

# Synthesis of Side-Chain Liquid Crystal Polymers by Living Ring-Opening Metathesis Polymerization. 3. Influence of Molecular Weight, Interconnecting Unit, and Substituent on the Mesomorphic Behavior of Polymers with Laterally Attached Mesogens

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Received February 21, 1992; Revised Manuscript Received July 6, 1992

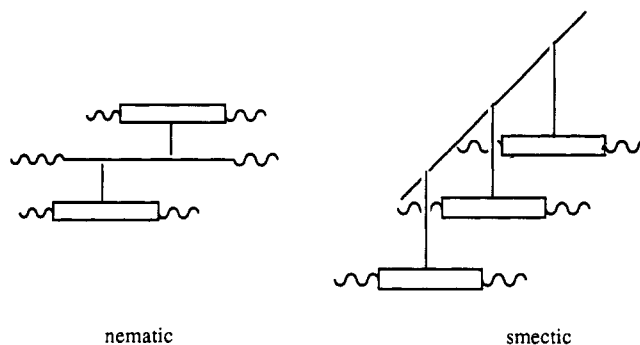
**ABSTRACT:** Norbornene derivatives containing laterally attached 2,5-bis[(4'-*n*-alkoxybenzoyl)oxy] mesogens were polymerized by controlled ring-opening metathesis polymerization to provide polymers in high yield with 5-100 repeat units and narrow molecular weight distributions. Monomers with *n* > 1 displayed monotropic or enantiotropic nematic mesophases. All polymers displayed enantiotropic nematic mesophases regardless of the spacer, molecular weight, or length of the *n*-alkoxy substituent. Constitutional isomers of poly[5-[[[2',5'-bis[(4''-methoxybenzoyl)oxy]benzyl]oxy]carbonyl]bicyclo[2.2.1]hept-2-ene]s containing laterally attached mixed phenyl ester/benzyl ester units are amorphous.

## Introduction

A new class of side-chain liquid crystalline polymers (SCLCPs) with the mesogen laterally attached to the polymer backbone have been synthesized recently.<sup>1-12</sup> In addition to the random coil conformation, laterally attached SCLCPs may conceivably orient with the mesogen either parallel to (nematic arrangement) or perpendicular to (smectic arrangement) the polymer backbone as shown in Chart I. Due to the large difference in size of the mesogen compared to the repeat unit along the polymer backbone, Zhou et al.<sup>2</sup> originally proposed that a nematic orientation of the mesogens should force the backbone into an extended helical conformation, thereby allowing the mesogens to wrap around it and form a cylindrical mesogen jacket. This was recently confirmed by small-angle neutron scattering analysis.<sup>9</sup> The nematic state is evidently favored based on the fact that almost all laterally attached SCLCPs prepared to date, including poly(methylsiloxanes),<sup>6-8</sup> polyacrylates,<sup>2,4,5</sup> polymethacrylates,<sup>1,3</sup> and poly(chloroacrylates),<sup>5</sup> exhibit only nematic mesophases regardless of the spacer length. However, two polymethacrylates containing laterally attached bis[[[4'-*n*-alkylcyclohexyl)carbonyl]oxy]naphthyl mesogens were recently shown to exhibit a smectic A mesophase in addition to the nematic mesophase.<sup>10,11</sup> In addition, X-ray analysis of a single-domain poly(methylsiloxane) sample revealed the presence of rather strong smectic C fluctuations in the nematic mesophase.<sup>12</sup>

Since these laterally attached SCLCPs have been prepared either by radical polymerization of mesogenic acrylic monomers or by hydrosilation of poly(methylsiloxane) backbones with mesogenic olefins, there is little information concerning the effect of molecular weight and polydispersity on their thermotropic behavior. However, it is well-known that the thermotropic behavior of conventional SCLCPs is influenced by a number of factors, including the molecular weight and thermal history of the polymer.<sup>13</sup> It is now possible to determine some of the structure/property relationships of SCLCPs using nearly monodisperse polymers prepared by living polymerization

Chart I  
Two Possible Orientations of the Mesogens and Polymer Backbone of Laterally Attached SCLCPs



