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Synthesis of Liquid Crystalline Polyesters of Various Types by Acyclic Diene Metathesis Polymerization

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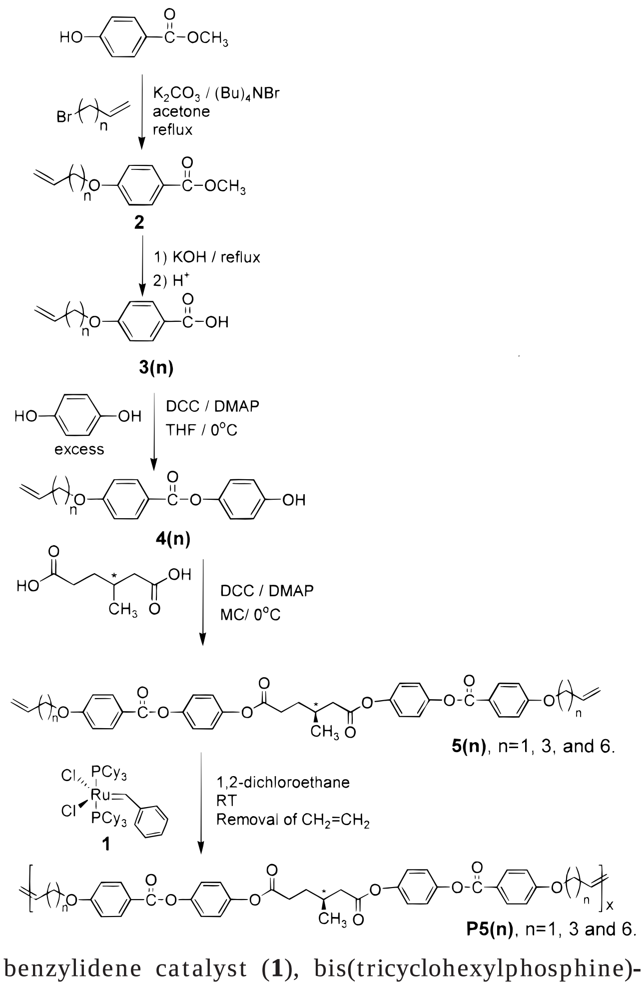
ABSTRACT: A series of liquid crystalline polyesters of different types were prepared by the acyclic diene metathesis polymerization method. These polymers are of main-chain, side-chain, and combined types. Polymerizations were conducted at 25−50 °C either in solution or in bulk using the so-called Grubbs' catalyst, bis(tricyclohexylphosphine)benzylideneruthenium dichloride. The monomers utilized in this investigation are all isolated dienes containing a built-in aromatic type mesogenic unit or an aromatic ester type mesogen bearing the cholesterol pendant through oxydodecyloxy spacer or monomesogenic terephthalate ester unit bearing the cholesterol pendant through a spacer. Bulk polymerization produced higher MW polymers than solution polymerization as expected from the known polymerization mechanism. Liquid crystallinity and phase transition properties of obtained polymers were studied by differential scanning calorimetry, optical microscopy, and X-ray diffraction.

Introduction

Studies on ring-opening metathesis polymerization (ROMP) of cycloalkenes[1−4] and cyclic polyenes[5−7] by metal carbene initiators have been not only clarifying the reaction mechanisms involved but also proving the importance of this relatively new polymerization method in synthetic polymer chemistry. Especially, discovery of many novel, highly efficient initiators by different research groups[8−13] has been enough to attract much scientific interest. In fact, presently there are several commercial products[14−17] available in the market produced by ROMP.

On the other hand, it was found by Wagener and co-workers[18] that the same initiators can be utilized in metathesis polymerization of open-chain isolated dienes such as 1,5-hexadiene and the like. In these cases, polymerization occurs in a step-growth manner with liberation of the gaseous side product of ethylene or other alkenes. Since many metathesis catalysts can be poisoned by the presence of polar functional groups, the ADMET method has been applied mainly to the polymerization of aliphatic and aromatic α,ω-dienes. Especially, Wagener and co-workers have been studying the ADMET polymerization of a wide variety of monomers including bis(alkenyl)silanes[19] and dienes containing ether[20] or ester groups.[21] Even dienes carrying hydroxyl groups could be polymerized by the ADMET method.[22] Recently, Grubbs et al.[23] reported the synthesis of main-chain liquid crystalline polymers (LCPs) from dienes containing aromatic ester type mesogenic structures by way of the ADMET reaction. There also are many reports[24−28] describing the synthesis of side-chain liquid crystalline polymers by ROMP of cycloalkenes bearing the mesogenic unit.

Scheme 1. Synthetic Route to Monomers 5(1), 5(3), and 5(6) and Polymers P5(1), P5(3), and P5(6)



We have prepared five isolated dienes as shown in Schemes 1−3, all of which contain one or two built-in mesogenic structural elements, and tried to polymerize them via ADMET polymerization. The catalyst utilized in this investigation was the Grubbs' ruthenium-based benzylidene catalyst (**1**), bis(tricyclohexylphosphine)benzylideneruthenium dichloride.[13] The polymers obtained were characterized for their structures and LC properties.

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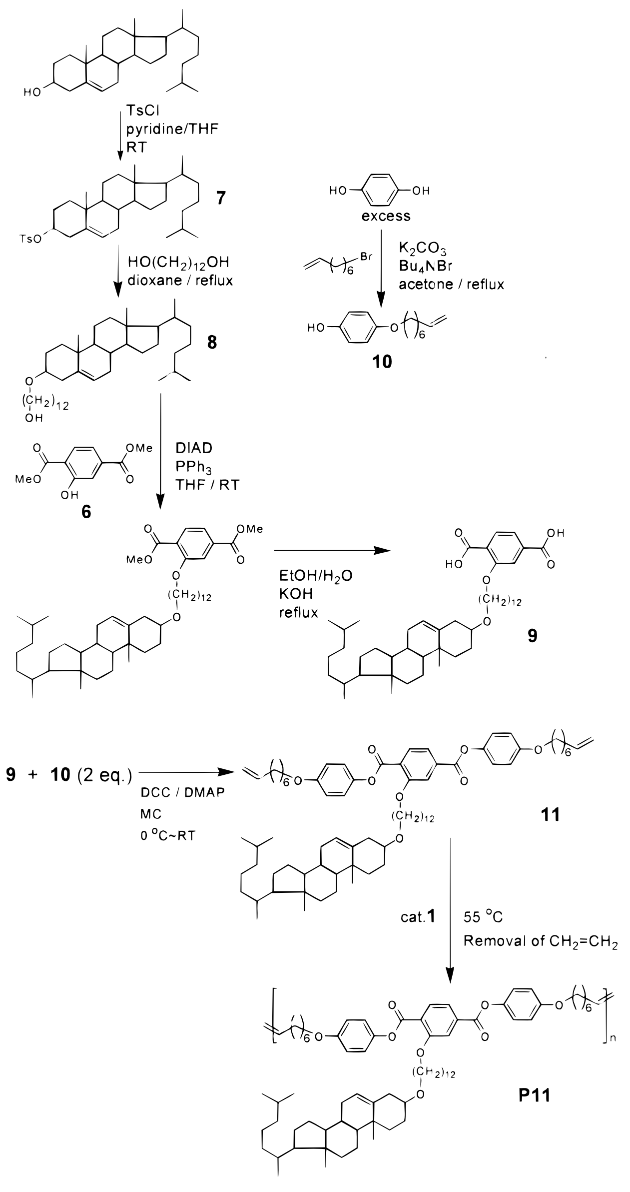
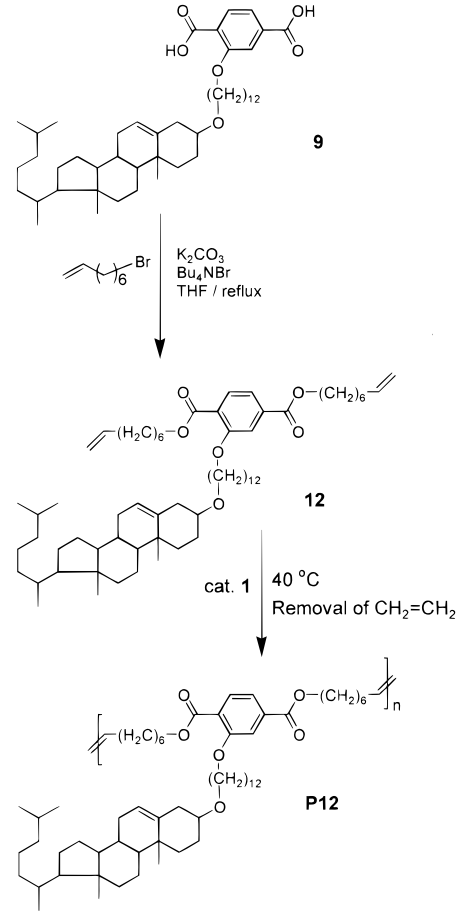
Scheme 2. Synthetic Route to Monomers 11 and P11



Scheme 3. Synthetic Route to Monomers 12 and P12



Experimental Section

A. Synthesis of Diene Monomers. Five monomers, **5(1)**, **5(3)**, **5(6)** **11**, and **12**, were prepared via multistep synthetic routes as shown in Schemes 1−3. Since compounds **5(1)**, **5(3)**, and **5(6)** were prepared in the same manner, a detailed synthetic procedure is given only for the preparation of **5(1)**.

