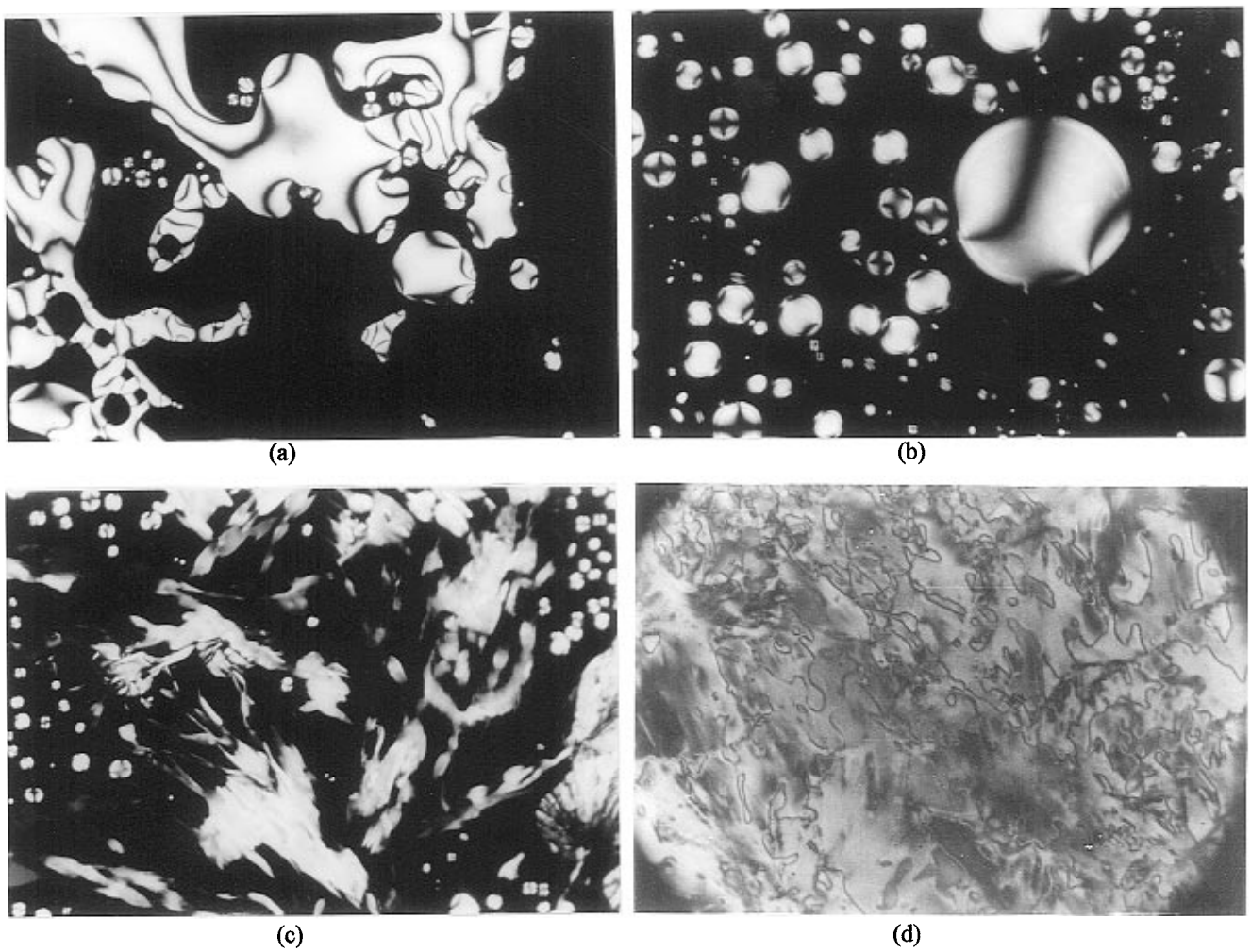
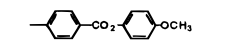
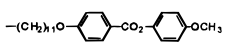
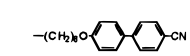
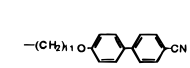


Figure 2. Microphotographs of polymers (a) taken for **Pa** at 220 °C, (b) taken for **Pa** at 150 °C, (c) taken for **Pa** at 143 °C, and (d) taken for **Pb** at 72 °C (magnification 500× for **Pa**, 250× for **Pb**). Note: The figure was reduced to 68% for publication.

Table 3. Phase Transitions of the Polymers

Polymers	Structures of LC mesogens	T_g, °C	T_m, °C	T_i, °C	LC
Pa		10	142	236	N [a]
Pb		-6.5	57	82	N
Pc		3.4	162	178	N
Pd		-6.4	84		

[a] N: nematic phase.

formed. At the temperature near T_m, the nematic droplet texture changed into the crystalline form (Figure 2c). Polymer **Pb** exhibits the typical nematic threaded texture (Figure 2d) at 72 °C on cooling. Polymer **Pc** also exhibited the nematic schlieren textures (not shown here). The reason for the formation of the well-developed nematic textures of these polymers is considered not only because of their low molecular weights but also because of the very mobile siloxane spacer backbone.

Conclusively, introduction of a siloxane spacer into the polymer backbone and of two symmetric mesogenic groups as side chains is an effective molecular design of the chemical structure of the polymer to give a better organized mesophase of lower transition temperature. T_m and T_i of the polymers were also decreased by increasing the flexible spacer length of the liquid crystalline mesogens. Thus, the spacer group actually decouples the motions of the side groups and the main chain of these polymers, and also a further lowering of glass transition temperature is possible by introducing the mesogenic units to a highly flexible siloxane backbone.

Acknowledgment. It is gratefully acknowledged that this research was supported by the Ministry of Science and Technology of Korea.

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MA961004K