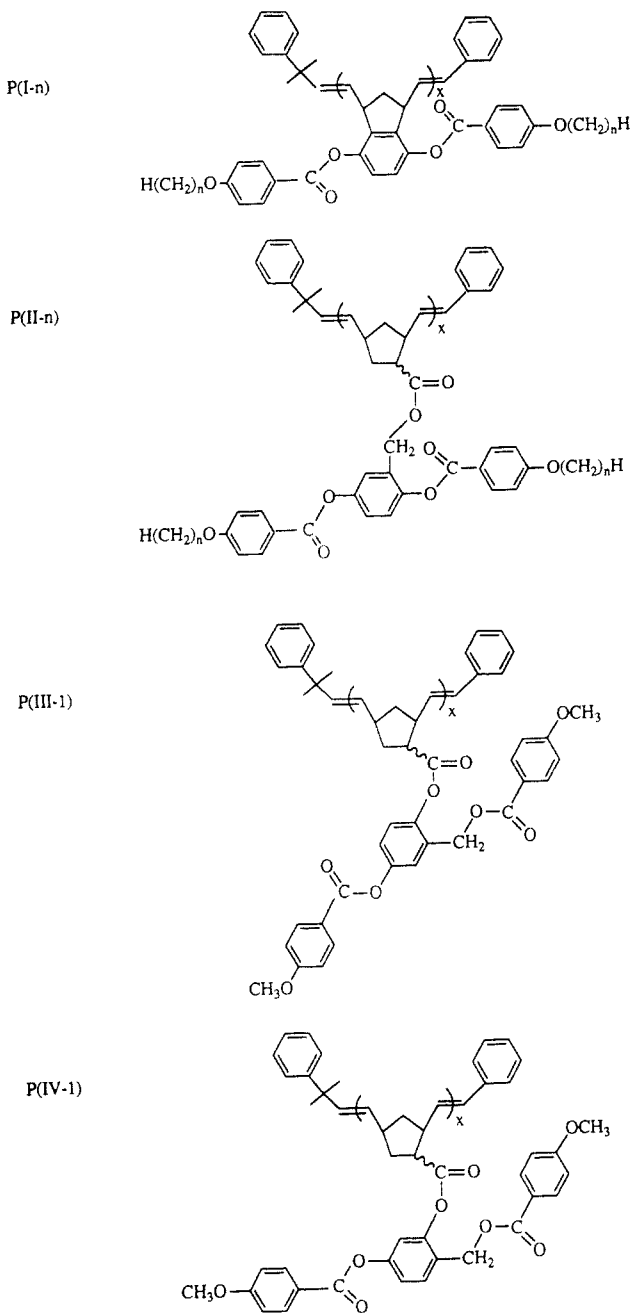
techniques. Such methods include group-transfer polymerization of certain mesogenic methacrylates,<sup>14</sup> cationic polymerization of vinyl ethers,<sup>15-24</sup> and ring-opening metathesis polymerization of norbornene derivatives.<sup>25,26</sup>

This paper presents the living ring-opening metathesis polymerization (ROMP) of laterally attached mesogenic norbornene monomers using Mo(CHCMe<sub>2</sub>Ph)(NAr)(O-*t*-Bu)<sub>2</sub><sup>27,28</sup> as the initiator to prepare the polymers shown in Chart II. The bis[(4'-*n*-alkoxybenzoyl)oxy]phenyl mesogen is fused to the polymer backbone in the poly(I-*n*) series, eliminating the possibility of a smectic orientation. The poly[5,8-bis[(4'-*n*-alkoxybenzoyl)oxy]-1,2,3,4-tetrahydronaphthalene]s were prepared to test the limits of the proposal that direct attachment of lateral mesogens should favor formation of a nematic mesophase,<sup>2</sup> in contrast to conventional SCLCPs in which a spacer is usually required. The poly[5-[[[2',5'-bis[(4''-*n*-alkoxybenzoyl)oxy]benzyl]oxy]carbonyl]bicyclo[2.2.1]hept-2-ene]s [series P(II-*n*)] are the direct analogues of the poly[[[2,5-bis[(4'-*n*-alkoxybenzoyl)oxy]benzyl]oxy]acrylate]s described previously.<sup>24</sup> Poly(III-1) and poly(IV-1) are constitutional isomers of poly(II-1). Both the smectic and nematic arrangements are possible with the last three polymer series. In addition to determining the effect of molecular weight on the thermotropic behavior of poly(II-1), this paper will also discuss the effects of the length of the *n*-alkoxy substituent, of the unit connecting the mesogen to the polymer backbone, and of constitutional

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**Chart II**  
**Laterally Attached SCLCPs Prepared by Ring-Opening**  
**Metathesis Polymerization of the Corresponding**  
**Norbornene Derivatives**



isomers on the thermotropic behavior of laterally substituted SCLCPs.