4-Hydroxyphenyl 4-Allyloxybenzoate, 4(1). 4-Allyloxybenzoic acid[29] (**3(1)**; 8.0 g, 44.9 mmmol) prepared from methyl *p*-hydroxybenzoate and allyl bromide, hydroquinone (Aldrich; 49.5 g, 4.49×10^{-1} mol), and 4-(dimethylamino)pyridine (Aldrich, DMAP; 0.7 g, 5.4 mmol) were dissolved in 100 mL of dry tetrahydrofuran (THF),[30] and the solution was cooled to 0 °C. A solution of *N*,*N*′-dicyclohexylcarbodiimide (Aldrich, DCC; 10.2 g, 49.4 mmol) dissolved in 30 mL of dry THF[30] was added dropwise to the above solution over a period of 1 h. The mixture was stirred at 0 °C for an additional 3 h. And then the mixture was allowed to warm to room temperature and was stirred for 20 h at room temperature. The precipitate (*N*,*N*′-dicyclohexylurea) formed was removed by filtration. The solvent (THF) was removed from the filtrate by using a rotavap. Dichloromethane (200 mL) was mixed with the residue. The insoluble part (hydroquinone) was removed by filtration. After dichloromethane was removed by distillation from the filtrate, the residue was again dissolved in 50 mL of ethanol. A small amount of precipitate (hydroquinone bis(4-allyloxybenzoate)) was removed by filtration. The filtrate was poured into excess water precipitating crude product, which was recrystallized twice from a mixture of dichloromethane and hexane (1:4 by volume). The product yield was 10.1 g (83%), mp 163 °C. ^{1}H NMR ($\mathrm{CDCl_3}$, δ ppm): 4.71−4.73 (d, 2H, $-\mathrm{OC}H_2-\mathrm{CH{=}CH_2}$), 5.28−5.49 (m, 2H, $-\mathrm{CH{=}C}H_2$), 6.05−6.17 (m, 1H, $-\mathrm{C}H\mathrm{{=}CH_2}$), 7.04−7.13 (d, 4H, Ar$\mathrm{C}H$), 8.09−8.12 (d, 2H, Ar$\mathrm{C}H$). IR (KBr, cm^{-1}): 3427 (O−H stretching), 3029 (aromatic C−H stretching), 2929 (aliphatic C−H stretching), 1701 (C=O stretching), 1652, 1604, 1508 (aromatic C=C stretching), 1255, 1172 (C−O stretching). Anal. Calcd for $\mathrm{C_{16}H_{14}O_4}$: C, 71.10; H, 5.22%. Found: C, 71.06; H, 5.61%.

4-Hydroxyphenyl 4-(4-Pentenyloxy)benzoate, 4(3); mp 116 °C. ^{1}H NMR ($\mathrm{CDCl_3}$, δ ppm): 1.87−1.96 (m, 2H, $-\mathrm{OCH_2C}H_2-$), 2.23−2.28 (q, 2H, $-\mathrm{OCH_2CH_2C}H_2-$), 4.13−4.17 (t, 2H, $-\mathrm{OC}H_2\mathrm{CH_2}-$), 4.97−5.11 (m, 2H, $-\mathrm{CH{=}C}H_2$), 5.84−5.97 (m, 1H, $-\mathrm{C}H\mathrm{{=}CH_2}$), 6.87−6.90 (d, 2H, Ar$\mathrm{C}H$), 7.05−7.11 (m, 4H, Ar$\mathrm{C}H$), 8.09−8.12 (d, 2H, Ar$\mathrm{C}H$). IR (KBr, cm^{-1}): 3429 (O−H stretching), 3070 (aromatic C−H stretching), 2924 (aliphatic C−H stretching), 1719 (C=O stretching), 1640 (aliphatic C=C stretching), 1603, 1506 (aromatic C=C stretching), 1291, 1184 (C−O stretching). Anal. Calcd for $\mathrm{C_{18}H_{18}O_4}$: C, 72.47; H, 6.08%. Found: C, 72.45; H, 6.07%.

4-Hydroxyphenyl 4-(7-Octenyloxy)benzoate, 4(6); mp 76 °C. ^{1}H NMR ($\mathrm{CDCl_3}$, δ ppm): 1.40−1.52 (m, 8H, $-\mathrm{CH_2}(\mathrm{C}H_2)\mathrm{CH_2{-}O}-$) 1.77−1.86 (m, 2H, $-\mathrm{OCH_2C}H_2-$), 2.04−2.10 (q, 2H, $-\mathrm{C}H_2\mathrm{CH{=}CH_2}$), 4.02−4.06 (t, 2H, $-\mathrm{OC}H_2-\mathrm{CH_2}-$), 4.93−5.04 (m, 2H, $-\mathrm{CH{=}C}H_2$), 5.76−5.90 (m, 1H, $-\mathrm{C}H\mathrm{{=}CH_2}$), 6.83−6.86 (d, 2H, Ar$\mathrm{C}H$), 6.98−7.06 (m, 4H, Ar$\mathrm{C}H$), 8.11−8.14 (d, 2H, Ar$\mathrm{C}H$). IR (KBr, cm^{-1}): 3394 (O−H stretching), 3074 (aromatic C−H stretching), 2935 (aliphatic C−H stretching), 1715 (C=O stretching), 1640 (aliphatic C=C stretching), 1610,-1511 (aromatic C=C stretching), 1290, 1250, 1165 (C−O stretching). Anal. Calcd for $\mathrm{C_{21}H_{24}O_4}$: C, 74.09; H, 7.11%. Found: C, 74.07; H, 7.36%.

Bis[4-{4-(allyloxy)benzoyloxy}phenyl] *R*-(+)-3-Methyladipate, 5(1). 4-Hydroxyphenyl 4-allyloxybenzoate (**4(1)**; 8.1 g, 29.8 mmol), *R*-(+)-3-methyladipic acid (Aldrich; 2.4 g, 14.9 mmol), and DMAP (Aldrich; 0.35 g, 2.9 mmol) were dissolved in 100 mL of dry dichloromethane,[30] and the solution was cooled to 0 °C. To this solution was added dropwise over a period of 1 h a solution of DCC (Aldrich; 6.1 g, 49.4 mmol) dissolved in 30 mL of dry dichloromethane.[30] The solution was stirred for 3 h at 0 °C and 20 h at room temperature. The precipitate (*N*,*N*′-dicyclohexylurea) was removed by filtration. And then the solvent was removed by distillation from the filtrate. The residue was redissolved in 50 mL of ethanol. Insolubles were removed by filtration. After ethanol was removed by using a rotavap from the solution, the crude product obtained was purified by recrystallization thrice from acetone. The yield was 11.5 g (58%), mp 111 °C. ^{1}H NMR ($\mathrm{CDCl_3}$, δ ppm): 1.13−2.73 (m, 10H, $-\mathrm{C}H_2-$, $-\mathrm{C}H_3$, $-\mathrm{COOC}H_2-$, $-\mathrm{CH(CH_3)}-$), 4.72−4.74 (m, 4H, $-\mathrm{OC}H_2-\mathrm{CH{=}CH_2}$), 5.28−5.49 (m, 4H, $-\mathrm{CH{=}C}H_2$), 6.05−6.18 (m, 2H, $-\mathrm{C}H\mathrm{{=}CH_2}$), 7.12−7.15 (m, 4H, ArC*H*), 7.21−7.33 (m, 8H, ArC*H*), 8.11−8.14 (m, 4H, ArC*H*). IR (KBr, cm^{-1}): 3066 (aromatic C−H stretching), 2923 (aliphatic C−H stretching), 1724 (C=O stretching), 1608, 1504 (aromatic C=C stretching), 1652 (aliphatic C=C stretching), 1280, 1250, 1190 (C−O stretching). Anal. Calcd for $\mathrm{C_{39}H_{36}O_{10}}$: C, 70.47; H, 5.46%. Found: C, 70.48; H, 5.41%.