## Experimental Section

**Materials.** Anisoyl chloride (99%), bromine (99.5+%), 2,5-dihydroxybenzaldehyde (97%), 4-*n*-ethoxybenzoic acid (99%), methylhydroquinone (99%), and tetrabutylammonium hydrogen sulfate (TBAH) (97%) were used as received from Aldrich. 4-*n*-Butoxybenzoyl chloride (99%), 4-(*n*-heptyloxy)benzoyl chloride (99%), 4-(*n*-hexyloxy)benzoyl chloride (98%), 4-(*n*-nonyloxy)benzoic acid (98%), 4-(*n*-octyloxy)benzoic acid (98%), 4-(*n*-pentyloxy)benzoyl chloride (98%), and 4-*n*-propoxybenzoic acid (98%) were used as received from Lancaster Synthesis. *n*-Alkoxybenzoyl chlorides not commercially available were prepared by reaction of the corresponding benzoic acid with  $\text{PCl}_5$ .<sup>29</sup> Bicyclo[2.2.1]hept-2-ene-5-carboxyl chloride<sup>30</sup> (86:14 endo:exo), 1,4,4a,8a-tetrahydro-endo-1,4-methanonaphthalene-5,8-dione,<sup>31</sup> 5,8-diacetoxy-1,4-dihydro-1,4-methanonaphthalene,<sup>32</sup> 5,8-dihydroxy-1,4-dihydro-1,4-methanonaphthalene,<sup>32</sup> and Mo(NAr)(CHCMe<sub>2</sub>Ph)(O-*t*-Bu)<sup>27</sup> (NAr = 2,6-diisopropylaniline) were

synthesized by literature procedures. Bicyclo[2.2.1]hept-2-ene-5-carboxylic acid (86:14 endo:exo) was prepared by hydrolysis of the corresponding carboxyl chloride. Potassium bicyclo[2.2.1]hept-2-ene-5-carboxylate was prepared by titrating a methanolic solution of the carboxylic acid with 1.5 M KOH in methanol using phenolphthalein as indicator. Benzaldehyde (Baker) was distilled under Ar before use. Triethylamine (Fisher Scientific, reagent) was distilled from KOH under Ar. Pentane was washed with 5%  $\text{HNO}_3$  in  $\text{H}_2\text{SO}_4$ , stored over  $\text{CaCl}_2$ , and then distilled from purple sodium benzophenone ketyl under  $\text{N}_2$ . Reagent-grade diethyl ether, tetrahydrofuran (THF), and toluene were dried by distillation from purple sodium benzophenone ketyl under  $\text{N}_2$ . THF used as a polymerization solvent was vacuum transferred from purple sodium benzophenone ketyl on a high vacuum line using standard Schlenk techniques immediately before use and then rigorously degassed by several freeze-pump-thaw cycles. All other reagents and solvents were commercially available and were used as received.

**Techniques.** All polymerizations were performed under a  $\text{N}_2$  atmosphere in a Vacuum Atmospheres drybox. All other reactions were performed outside the drybox under an Ar atmosphere. 300-MHz  $^1\text{H}$ -NMR spectra ( $\delta$ , ppm) were recorded on a Varian XL-300 spectrometer. All spectra were recorded in  $\text{CDCl}_3$  with TMS as internal standard. UV/vis spectra of THF solutions were recorded on a Hewlett-Packard 8451A diode-array spectrophotometer in the range of 190–820 nm. Relative molecular weights were determined by gel permeation chromatography (GPC) at room temperature using THF as solvent, a set of 700,  $2 \times 10^3$ ,  $2 \times 10^4$ , and  $10^5$  Å Shodex columns, a Knauer differential refractometer detector and a Spectroflow 757 absorbance detector set at 290 nm, and a calibration plot determined with polystyrene standards (Polymer Laboratories Ltd.). The reported molecular weights and polydispersities are the mean values using both detectors.

The thermotropic behavior of all compounds was determined by a combination of differential scanning calorimetry (DSC) and polarized optical microscopy. A Perkin-Elmer DSC-7 differential scanning calorimeter was used to determine the thermal transitions which were read as the maximum or minimum of the endothermic or exothermic peaks. Glass transition temperatures ( $T_g$ s) were read as the middle of the change in heat capacity. All heating and cooling rates were 10 °C/min. Unless stated otherwise, thermal transitions were read from reproducible second or later heating scans and first or later cooling scans. Both enthalpy changes and transition temperatures were determined using indium and zinc as calibration standards. A Nikon polarized optical microscope (magnification 160×) equipped with a Mettler FP 82 hot stage and a Mettler FP 800 central processor was used to observe the thermal transitions and to analyze the anisotropic textures.<sup>33,34</sup> Thin samples were prepared by melting a minimum amount of compound between a clean glass slide and a cover slip and rubbing the cover slip with a spatula. Thermal gravimetric analyses (TGA) were conducted with a Seiko II TGA at a heating rate of 5 °C/min under  $\text{N}_2$ . The decomposition temperature range was calculated by extrapolation of the constant-weight regions to the tangent of the weight loss.

**Synthesis of Monomers and Precursors.** 5,8-Bis[(4'-*n*-alkoxybenzoyloxy)]-1,2,3,4-tetrahydronaphthalene ( $n = 1-9$ ). Monomers I-*n* were prepared in 41–94% yield as in the following example. While cooling the reaction in an ice bath, 4-methoxybenzoyl chloride (5.6 g, 33 mmol) was added dropwise over 10 min to a solution of 5,8-dihydroxy-1,2,3,4-tetrahydronaphthalene (2.0 g, 23 mmol of OH) and  $\text{NEt}_3$  (6.5 mL, 47 mmol) in THF (150 mL). Triethylammonium chloride precipitated immediately. After stirring for 19 h at room temperature, the reaction mixture was poured into 450 mL of cold water and the precipitate was collected. Recrystallization from 150 mL of ethanol/toluene (2:1), followed by chromatography on silica gel using  $\text{CH}_2\text{Cl}_2$  as eluent, and finally recrystallization from 100 mL of toluene/THF (1:1) in the drybox yielded 4.3 g (84%) of white crystals; mp (DSC) 185.5 °C;  $^1\text{H}$  NMR  $\delta$  2.24 (d, C(7) $\text{H}_2$ , 1 H), 2.35 (d, C(7) $\text{H}_2$ , 1 H), 3.96 (s, OCH<sub>3</sub>, 6 H), 4.02 (s, bridgehead, 2 H), 6.87 (s, olefinic methine, 2 H), 6.91 (s, 2 aromatic H ortho to OOCAr), 7.06 (d, 4 aromatic H ortho to OR), 8.24 (4 aromatic H meta to OR).

1-2:  $^1\text{H}$  NMR  $\delta$  1.52 (t,  $\text{CH}_3$ , 6 H), 2.24 (d,  $\text{C}(7)\text{H}_2$ , 1 H), 2.34 (d,  $\text{C}(7)\text{H}_2$ , 1 H), 3.99 (s, bridgehead, 2 H), 4.16 (q,  $\text{OCH}_2$ , 4 H), 6.83 (s, olefinic methine, 2 H), 6.88 (s, 2 aromatic H ortho to  $\text{OOCAR}$ ), 7.01 (d, 4 aromatic H ortho to OR), 8.20 (d, 4 aromatic H meta to OR).

The  $^1\text{H}$ -NMR spectra of monomers 1- $n$  with  $n = 3-5$  are identical: 1.04 (t,  $\text{CH}_3$ , 6 H), 1.54 (m,  $[\text{CH}_2]_{n-3}$ ,  $2[n-3]$  H), 1.87 (m,  $\text{OCH}_2\text{CH}_2$ , 4 H), 2.23 (d,  $\text{C}(7)\text{H}_2$ , 1 H), 2.35 (d,  $\text{C}(7)\text{H}_2$ , 1 H), 3.99 (s, bridgehead, 2 H), 4.08 (t,  $\text{OCH}_2$ , 4 H), 6.84 (s, olefinic methine, 2 H), 6.89 (s, 2 aromatic H ortho to  $\text{OOCAR}$ ), 7.02 (d, 4 aromatic H ortho to OR), 8.20 (d, 4 aromatic H meta to OR).

The  $^1\text{H}$ -NMR spectra of monomers 1- $n$  with  $n = 4-9$  are identical: 0.92 (t,  $\text{CH}_3$ , 6 H), 1.34 (m,  $[\text{CH}_2]_{n-4}$ ,  $2[n-4]$  H), 1.49 (m,  $\text{OCH}_2\text{CH}_2\text{CH}_2$ , 4 H), 1.83 (m,  $\text{OCH}_2\text{CH}_2$ , 4 H), 2.23 (d,  $\text{C}(7)\text{H}_2$ , 1 H), 2.35 (d,  $\text{C}(7)\text{H}_2$ , 1 H), 3.97 (s, bridgehead, 2 H), 4.08 (t,  $\text{OCH}_2$ , 4 H), 6.82 (s, olefinic methine, 2 H), 6.87 (s, 2 aromatic H ortho to  $\text{OOCAR}$ ), 7.01 (d, 4 aromatic H ortho to OR), 8.19 (d, 4 aromatic H meta to OR).