Bis[4-{4-(4-pentenyloxy)benzoyloxy}phenyl] *R*-(+)-3-Methyladipate, 5(3), mp 141 °C. ^{1}H NMR ($\mathrm{CDCl_3}$, δ ppm): δ 1.13−2.70 (m, 24H, $-\mathrm{C}H_2-$, $-\mathrm{C}H\mathrm{(CH_3)}-$, $-\mathrm{CH(C}H_3)-$), 4.04−4.08 (t, 4H, $-\mathrm{OC}H_2\mathrm{CH_2}-$), 4.95−5.12 (m, 4H, $-\mathrm{CH{=}C}H_2$), 5.80−5.93 (m, 2H, $-\mathrm{C}H\mathrm{{=}CH_2}$), 6.95−6.98 (d, 4H, ArC*H*), 7.16−7.26 (m, 8H, ArC*H*), 8.11−8.14 (d, 4H, ArC*H*). IR (KBr, cm^{-1}): 3080 (aromatic C−H stretching), 2926 (aliphatic C−H stretching), 1728 (C=O stretching), 1640 (aliphatic C=C stretching), 1604, 1506 (aromatic C=C stretching), 1280, 1255, 1172 (C−O stretching). Anal. Calcd for $\mathrm{C_{43}H_{44}O_{10}}$: C, 71.65; H, 6.15%. Found: C, 71.62; H, 6.17%.

Bis[4-{4-(7-octenyloxy)benzoyloxy}phenyl] *R*-(+)-3-Methyladipate, 5(6), mp 114 °C. ^{1}H NMR ($\mathrm{CDCl_3}$, δ ppm): 1.13−2.78 (m, 36H, $-\mathrm{C}H_3$, $-\mathrm{C}H\mathrm{(CH_3)}-$, $-\mathrm{C}H_2-$), 4.02−4.06 (t, 4H, $-\mathrm{OC}H_2-\mathrm{CH_2}-$), 4.93−5.04 (m, 4H, $-\mathrm{CH{=}C}H_2$), 5.76−5.90 (m, 2H, $-\mathrm{C}H\mathrm{{=}CH_2}$), 6.95−6.98 (d, 4H, ArC*H*), 7.13−7.26 (m, 8H, ArC*H*), 8.12−8.15 (d, 4H, ArC*H*). IR (KBr, cm^{-1}): 3075 (aromatic C−H stretching), 2930 (aliphatic C−H stretching), 1728 (C=O stretching), 1640 (aliphatic C=C stretching), 1604, 1506 (aromatic C=C stretching), 1255, 1172 (C−O stretching). Anal. Calcd for $\mathrm{C_{49}H_{56}O_{10}}$: C, 73.11; H, 7.01%. Found: C, 73.05; H, 7.08%.

12-Cholesteryloxydodecanol, 8. Cholesteryl tosylate (**7**; 20.8 g, 38.5 mmol) prepared from cholesterol (Aldrich) and tosyl chloride (Aldrich) was refluxed for 24 h with 1,12-dodecanediol (Aldrich; 39.0 g, 192.8 mmol) in 300 mL of dry dioxane.[30] The insolubles were removed by filtration. The residue obtained after removing the dioxane solvent from the filtrate using a rotavap was redissolved in dichloromethane. The insoluble precipitate, mostly 1,12-dodecanediol, was removed by filtration. The dichloromethane solvent was removed by distillation, and the solid product was purified by recrystallization from acetone. The yield was 13.6 g (62%), mp 81 °C. ^{1}H NMR ($\mathrm{CDCl_3}$, δ ppm): 0.67−2.40 (m, 63H, $-\mathrm{C}H_3$, $-\mathrm{C}H\mathrm{(CH_3)}-$, $-\mathrm{C}H-$, $-\mathrm{C}H_2-$), 3.12 (m, 1H, $-\mathrm{C}H\mathrm{O}-$), 3.42−3.46 (t, 2H, $-\mathrm{C}H_2-\mathrm{O}-\mathrm{CH}-$), 3.62−3.66 (t, 2H, $-\mathrm{C}H_2-\mathrm{OH}$), 5.33−5.35 (d, 1H, $-\mathrm{C(CH_2-){=}C}H-$). IR (KBr, cm^{-1}): 3451 (O−H stretching), 2840 (aliphatic C−H stretching), 1095 (C−O stretching). Anal. Calcd for $\mathrm{C_{39}H_{70}O_2}$: C, 82.04; H, 12.36%. Found: C, 82.05, H; 12.45%.

2-{12-(Cholesteryloxy)dodecyloxy}terephthalic Acid, 9. This compound was prepared in two steps: synthesis of dimethyl ester followed by hydrolysis to the dicarboxylic acid. 12-Cholesteryloxydodecanol (**8**; 4.3 g, 7.5 mmol), dimethyl 2-hydroxyterephthalate[31] (1.4 g, 6.85 mmol), and triphenylphosphine (Aldrich; 2.7 g, 10.3 mmol) were dissolved in 100 mL of dry THF,[30] and the solution was cooled to 0 °C. To this solution was added slowly over a period of 30 min diisopropyl azodicarboxylate[32,33] (Aldrich; 2.1 g, 10.3 mmol). The mixture was stirred for 3 h at 0 °C and then for 12 h at room temperature. After the solvent was removed by distillation from the reaction mixture, the crude product was recrystallized from acetone. The yield was 4.8 g (90%), mp 67 °C. Spectroscopic (^{1}H NMR and IR spectra) and elemental analysis data confirmed the structure and purity of the compound, dimethyl 2-{12-(cholesteryloxy)dodecyloxy}terephthalate. This diester (3.2 g, 4.11 mmol), potassium hydroxide (Aldrich; 3.2 g, 57.5 mmol), and 5 mL of distilled water were dissolved in 100 mL of ethanol. The mixture was refluxed for 24 h and was poured into 500 mL of distilled water. The solution was acidified to pH 1 by adding concentrated hydrochloric acid. The precipitate formed was collected on a filter and washed thoroughly with distilled water. The product (3.0 g, 98%, mp 197 °C) was proved to be pure enough to be used in the next step. ^{1}H NMR ($\mathrm{CDCl_3}$, δ ppm): 0.67−2.40 (m, 63H, $-\mathrm{C}H_3$, $-\mathrm{C}H\mathrm{(CH_3)}-$, $-\mathrm{C}H-$, $-\mathrm{C}H_2-$), 3.12 (m, 1H, $-\mathrm{C}H\mathrm{O}-$), 3.44−3.49 (t, 2H, $-\mathrm{C}H_2-\mathrm{O}-\mathrm{CH}-$), 4.31−4.35 (t, 2H, $-\mathrm{C}H_2-\mathrm{O}-\mathrm{Ar}$), −5.33−5.35 (d, 1H, $-\mathrm{C(CH_2-){=}C}H-$), 7.76−8.28 (m, 3H, ArC*H*). IR (KBr, cm^{-1}): 3300−2500 (O−H stretching), 2929 (aliphatic C−H stretching), 1699 (C=O stretching), 1610, 1496 (aromatic C=C stretching), 1245, 1107 (C−O stretching). Anal. Calcd for $\mathrm{C_{47}H_{74}O_6}$: C, 76.79; H, 10.15%. Found: C, 76.75; H, 10.16%.

Bis{4-(7-octenyloxy)phenyl} 2-{12-(Cholesteryloxy)dodecyloxy}terephthalate, 11. Compound **9** (4.5 g, 6.0 mmol), 4-(7-octenyloxy)phenol (**10**; 26 g, 12.0 mmol) separately prepared by reacting hydroquinone and 8-bromo-1-octene (Aldrich) in acetone in the presence of potassium carbonate, and DMAP (Aldrich; 0.18 g, 1.5 mmol) were dissolved in 50 mL of dry dichloromethane.[30] To this solution was added at 0 °C slowly over a period of 1 h a solution of DCC (Aldrich; 3.1 g, 15.0 mmol) dissolved in 10 mL of dry dichloromethane.[30] The reaction mixture was stirred for 3 h at 0 °C and for 20 h at room temperature. *N*,*N*′-Dicyclohexylurea formed was removed by filtration, and the solvent was distilled out of the filtrate. The residue was redissolved in 100 mL of acetone, and the solution was cooled to −5 °C. The precipitate formed was removed by filtrate, and the volume of the filtrate was reduced to 5 mL using a rotavap. Hexane (100 mL) was mixed with the acetone solution, and then the whole mixture was cooled to and kept for 24 h at −5 °C. The precipitate formed was collected on a filter and washed thoroughly with chilled hexane. The final product was dried at 40 °C in a vacuum oven (0.1 Torr). The yield was 3.8 g (56%), mp 64.4 °C. ^{1}H NMR ($\mathrm{CDCl_3}$, δ ppm): δ 0.67−2.40 (m, 83H, $-\mathrm{C}H_3$, $-\mathrm{C}H\mathrm{(CH_3)}-$, $-\mathrm{C}H-$, $-\mathrm{C}H_2-$), 3.12 (m, 1H, $-\mathrm{C}H\mathrm{O}-$), 3.41−3.46 (t, 2H, $-\mathrm{C}H_2-\mathrm{O}-\mathrm{CH}-$), 3.94−3.99 (m, 4H, $\mathrm{Ar}-\mathrm{O}-\mathrm{C}H_2-$), 4.13−4.18 (t, 2H, $-\mathrm{C}H_2-\mathrm{O}-\mathrm{Ar}$), 4.93−5.04 (m, 4H, $-\mathrm{CH{=}C}H_2$), 5.33−5.35 (d, 1H, $-\mathrm{C(CH_2-){=}C}H-$), 5.76−5.89 (m, 2H, $-\mathrm{C}H\mathrm{{=}CH_2}$), 6.91−8.03 (m, 11H, ArC*H*). IR (KBr, cm^{-1}): 3077 (aromatic C−H stretching), 2929 (aliphatic C−H stretching), 1728 (C=O stretching), 1639 (aliphatic C=C stretching), 1625, 1511 (aromatic C=C stretching), 1280, 1191, 1105 (C−O stretching). Anal. Calcd for $\mathrm{C_{75}H_{110}O_8}$: C, 79.04; H, 9.73%. Found: C, 79.03; H, 9.70%.