**2,4- and 2,5-Bis[(4'-methoxybenzoyl)oxy]benzaldehydes.** In a typical procedure, *p*-anisoyl chloride (8.5 g, 50 mmol) was added dropwise to an ice-cooled solution of 2,5-dihydroxybenzaldehyde (3.0 g, 44 mmol of OH) and  $\text{NEt}_3$  (7.4 mL, 52 mmol) in dry THF (250 mL). The reaction mixture was stirred at room temperature for 20.5 h and then poured into 500 mL of cold water. The resulting precipitate was collected and recrystallized from 850 mL of ethanol/toluene (1:1) to yield 7.4 g (83%) of 2,5-bis[(4'-methoxybenzoyl)oxy]benzaldehyde as fine white crystals: DSC k 186.6 n 249.3 i (lit.<sup>24</sup> DSC k 192 n 224 i);  $^1\text{H}$  NMR  $\delta$  3.96 (s,  $\text{OCH}_3$ , 6 H), 7.06 (t, 4 aromatic H ortho to OR), 7.45 (d) and 7.57 (d, 2 aromatic H ortho to  $\text{OOCAR}$ ), 7.84 (s, 1 aromatic H ortho to CHO), 8.22 (t, 4 aromatic H meta to OR), 10.3 (s, CHO, 1 H).

2,4-Bis[(4'-methoxybenzoyl)oxy]benzaldehyde; 86% yield; mp (DSC) 149.8 °C;  $^1\text{H}$  NMR  $\delta$  3.92 (m,  $\text{OCH}_3$ , 6 H), 7.02 (dd, 4 aromatic H ortho to OR), 7.33 (s, 2 aromatic H ortho to  $\text{OOCAR}$ ), 8.08 (d, 1 aromatic H ortho to CHO), 8.18 (dd, 4 aromatic H meta to OR), 10.2 (s, CHO, 1 H).

**2,5-Bis[(4'-*n*-alkoxybenzoyl)oxy]toluenes ( $n = 1-6$ ).** The 2,5-bis[(4'-*n*-alkoxybenzoyl)oxy]toluenes were prepared in 78-86% yield as in the previous procedure.

2,5-Bis[(4'-methoxybenzoyl)oxy]toluene:  $^1\text{H}$  NMR  $\delta$  2.30 (s,  $\text{ArCH}_3$ , 3 H), 3.95 (s,  $\text{OCH}_3$ , 6 H), 7.05 (dd, 4 aromatic H ortho to OR), 7.18 (m, 3 aromatic H of central ring), 8.22 (dd, 4 aromatic H meta to OR); DSC k 172 n 255 i (lit.<sup>35</sup> DSC k 166 n 252 i).

2,5-Bis[(4'-*n*-ethoxybenzoyl)oxy]toluene:  $^1\text{H}$  NMR  $\delta$  1.48 (t,  $\text{CH}_3$ , 6 H), 2.26 (s,  $\text{ArCH}_3$ , 3 H), 4.14 (q,  $\text{OCH}_2$ , 4 H), 6.99 (dd, 4 aromatic H ortho to OR), 7.14 (m, 3 aromatic H of central ring), 8.16 (dd, 4 aromatic H meta to OR); DSC k 191 n 256 i (lit.<sup>35</sup> DSC k 187 n 248 i).

The  $^1\text{H}$ -NMR spectra of the 2,5-bis[(4'-*n*-alkoxybenzoyl)oxy]toluenes with  $n = 3-6$  are identical: 0.99 (t,  $\text{CH}_3$ , 6 H), 1.37 (m,  $[\text{CH}_2]_{n-4}$ ,  $2[n-4]$  H), 1.49 (m,  $\text{OCH}_2\text{CH}_2\text{CH}_2$ , 4 H), 1.84 (m,  $\text{OCH}_2\text{CH}_2$ , 4 H), 2.25 (s,  $\text{ArCH}_3$ , 3 H), 4.05 (t,  $\text{OCH}_2$ , 4 H), 6.98 (dd, 4 aromatic H ortho to OR), 7.14 (m, 3 aromatic H of central ring), 8.16 (dd, 4 aromatic H meta to OR); DSC  $n = 3$ , k 140 n 213 i (lit.<sup>35</sup> DSC k 138 n 209 i);  $n = 4$ , k 113 n 204 i (lit.<sup>35</sup> DSC k 115 n 206 i);  $n = 5$ , k 85 n 180 i (lit.<sup>35</sup> DSC k 90 n 178 i);  $n = 6$ , k 88 n 173 i.

**2,5-Bis[(4'-methoxybenzoyl)oxy]benzyl Alcohol and 2-[[[(4'-Methoxybenzoyl)oxy]methylene]-4-[(4'-methoxybenzoyl)oxy]phenol.** The following procedure was used to synthesize the benzyl alcohol in 37-68% yield; the phenol was a side product. A solution of 2,5-bis[(4'-methoxybenzoyl)oxy]benzaldehyde (4.2 g, 10 mmol) in a mixture of dry THF (170 mL) and DMSO (10 mL) was added all at once to an ice-cooled solution of  $\text{NaBH}_4$  (0.15 g, 4.0 mmol) in DMSO (5 mL). After stirring in an ice bath for 30 min, the reaction mixture was quenched with 5 drops of HCl and poured into 400 mL of aqueous NaCl. This was extracted four times with ether and dried over  $\text{Na}_2\text{SO}_4$ . After filtration and removal of the solvent on a rotary evaporator, the residue was recrystallized from 150 mL of ethanol to yield 1.8 g (42%) of 2,5-bis[(4'-methoxybenzoyl)oxy]benzyl alcohol: DSC k 151 n 156 i (lit.<sup>24</sup> DSC mp 159-160 °C);  $^1\text{H}$  NMR  $\delta$  2.16 (bs,  $\text{CH}_2\text{OH}$ , 1 H), 3.95 (s,  $\text{OCH}_3$ , 6 H), 4.69 (s,  $\text{CH}_2\text{OH}$ , 2 H), 7.04 (d, 4 aromatic H ortho to OR), 7.26 (s, 2 aromatic H ortho to  $\text{OOCAR}$ ), 7.47 (s, 1 aromatic H ortho to  $\text{CH}_2\text{OH}$ ), 8.21 (d, 4 aromatic H meta to

OR). 2-[[[(4'-Methoxybenzoyl)oxy]methylene]-4-[(4'-methoxybenzoyl)oxy]phenol (1.4 g, 33%) was collected from the reduced filtrate (50 mL): mp (DSC) 159.0 °C;  $^1\text{H}$  NMR  $\delta$  3.89 (s,  $\text{OCH}_3$ , 3 H), 3.94 (s,  $\text{OCH}_3$ , 3 H), 5.36 (s,  $\text{ArCH}_2\text{OOC}$ , 2 H), 6.95 (d, 2 aromatic H ortho to OR), 7.04 (m, 2 aromatic H ortho to OR and 1 aromatic H ortho to  $\text{OOCAR}$  and meta to OH), 7.14 (dd, 1 aromatic H ortho to OH), 7.26 (d, 1 aromatic H ortho to  $\text{CH}_2$  and  $\text{OOCAR}$ ), 8.05 (d, 2 aromatic H meta to OR), 8.21 (d, 2 aromatic H ortho to OR), 8.38 (s, OH, 1 H).

**2-[[[(4'-Methoxybenzoyl)oxy]methylene]-5-[(4'-methoxybenzoyl)oxy]phenol.** A solution of 2,4-bis[(4'-methoxybenzoyl)oxy]phenol (3.4 g, 8.3 mmol) in a mixture of THF (110 mL) and DMSO (11 mL) was added all at once to an ice-cooled slurry of  $\text{NaBH}_4$  (0.15 g, 4.0 mmol) in DMSO (10 mL). The solution rapidly became heterogeneous. It was allowed to warm slowly to room temperature and was stirred until  $^1\text{H}$  NMR showed that all CHO and  $\text{CH}_2\text{OH}$  resonances had been converted to  $\text{CH}_2\text{OOCAR}$  resonances (3.5 h). After stirring at room temperature for an additional 1.5 h, the reaction mixture was quenched with saturated  $\text{NH}_4\text{Cl}$  (5 mL) and poured into 300 mL of aqueous NaCl. This was extracted three times with ether and dried over  $\text{Na}_2\text{SO}_4$ . An oil was obtained by filtration and removal of the solvent on a rotary evaporator. This crystallized by stirring with ethanol (50 mL). The resulting white solid was collected and recrystallized from ethanol to yield 2.1 g (63%) of 2-[[[(4'-methoxybenzoyl)oxy]methylene]-5-[(4'-methoxybenzoyl)oxy]phenol: mp (DSC) 153 °C;  $^1\text{H}$  NMR  $\delta$  3.87 (s,  $\text{OCH}_3$ , 3 H), 3.89 (s,  $\text{OCH}_3$ , 3 H), 5.3 (s,  $\text{ArCH}_2\text{OOC}$ , 2 H), 6.81 (m, 2 aromatic H meta to  $\text{CH}_2\text{OOC}$ ), 6.92 (d, 2 aromatic H ortho to OR), 6.98 (d, 2 aromatic H ortho to OR), 7.39 (d, 1 aromatic H ortho to  $\text{CH}_2\text{OOC}$ ), 8.02 (d, 2 aromatic H meta to OR), 8.13 (d, 2 aromatic H meta to OR), 8.67 (s, OH, 1 H).