Bis(*ω*-octenyl) 2-{12-(Cholesteryloxy)dodecyloxy}terephthalate, 12. 2-{12-(Cholesteryloxy)dodecanoyloxy}terephthalic acid (**9**; 1.0 g, 1.3 mmol), 8-bromo-1-octene (Aldrich; 0.55 g, 2.9 mmol), potassium carbonate (0.91 g, 6.7 mmol), and tetra-*n*-butylammonium bromide (Aldrich; 0.05 g, 0.15 mmol) were dissolved in 50 mL of THF. The mixture was refluxed for 48 h. The insoluble products were removed by filtration, and the filtrate was kept at −5 °C for 6 h. The precipitate formed was again removed by filtration. Acetone was distilled out of the filtrate using a rotavap. The residual liquid was chromatographed through a silica gel column using a mixture of ethyl acetate and hexane (1:1 by volume) as a eluent. Chromatographic purification was repeated twice more. Removal of the eluent produced the oily product (0.68 g, 53%). ^{1}H NMR ($\mathrm{CDCl_3}$, δ ppm): 0.67−2.40 (m, 83H, $-\mathrm{C}H_3$, $-\mathrm{C}H\mathrm{(CH_3)}-$, $-\mathrm{C}H-$, $-\mathrm{C}H_2-$), 3.12 (m, 1H, $-\mathrm{C}H\mathrm{O}-$), 3.42−3.47 (t, 2H, $-\mathrm{C}H_2-\mathrm{O}-\mathrm{Ar}-$), 4.06−4.10 (m, 4H, $\mathrm{Ar}-\mathrm{O}-\mathrm{C}H_2-$), 4.28−4.35 (m, 4H, $-\mathrm{C}H_2-\mathrm{O}-\mathrm{Ar}$), 4.92−5.02 (m, 4H, $-\mathrm{CH{=}C}H_2$), 5.33−5.35 (d, 1H, $-\mathrm{C(CH_2-){=}C}H-$), 5.74−5.88 (m, 2H, $-\mathrm{C}H\mathrm{{=}CH_2}$), 7.59−7.78 (m, 3H, ArC*H*). IR (KBr, cm^{-1}): 3077 (aromatic C−H stretching), 2927 (aliphatic C−H stretching), 1722 (C═O stretching), 1639 (aliphatic C═C stretching), 1614, 1500 (aromatic C═C stretching), 1285, 1101 (C−O stretching). Anal. Calcd for $C_{63}H_{102}O_6$: C, 79.19; H, 10.76%. Found: C, 79.17; H, 10.79%.

B. Preparation of Polymers. General Procedure. All of the polymerizations were performed using a Schlenk line. Other operations were performed in a glovebox. Argon gas was purified by Drierite (Aldrich) and R3-11 (BASF). All the monomers, with the exception of the oily monomer **12**, were purified by recrystallization from acetone. When necessary, repeated recrystallization was conducted until a pure product could be obtained. Their purity was checked mainly by thin-layer chromatography (TLC) and ^{1}H NMR spectroscopy. Reaction conversion was estimated by comparing the ^{1}H NMR peak intensity of the newly formed internal ethylenic unit, −CH═CH−, to that of unreacted, remaining terminal vinylene unit, $-CH{=}CH_2$. Resonance positions of these protons are given in ^{1}H NMR data provided for each monomers and polymers.

Preparation of P5(1), P5(3), and P5(6). Monomer (**5(1)**, **5(3)**, **5(6)** each; 1.21 mmol) was placed in a Schlenk tube, into which 5 mL of purified 1,2-dichloroethane[30] was injected under a dry argon atmosphere using a syringe. The solution was warmed to and maintained at 40 °C. Bis(tricyclohexylphosphine)benzylideneruthenium(IV) dichloride (**1**; 10 mg, 1.21×10^{-2} mmol), the so-called Grubbs' catalyst, prepared by a known method[13] and dissolved in 3 mL of purified 1,2-dichloroethane,[30] was injected into the monomer solution in three portions every 2 h. After the final injection of the catalyst, the reaction mixture was stirred at 40 °C for an additional 3 h, and the pressure in the reaction tube was slowly reduced to 1×10^{-3} Torr. Under this pressure the mixture was stirred for 12 h at 40 °C. Ethyl vinyl ether (Aldrich, 0.1 mL) was injected into the reaction mixture to stop the polymerization.[34−36] The gelly mixture was dissolved in 10 mL of 1,1,2,2-tetrachloroethane, to which 50 mL of acetone was mixed with stirring. The precipitate was collected and was subjected to Soxhlet extraction for 24 h using acetone. Reaction conversion estimated by comparing the area of ^{1}H NMR peak at δ 6.04 ppm for the protons in the internal −CH═CH− unit and that at δ 5.28−5.49 ppm for the protons in the terminal $-CH{=}CH_2$ groups was 90%. The recovered yield after acetone extraction was 530 mg (66%). ^{1}H NMR (tetrachloroethane-d_2, δ ppm): 1.02−2.59 (m, 10H, $-CH_2-$, $-CH_3$, $-COOCH_2-$, $-CH(CH_3)-$), 4.72−4.74 (m, 4H, $-OCH_2-CH{=}CH-$), 5.28−5.49 (m, $-CH{=}CH_2$), 6.04 (m, 2H, $-CH{=}CH-$) 6.05−6.18 (m, $-CH{=}CH_2$), 7.12−7.15 (m, 4H, ArC*H*), 7.21−7.33 (m, 8H, ArC*H*), 8.11−8.14 (m, 4H, ArC*H*). IR (KBr, cm^{-1}): 3077 (aromatic C−H stretching), 2927 (aliphatic C−H stretching), 1727 (C═O stretching), 1649 (vinylene C═C stretching), 1603, 1511 (aromatic C═C stretching), 1280, 1250, 1190 (C−O stretching). Anal. Calcd for $(C_{37}H_{32}O_{10})_n$: C, 69.80; H, 5.07%. Found: C, 70.77; H, 5.03%.

The reaction conversion of **5(3)** after polymerization in the exact same manner was 95%. Recovered yield after acetone extraction was 640 mg (73%). ^{1}H NMR (CDCl$_3$, δ ppm): δ 1.13−2.70 (m, 24H, $-CH_2-$, $-CH(CH_3)-$, $-CH(CH_3)-$), 4.04−4.08 (t, 4H, $-OCH_2CH_2-$), 4.95−5.12 (m, $-CH{=}CH_2$), 5.52 (m, 2H, $-CH{=}CH-$), 5.80−5.93 (m, $-CH{=}CH_2$), 6.95−6.98 (d, 4H, ArC*H*), 7.16−7.26 (m, 8H, ArC*H*), 8.11−8.14 (d, 4H, ArC*H*). IR (KBr, cm^{-1}): 3074 (aromatic C−H stretching), 2926 (aliphatic C−H stretching), 1728 (C═O stretching), 1640 (vinylene C═C stretching), 1604 1506 (aromatic C═C stretching), 1280, 1255, 1172 (C−O stretching). Anal. Calcd for $(C_{41}H_{40}O_{10})_n$: C, 71.09; H, 5.82%. Found: C, 71.91; H, 5.80%.

The reaction conversion of **5(6)** was found to be higher than 99% after polymerization. Recovered yield after acetone extraction was 730 mg (83%). ^{1}H NMR (CDCl$_3$, δ ppm): 1.13−2.78 (m, 36H, $-CH_3$, $-CH(CH_3)-$, $-CH_2-$), 4.02−4.06 (t, 4H, $-OCH_2-CH_2-$), 4.93−5.04 (m, $-CH{=}CH_2$), 5.51 (m, 2H, $-CH{=}CH-$), 5.76−5.90 (m, $-CH{=}CH_2$), 6.95−6.98 (d, 4H, ArC*H*), 7.13−7.26 (m, 8H, ArC*H*), 8.12−8.15 (d, 4H, ArC*H*). IR (KBr, cm^{-1}): 3075 (aromatic C−H stretching), 2930 (aliphatic C−H stretching), 1728 (C═O stretching), 1640 (vinylene C═C stretching), 1604,1506 (aromatic C═C stretching), 1255, 1172 (C−O stretching). Anal. Calcd for $(C_{47}H_{52}O_{10})_n$: C, 72.66; H, 6.75%. Found: C, 73.11; H, 6.68%.