**2,5-Bis[(4'-*n*-alkoxybenzoyl)oxy]benzyl Bromide ( $n = 1-6$ ).** The benzyl bromides were prepared in 69-94% yield as in the following example. A solution of bromine (1.5 mL, 29 mmol) in  $\text{CCl}_4$  (180 mL) was added dropwise over 2 h to a refluxing solution of 2,5-bis[(4'-methoxybenzoyl)oxy]toluene (7.1 g, 18 mmol) in  $\text{CCl}_4$  (1600 mL). The resulting red solution was stirred at reflux for an additional 2 h and then poured immediately onto 2000 mL of ice. The orange organic layer was separated from the aqueous layer and washed two times with 5% aqueous  $\text{NaHSO}_3$  (400 mL total). The resulting colorless organic layer was dried over  $\text{Na}_2\text{SO}_4$  and filtered, and the solvent was removed by rotary evaporation. The beige solid was recrystallized from a mixture of ethanol (200 mL) and toluene (100 mL) to yield 6.9 g (82%) of 2,5-bis[(4'-methoxybenzoyl)oxy]benzyl bromide as white crystals:  $^1\text{H}$  NMR  $\delta$  3.91 (s,  $\text{OCH}_3$ , 6 H), 4.46 (s,  $\text{CH}_2\text{Br}$ , 2 H), 7.02 (m, 4 aromatic H ortho to OR), 7.30 (m, 3 aromatic H of central ring), 8.19 (m, 4 aromatic H meta to OR).

2,5-Bis[(4'-ethoxybenzoyl)oxy]benzyl bromide:  $^1\text{H}$  NMR  $\delta$  1.51 (t,  $\text{CH}_3$ , 6 H), 4.18 (q,  $\text{OCH}_2$ , 4 H), 4.49 (s,  $\text{CH}_2\text{Br}$ , 2 H), 7.03 (dd, 4 aromatic H ortho to OR), 7.33 (m, 3 aromatic H of central ring), 8.18 (d, 2 aromatic H ortho to OR), 8.25 (d, 2 aromatic H ortho to OR).

The  $^1\text{H}$ -NMR spectra of the 2,5-bis[(4'-*n*-alkoxybenzoyl)oxy]benzyl bromides with  $n = 3-6$  are identical: 1.00 (t,  $\text{CH}_3$ , 6 H), 1.49 (m,  $[\text{CH}_2]_{n-3}$ ,  $2[n-3]$  H), 1.84 (m,  $\text{OCH}_2\text{CH}_2$ , 4 H), 4.07 (t,  $\text{OCH}_2$ , 4 H), 4.46 (s,  $\text{CH}_2\text{Br}$ , 2 H), 7.01 (dd, 4 aromatic H ortho to OR), 7.31 (m, 3 aromatic H of central ring), 8.16 (d, 2 aromatic H meta to OR), 8.22 (d, 2 aromatic H ortho to OR). In addition to the above resonances, all spectra contained trace singlets at 6.85 and 7.77 ppm, presumably due to  $\text{ArBr}$  and  $\text{ArCHBr}_2$ . These compounds were used without further purification.