Preparation of P11. Monomer **11** (500 mg, 0.44 mmol) was placed in a Schlenk tube under a dry argon atmosphere and heated to 70 °C. It was cooled to 55 °C. While the monomer (mp 65 °C) is still in a liquid state at 55 °C because of supercooling, bis(tricyclohexylphosphine)benzylideneruthenium(IV) dichloride (**1**; 3.6 mg, 4.4×10^{-3} mmol) dissolved in 1 mL of dry dichloromethane[30] was injected into the reaction tube. The pressure inside the polymerization tube was slowly reduced to and maintained at 1×10^{-3} Torr for 24 h. Ethyl vinyl ether (Aldrich, 0.1 mL) was injected into the tube to terminate the reaction.[34−36] The solidified product was dissolved in 10 mL of dichloromethane, to which 50 mL of acetone was added precipitating the product. The fibrous polymer was subjected to Soxhlet extraction for 24 h using acetone. The reaction conversion estimated from the NMR spectroscopy was 100% within the detection limit of NMR analysis. Recovered yield was 453 mg (91%). ^{1}H NMR (CDCl$_3$, δ ppm): 0.67−2.40 (m, 83H, $-CH_3$, $-CH(CH_3)-$, $-CH-$, $-CH_2-$), 3.12 (m, 1H, $-CHO-$), 3.41−3.46 (t, 2H, $-CH_2-O-CH-$), 3.94−3.99 (m, 4H, $Ar-O-CH_2-$), 4.13−4.18 (t, 2H, $-CH_2-O-Ar$), 5.38−5.43 (m, 2H, $-CH{=}CH-$), 5.33−5.35 (d, 1H, $-C(CH_2-){=}CH-$), 6.91−8.03 (m, 11H, ArC*H*).

IR (KBr, cm^{-1}): 3046 (aromatic C−H stretching), 2933 (aliphatic C−H stretching), 1728 (C═O stretching), 1639 (vinylene C═C stretching), 1614, 1505 (aromatic C═C stretching), 1280, 1191, 1105 (C−O stretching). Anal. Calcd for $(C_{73}H_{106}O_8)_n$: C, 78.87; H, 9.61%. Found: C, 78.17; H, 10.79%.

Preparation of P12. Monomer **12** (500 mg, 0.52 mmol) was placed in a Schlenk tube under an dry argon atmosphere and was heated to 40 °C. The polymerization catalyst (**1**; 4.2 mg, 5.2×10^{-3} mmol) dissolved in 1 mL of dry dichloromethane[30] was introduced into the polymerization tube using a syringe. The pressure inside the tube was slowly reduced to and maintained at 1×10^{-3} Torr. After polymerizing the mixture at 40 °C for 24 h under the reduced pressure, the mixture was mixed with ethyl vinyl ether (0.1 mL). Crude polymer was obtained by evaporating the solvent. Reaction conversion was found to be quantitative by NMR analysis, and the recovered yield was 490 mg (98%) after purification by Soxhlet extraction with acetone. ^{1}H NMR (CDCl$_3$, δ ppm): 0.67−2.40 (m, 83H, $-CH_3$, $-CH(CH_3)-$, $-CH-$, $-CH_2-$), 3.12 (m, 1H, $-CHO-$), 3.42−3.47 (t, 2H, $-CH_2-O-Ar-$), 4.06−4.10 (m, 4H, $Ar-O-CH_2-$), 4.28−4.35 (m, 4H, $-CH_2-O-Ar$), 5.42 (m, 2H, $-CH{=}CH-$), 5.33−5.35 (d, 1H, $-C(CH_2-){=}CH-$), 7.59−7.78 (m, 3H, ArC*H*). IR (KBr, cm^{-1}): 2933 (aliphatic C−H stretching), 1722 (C═O stretching), 1649 (vinylene C═C stretching), 1608, 1500 (aromatic C═C stretching), 1285, 1101 (C−O stretching). Anal. Calcd for $(C_{61}H_{98}O_6)_n$: C, 79.00; H, 10.65%. Found: C, 79.49; H, 9.98%.

C. Instrumentation and Characterization. ^{1}H NMR spectra of intermediates, monomers, and polymers were obtained on a Varian AM 300 spectrometer. ^{13}C NMR spectra of polymers were recorded on the same instrument in the CDCl$_3$ and 1,1,2,2-tetrachloroethane-d_2 solvents. Their IR spectra were recorded on a Bomem MB FT-IR instrument. Elemental analyses were performed by the Center for Organic Reactions, Sogang University, Seoul, Korea, using an Eager 200 elemental analyzer. Thermal properties were studied under a nitrogen atmosphere on a Mettler DSC 821^e instrument. The heating and cooling rates were maintained at 10 °C/min. Indium was utilized for temperature calibration and enthalpy changes involved in the phase transitions. Optical textures and thermal transitions were examined on a polarizing microscope (Olympus BH-2) equipped with the Mettler FP-82HT hot stage and Mettler FP-90 controller. X-ray diffractograms were obtained using Rigaku tabletop rotating anode X-ray generator (RINT 2000 series) equipped with a Pt, Ni double mirror focusing system. The nickel-filtered Cu Kα line (λ = 0.1542 nm) was utilized as a radiation source. SAXS was performed in a vacuum chamber (sample-to-detector distance is 500 mm), and WAXS was recorded with four-circle goniometer (sample-to-detector distance is 200 mm). Relative molecular weights and molecular weight distributions were

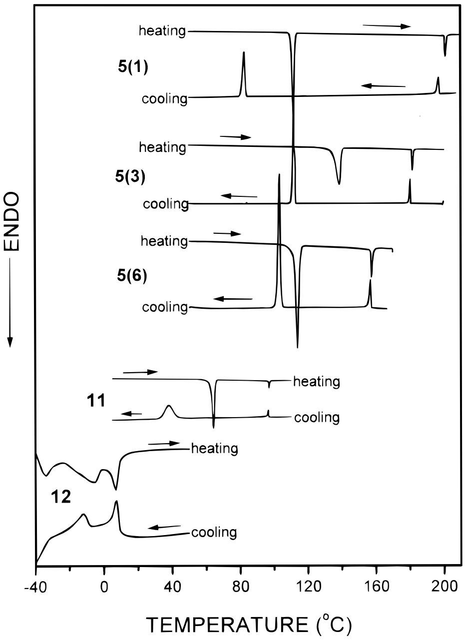


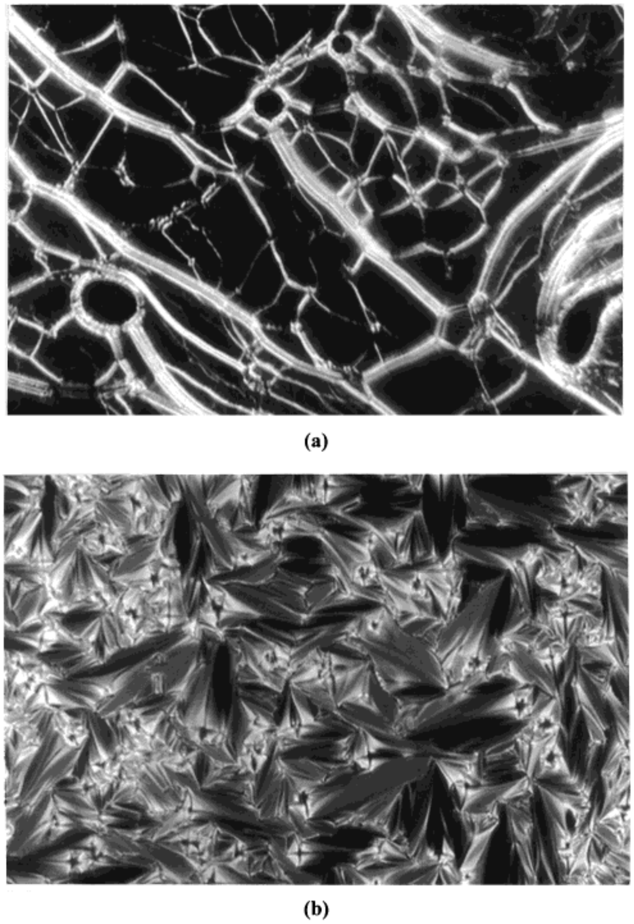
Figure 1. DSC thermograms of monomers **5(1), 5(3)**, **5(6)**, **11**, and **12**.

determined by gel permeation chromatography (GPC) with a Waters R401 instrument equipped with Stragel HR3, 4, and 4E columns, M7725i manual injector, column heating chamber, and 2010 millennium data station. Measurements were made by using an UV detector, with $CHCl_3$ as solvent (1.0 mL min^{-1}).

Results and Discussion

Synthesis and LC Properties of Monomers. Monomers were prepared via the synthetic routes shown in Schemes 1−3. Bis[4-{4-ω-(alkenyloxy)benzoyloxyphenyl}] *R*-(+)-3-methyladipates (**5(n)**'s, Scheme 1) could be synthesized by condensing 4-hydroxyphenyl 4-ω-alkenyloxybenzoates (**4(n)**'s) with *R*-(+)-3-methyladipic acid in methylene chloride using the pair of *N*,*N'*-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)-pyridine (DMAP) as condensing agents.[37,38] Bis{4-(7-octenyl)phenyl} 2-{12-(cholesteryloxy)dodecyloxy}terephthalate (**11**, Scheme 2) could be readily obtained by condensing 2-{12-(cholesteryloxy)dodecyloxy}terephthalic acid (**9**) with 4-(7-octenyloxy)phenol (**10**) using the DCC/DMAP condensing agent pair. Bis(7-octenyl) 2-{12-(cholesteryloxy)dodecyloxy}terephthalate (**12**, Scheme 3) was prepared by esterification of the dicarboxylic acid **9** by refluxing it in tetrahydrofuran with 8-bromo-1-octene in the presence of potassium carbonate and tetrabutylammonium bromide. The last compound was utilized as a phase transfer catalyst.[39,40] Compound **12** was obtained in the form of a viscous liquid.

Figure 1 compares the thermograms of monomers **5(1)**, **5(3)**, and **5(6)** obtained by differential scanning calorimetry (DSC) at the heating and cooling rates of 10 °C/min. All of the three compounds show two transition peaks. The lower temperature ones correspond to melting transition, and they appear respectively at 111.4, 140.6, and 113.8 °C. The higher temperature peaks at 200.9, 181.9, and 157.5 °C respectively for **5(1)**, **5(3)**, and **5(6)** correspond to mesophase-to-isotropic phase transitions, i.e., isotropization. It is noted that as the length of tails increases, the isotropization temperature decreases. This phenomenon is very often observed in the LC homologous series with varying alkyl tail length.[41−44] This implies that a longer tail destabilizes the mesophase in melt due to enhanced conformational freedom of longer alkyl groups. Their optical textures observed for melts through a polarizing microscope indicate that these compounds form the cholesteric mesophase. Figure 2 shows either oily streaks or fan textures characteristic of cholesteric phases.


(a)

(b)

Figure 2. Optical photomicrographs of (a) oily streak texture (first heating, 144 °C) and (b) cholesteric fan texture (first cooling, 144 °C) of monomer **5(3)** (magnification 200×).

Monomer **11** has a unique structure in which two mesogenic units are included: an aromatic ester type mesogenic unit and the cholesteryl unit in the side branch. This monomer also undergoes two thermal transitions (Figure 1) before reaching the isotropic state: melting transition at 64.4 °C and isotropization at 97.1 °C. The LC phase formed by this compound is identified to be cholesteric by its observed fanlike and oily streaks optical textures. Different from monomers, **5(1)**, **5(3)**, **5(6)** and **11**, discussed above, the last monomer **12** contains the cholesteryl moiety in a branched molecular architecture. This compound exhibits rather broad melting and isotropization tranitions respectively at −5.4 and 6.8 °C as shown in Figure 1. This compound forms the cholesteric phase in melt. The LC temperature range of this compound is much narrower than other monomers dealt with in this investigation. This can be ascribed to the bulkiness of the nonmesogenic structure attached to the cholesterol moiety. The reversible transition occurring around −30 °C is conjectured to correspond to glass transition of the viscous liquid. In general, all the monomers revealed much broader LC temperature range in cooling cycle than in heating cycle. This is mainly due to significantly higher extent of supercooling for crystallization, i.e., LC-to-crystal phase transition, than supercooling for isotropic-to-LC phase

Table 1. Thermodynamic Data for the Phase Transitions of Monomers[a]

monomers	T_m (°C)	T_i (°C)	$\Delta H_m{}^c$	$\Delta H_i{}^c$	$\Delta S_m{}^c$	$\Delta S_i{}^c$
5(1)	111.4	200.9	93.5	15.2	35.9	7.2
5(3)	140.6	181.9	96.6	10.8	40.0	5.1
5(6)	113.8	157.5	65.8	7.9	25.5	3.4
11	64.4	97.1	35.6	1.6	12.0	0.6
12	−5.4	6.8	*b*	*b*	*b*	*b*

[a] All the data were obtained from first heating DSC curves under N_2 atmosphere. Heating rate was 10 °C/min. [b] Peaks were too broad to estimate the values correctly. In addition, baseline shift was exceptionaly high. [c] ΔH values are in kJ/mol and ΔS in J/(mol K).

transition. Such phenomena are very commonly observed for other LC compounds[43,45−48] and can be rationalized by the fact that a more drastic change in molecular ordering is required for LC-to-crystal transition than for isotropic liquid-to-LC transition. This is very well reflected by much smaller enthalpy changes (ΔH_i) for the latter transition than the former (ΔH_m) (see Table 1).

According to the data shown in Table 1, the ΔH_i value of monomers **5(n)**'s decreases steadily with the length of the terminal alkenyl tails. The same trend is observed for the entropy changes (ΔS_i) involved in isotropization. This observation can be explained by the assumption that the longer the tail of a compound, the less ordered or less stable its mesophase becomes. In fact, similar phenomena have been observed for many other monomesogenic homologues.[49,50] This phenomenon can be ascribed to reduced intermolecular attractions and increased conformational freedom with increasing length of terminal tails.

Another observation to be noted is that the ΔH_m (35.6 kJ/mol) and ΔH_i (1.6 kJ/mol) values of compound **11** (Table 1) are much less than the corresponding values (65.8 and 7.9 kJ/mol) of compound **5(6)**, which can be ascribed to the side-branched shape of the former in contrast to the latter's linear structure. The melting transition and clearing point of compound **12** are particularly low when compared with those of other compounds. This compound is not only monomesogenic, i.e., contains only one mesogenic unit, but also is of side-branched shape. These two structural features appear to be major reasons for the low transition temperatures.

Synthesis and General Properties of Polymers. Polymers prepared in this investigation are of three different types of LCPs. Polymers **P5(1)**, **P5(3)**, and **P5(6)** prepared from the respective monomers of **5(1)**, **5(3)**, and **5(6)** belong to main-chain LCPs, whereas **P11** and **P12** synthesized from monomers **11** and **12**, respectively, are combined type and side-chain LCPs. Tables 2 and 3 tabulate molecular weights and thermal properties of the polymers prepared in this investigation. Conversion or extent of polymerization was determined by ^{1}H NMR analysis of polymerization mixtures in $CDCl_3$ or 1,1,2,2-tetrachloroethane-d_2. The terminal methylene and vinyl protons in monomers show ^{1}H resonance peaks in multiplets at $\delta = 4.92{-}5.12$ and 5.74−5.93, respectively, whereas the vinylene protons newly formed in the backbones of polymers show resonance peaks at $\delta = 5.38{-}5.52$.

Therefore, comparison of integration of resonance peaks of unreacted terminal vinyl protons with that of newly formed vinylene protons in polymer backbone provides us with monomer conversion to polymers. Within the NMR detection limit, all of the polymerizations proceeded to high conversions (95−100%) with the exception (90%) of **P5(1)**, which precipitated out of the reaction mixture as it formed. All the monomers **5(n)**'s, due to their high melting points, were polymerized in solution, whereas monomers **11** and **12** could be polymerized in bulk because they are in the liquid form at the polymerization temperature (55 and 40 °C, respectively). Monomer **11**, whose melting point (64.4 °C) is higher than polymerization temperature (55 °C), was heated to 70 °C, and the melt was cooled to 55 °C in a supercooled state. It was then polymerized in the supercooled state.

ADMET is known to proceed in a step-reaction mechanism[18] and, therefore, produces high molecular weight polymers only at high conversion. The molecular weights of polymers and conversion data given in Table 2 are well in line with what are expected in such step-reaction polymerizations. **P11** that was formed by bulk polymerization with quantitative conversion in the NMR detection limit revealed the highest apparent molecular weight ($\overline{M}_n = 53\,200$ and $\overline{M}_w = 151\,800$) among the present polymers, whereas **P5(1)** formed with lowest conversion (90%) was of the lowest MW ($\overline{M}_n = 3500$ and $\overline{M}_w = 4600$). As already pointed out above, **P5(1)** precipitated out of the dichloroethane polymerization solvent as it was formed, which must be the main reason for its low molecular weight. In addition, there is an earlier report[51] saying that the double bond in the allyloxy ($CH_2{=}CHCH_2O{-}$) structure as is in monomer **5(1)** shows a diminished reactivity in ADMET polymerization. **P12** was formed by bulk polymerization, and its molecular weight is relatively high, $\overline{M}_n = 26\,900$ and $\overline{M}_w = 54\,300$. Polydispersity index (PDI) values for the present polymers range from 1.3 to 2.0, which is considered to be rather narrow when compared with those for the polyesters prepared by conventional step-reaction polymerization. The only exception was **P11** whose PDI value was the highest, 2.8. Purification of polymers by Soxhlet extraction using acetone must have removed low molar mass fractions, resulting in narrow MW distribution. Significant differences between conversions and recovered yields support this supposition. The situation for **P11**, however, is a little different. Since its molecular weight is high, the extraction process removes very little low molar

Table 2. Molecular Weights of Polymers

polymers	yield (%) conversion	yield (%) recovered	$\eta_{inh}{}^a$ (dL/g)	mol wt (GPC[b]) $\overline{M}_n{}^b$	mol wt (GPC[b]) $\overline{M}_w{}^b$	PDI	$\overline{DP}^b$
P5(1)	90	66	0.37	3 500	4 600	1.3	5
P5(3)	95	73	0.82	18 000	31 300	1.7	25
P5(6)	99	83	0.62	16 100	30 800	1.9	20
P11	100	91	1.73	53 200	151 800	2.9	134
P12	100	98	0.45	26 900	54 300	2.0	57

[a] Solution viscosities were measured at 30 ± 1 °C on a 0.20 g/dL solution in a mixed solvent of 1,1,2,2-tetrachloroethane and phenol (1:1 by volume). [b] Molecular weights were measured by GPC on chloroform solution. Polystyrene was used for calibration. Therefore, these values should be taken only as approximations.

Table 3. Transition Temperatures and Trans Contents of Polymers[a]

polymers	T_g (°C)	T_m (°C)	T_i (°C)	trans[c] (%)
P5(1)	62	243−260[b]	275−292[b]	
P5(3)	43	150	225	80
P5(6)	14	175	217	83
P11	36	68	132	82
P12	−30	19.5	54	

[a] All the thermal data, with the exception of the T_g values, were obtained from first DSC heating curves obtained under N_2 atmosphere. Heating rate was 10 °C/min. The T_g values were estimated from the first cooling DSC curves. The temperatures where the initial slope changes occur on the thermograms were taken as T_g. [b] The T_m and T_i values of **P5(1)** were obtained from microscopic observation under crossed polars (magnification ×200). The T_m values in this case corresponds more to the flowing temperature rather than to the crystalline melting temperature. [c] Calculated from the heights of cis and trans vinylene peaks on ^{13}C NMR spectra.

mass fraction. Thus, its PDI value is the highest among the polymers being reported in this paper. It, however, should be emphasized that the values reported for the molecular weight and, thus, degree of polymerization of the present polymers must be only approximated values since they were determined by GPC. In fact, the ratio of the vinyl end groups to the vinylene groups in the main chain can be determined by NMR analysis to obtain molecular weight of polymers assuming that there are two vinyl groups per chain. The $\overline{M}_n$ value of **P5(1)** determined by this NMR analysis method was 4300, which corresponds to the degree of polymerization of 7. These values are higher than those determined by the GPC method.

Although they are not given here, wide-angle X-ray diffractograms (WAXD) of the present polymers suggest that all of them are semicrystalline. The WAXD of **P5(1)** indicated that the polymer is either amorphous or semicrystalline with extremely low degree of crystallinity. **P5(1)** does not crystallize readily probably due to its low molecular weight which corresponds to a degree of polymerization of only 5. All of the polymers, with the only exception of **P5(1)**, exhibited clear melting endotherms in the heating DSC thermograms (Figure 3), indicating again that they are semicrystalline. Their melting transition could be confirmed by observing them on a hot stage attatched to a polarizing microscope. Melting temperatures of polymers **P5(3)** and **P5(6)**, 150 and 175 °C, respectively, are much higher than those of **P11** (68 °C) and **P12** (19.5 °C). The presence of nonpolar bulky substituents is accountable for the latters' low mp's. The most flexible nature of the backbone of **P12** causes additional lowering in mp. Since the mp of **P12** is only 19.5 °C, it is already in a fluid state at room temperature. These polymers revealed relatively low glass transition temperatures (T_g's, Table 3) ranging from −30 to 62 °C. This is ascribed to the presence of long alkenic spacer structures along the backbones. As expected, as the length of the spacer part increases in **P5** polymers, the T_g value steadily drops down from 62 °C (for **P(1)**) to 14 °C (for **P5(6)**). **P12** which is composed of the most flexible main-chain and bulky pendants reveals the lowest T_g values of −30 °C. In fact, this polymer reveals a physical behavior very much alike the one expected from very lightly cross-linked natural rubbers.

Since new double bonds are formed along the polymer backbone during polymerization of the α,ω-diene monomers, it is interesting to analyze the contents of trans and cis configuration. As shown in Figure 4b, the trans vinylene carbons (^{13}C) in the polymers resonate at 129.9 ppm in the ^{13}C NMR spectrum, whereas the cis vinylene carbons resonate at 129.5 ppm. Table 2 shows the content of trans configuration of double bonds in the polymers prepared. The trans content ranges from 80 to 83%, with only a little variation among the polymers investigated. It has been reported by others[18,52−54] that the trans contents in other polymers prepared by ADMET reaction are about 60−90%.

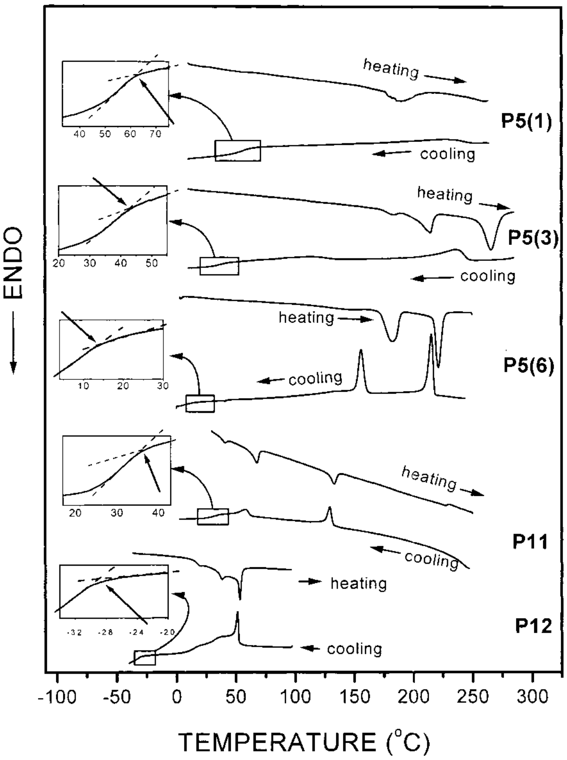
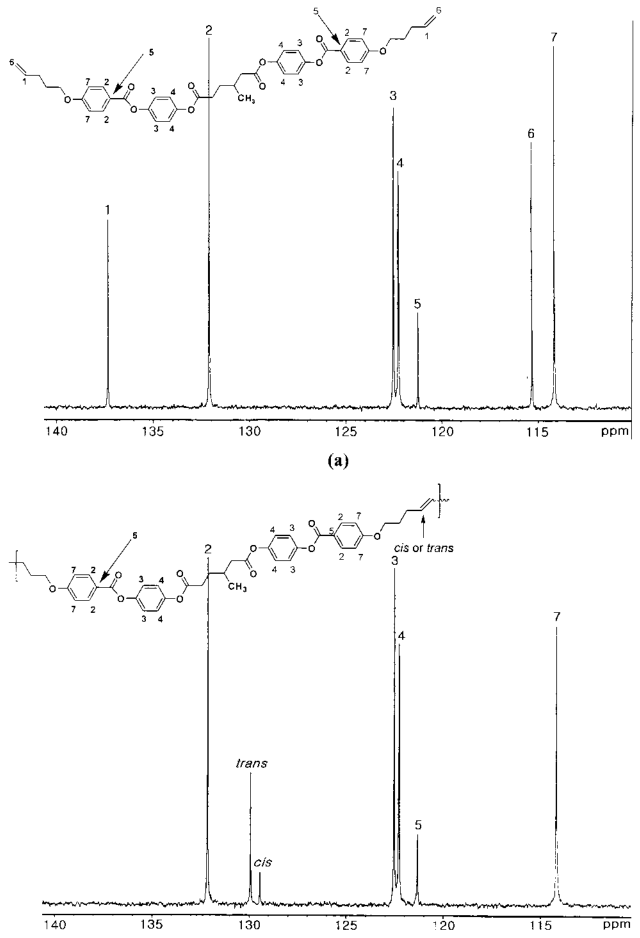


Figure 3. DSC thermograms for polymers **P5(1)**, **P5(3)**, **P5(6)**, **P11**, and **P12**.

LC Properties of Polymers. According to the DSC thermograms of the present polymers presented in Figure 3, all of them, with an exception of **P5(1)**, exhibit either one (**P5(3)**, **P5(6)**, and **P11**) or two (**P12**) additional endothermic peaks after melting transition. This is an indication that they may be thermotropic. This could be confirmed by observing their optical textures on a hot stage under a polarizing microscope. The four polymers **P5(1)**, **P5(3)**, and **P5(6)** exhibited either oily streak or fan textures (Figure 5) characteristic of the cholesteric mesophase. They tended to show oily streak textures on heating, whereas they formed focal conic textures on cooling. **P11**, however, exhibited only polished marble textures, indicating that it forms the nematic phase (Figure 5b).

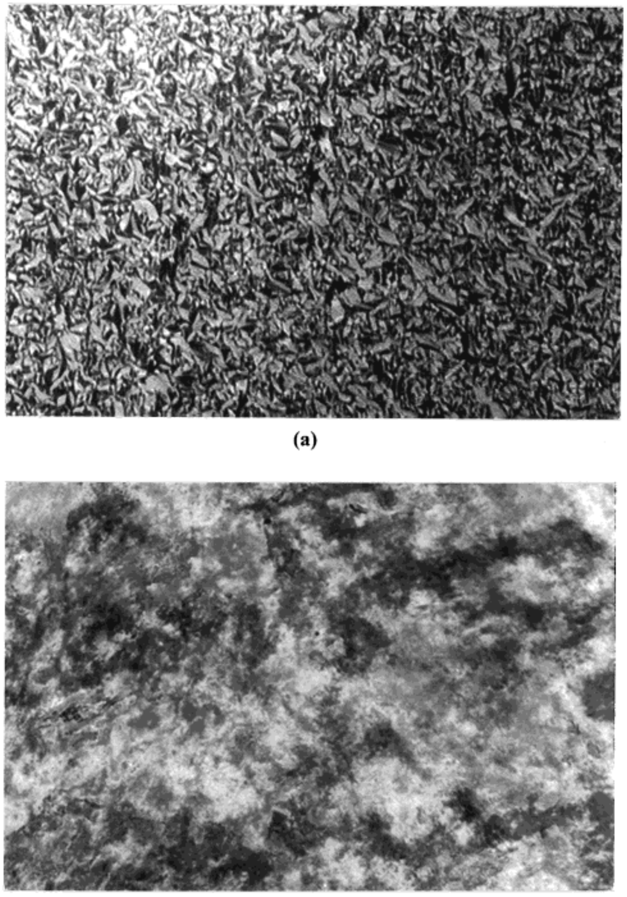
Thermal and LC behavior of **P12** is unique in that it showed three endothermic peaks as shown by the heating DSC thermogram in Figure 3. On the first heating DSC thermogram the first peak at 19.5 °C corresponds to melting transition, the one at 37 °C to the mesophase 1-to-mesophase 2 transition, and the last one at 54 °C to isotropization. These three peaks reappear in the reverse mode on the cooling DSC thermogram. In the other words, the three transitions are reversible, and thus, this compound forms two mesophases enantiotropically. When the change in optical textures of this polymer was observed through a polarizing microscope, its optical texture at room temperature was not well defined. This polymer, how-



(a)

(b)

Figure 4. Changes of alkenyl peaks on 75 MHz ^{13}C NMR spectrum after polymerization: (a) monomer **5(3)**; (b) polymer **P5(3)**.



(a)

(b)

Figure 5. Optical photomicrographs of (a) cholesteric fan texture (first cooling, 199 °C, magnification 200×) of **P5(3)** and (b) polished marble texture of **P11** (second cooling, 122 °C, magnification 200×).

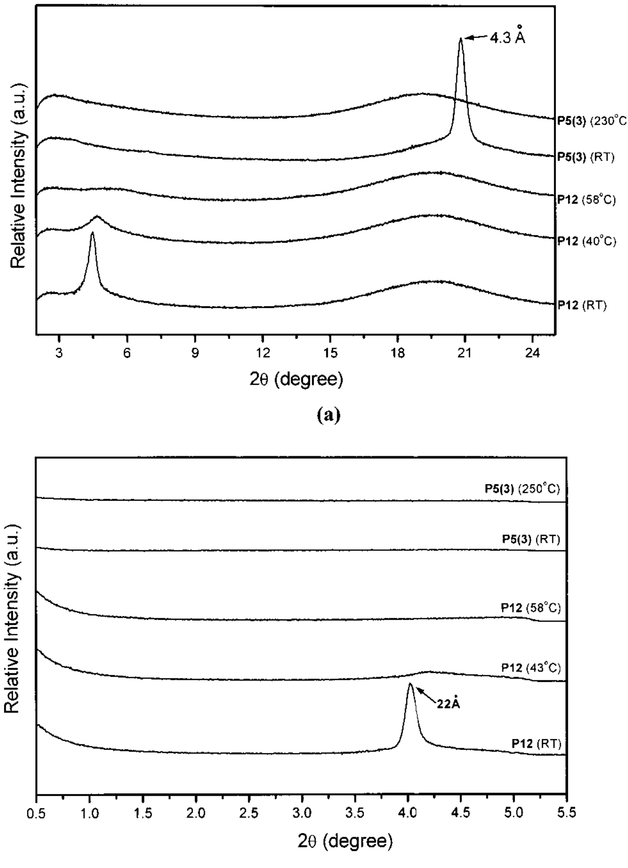
ever, exhibited the so-called polished marble texture above 37 °C, indicating that it forms a nematic phase as the second mesophase. The nematic texture disappeared when heated above its isotropization temperature (54 °C).

To study further the nature of mesophases formed by these polymers, the temperature dependence of wide- (WAXD) and small-angle X-ray diffractions (SAXD) of **P5(3)** and **P12** was examined, and the resulting diffractograms are shown in Figure 6. The WAXD of **P5(3)** obtained at room temperature shows a rather sharp peak at $2\theta = 20.83°$ (4.3 Å), whereas that obtained at 230 °C, which is within the temperature range of the mesophase, shows only a very broad and weak diffraction at $2\theta = 16.38{-}22.15°$ (4.0−5.4 Å). This polymer, however, did not show any diffraction in SAXD (Figure 6b). Such a diffraction character is consistent with the nematic or cholesteric phase. Since this polymer exhibits the oily streaks texture, it is concluded that this polymer forms the cholesteric phase. In contrast, the X-ray diffractogram obtained for **P12** at room temperature that is located within the temperature range of the first mesophase shows one diffraction in the small-angle region, at $2\theta = 4.02°$. This corresponds to the spacing of 22 Å. The spacing of 22 Å happens to be slightly longer than the length (20 Å) of the cholesteryl moiety.[55] The broad peak around at $2\theta = 19.54°$ (4.5 Å) must correspond to the short spacing, i.e., interchain distance. Although much more systematic structural analysis is required before a firm conclusion is made, it can be conjectured that **P12** forms a smectic ordering at lower temperature where the cholesterol moieties are oriented in such a way that they result in a layered morphology. The backbones as well as the side-chain spacers are flexible ($T_g = -30$ °C) enough to allow the cholesterol moieties to form smectic layers. The flexible parts in the polymer must swarm around the smectic layers. Moreover, this polymer was found to easily show the homeotropic texture. This can be taken as a strong suggestion that this polymer forms a smectic A phase where the main chain passes through the smectic layer and side-group spacers are bent so that the cholesterol moieties align themselves in a layered structure. Lindau et al.[56] recently proposed a similar morphology for side-group LCPs consisting of flexible main-chain and side-group spacers.

When the sample is further heated, it loses the smectic ordering, as one can see from the X-ray diffractogram obtained at 40 and 43 °C, close to the second transition temperature (37 °C), and becomes nematic afterward. The diffractogram obtained at 58 °C shows only a very broad diffraction over the wide-angle region, indicating the polymer is in an isotropic state.

Conclusion

We could employ successfully the ADMET polymerization method in the preparation of various types of thermotropic liquid crystalline (LC) polymers containing ester groups. The present investigation demonstrates the usefulness of this polymerization method in the



(a)

(b)

Figure 6. X-ray diffractograms [(a) WAXS and (b) SAXS] of **P5(3)** and **P12**.

synthesis of condensation type LC polymers from isolate diene monomers with built-in mesogenic units that can be easily prepared. The advantage of this particular method lies in the fact that reasonably high molecular weight polymers can be prepared at a low temperature under very mild conditions. Therefore, it can be envisaged that one may be able to synthesize LC polymers containing functional groups that do not interfere with the catalyst activity. In fact, all of the present polymers are cross-linkable or vulcanizable polymers due to the presence of double bonds along their backbones. Effective removal of the side product, ethylene, and running the polymerization in a homogeneous melt state ensure the production of high molecular weight polymers.

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