**Synthesis of 5-[[[2,5-Bis[(4'-methoxybenzoyl)oxy]benzyl]oxy]carbonyl]bicyclo[2.2.1]hept-2-ene (II-1), 5-[[[2-[[[(4'-Methoxybenzoyl)oxy]methylene]-4-[(4'-methoxybenzoyl)oxy]phenyl]oxy]carbonyl]bicyclo[2.2.1]hept-2-ene (III-1), and 5-[[[2-[[[(4'-Methoxybenzoyl)oxy]methylene]-5-[(4'-methoxybenzoyl)oxy]phenyl]oxy]carbonyl]bicyclo[2.2.1]hept-2-ene (IV-1) by Esterification of the Corresponding Benzyl Alcohol or Phenols.** In a typical procedure, a solution of bicyclo[2.2.1]hept-2-ene-5-carboxyl chloride (1.3 g, 8.2 mmol) in dry THF (5 mL) was added dropwise simultaneously with a solution of  $\text{NEt}_3$  (1.2 mL, 8.6 mmol) in dry THF (5 mL) to an ice-cooled solution of 2,5-bis[(4'-methoxybenzoyl)oxy]benzyl alcohol (2.2 g, 5.3 mmol) in dry THF (55 mL). Triethylammonium

chloride immediately precipitated. After stirring at room temperature for 18.5 h, the reaction mixture was poured into 250 mL of cold water. An oil separated which crystallized with further stirring. This precipitate was collected, dried, and recrystallized from a mixture of ethanol (120 mL) and toluene (20 mL) to yield 2.3 g (83%) 5-[[[2',5'-bis[(4'-methoxybenzoyl)oxy]benzyl]oxy]carbonyl]bicyclo[2.2.1]hept-2-ene. Monomer II-1 was purified for polymerization by chromatography on a silica gel (6-in.) column topped with basic activated  $\text{Al}_2\text{O}_3$  (1.5 in.) using  $\text{CH}_2\text{Cl}_2$  as eluent, followed by recrystallization in the drybox from a mixture of pentane (20 mL) and toluene (35 mL) with a hot filtration:  $^1\text{H}$  NMR  $\delta$  resonances at 1.23 (d), 1.38 (m), 1.85 (m), 2.87 (s overlapped with m) and 3.15 (s) are due to the non-olefinic norbornene protons of both isomers; 3.93 (s,  $\text{OCH}_3$ , 6 H), 5.10 (d) and 5.16 (d,  $\text{COOCH}_2\text{Ar}$ , 2 H), 5.82 (m) and 6.12 (m, olefinic methine of endo isomer), 6.04 (m) and 6.12 (m, olefinic methine of exo isomer), 7.01 (d, 4 aromatic H ortho to OR), 7.28 (s, 2 aromatic H ortho to  $\text{OOCAr}$ ), 7.35 (s, 1 aromatic H ortho to  $\text{CH}_2\text{OOCAr}$ ), 8.18 (d, 4 aromatic H meta to OR). The ratio of endo to exo isomers calculated from the ratio of the corresponding olefinic resonances is 86:14.

Monomer III-1: 84% yield; mp (DSC) 109 °C;  $^1\text{H}$  NMR resonances at  $\delta$  1.39 (d), 1.57 (dd), 2.03 (dt), 3.00 (s), 3.28 (m), and 3.42 (s) are due to the non-olefinic norbornene protons of both isomers; 3.90 (s,  $\text{OCH}_3$ , 3 H), 3.94 (s,  $\text{OCH}_3$ , 3 H), 5.33 (d,  $\text{COOCH}_2\text{Ar}$ , 2 H), 6.14 (m) and 6.28 (m, olefinic methine of endo isomer), 6.20 (m) and 6.23 (m, olefinic methine of exo isomer), 6.96 (d, 2 aromatic H ortho to OR), 7.03 (d, 2 aromatic H ortho to OR), 7.17 (d, 1 aromatic H ortho to  $\text{OOCAr}$  and meta to  $\text{OOCNBE}$ ), 7.26 (dd, 1 aromatic H ortho to  $\text{OOCNBE}$ ), 7.41 (d, 1 aromatic H ortho to  $\text{CH}_2$ ), 8.05 (d, 2 aromatic H meta to OR), 8.19 (d, 2 aromatic H meta to OR). The ratio of endo to exo isomers calculated from the olefinic resonances is 79:21.

Monomer IV-1: 88% yield; mp (DSC) 120 °C;  $^1\text{H}$  NMR resonances at  $\delta$  1.39 (d), 1.56 (dd), 2.03 (dt), 2.99 (s), 3.26 (dd), and 3.40 (s) are due to the non-olefinic norbornene protons of both isomers; 3.92 (s,  $\text{OCH}_3$ , 3 H), 3.96 (s,  $\text{OCH}_3$ , 3 H), 5.34 (d,  $\text{COOCH}_2\text{Ar}$ , 2 H), 6.13 (m) and 6.26 (m, olefinic methine of endo isomer), 6.15 (m) and 6.21 (m, olefinic methine of exo isomer), 6.97 (d, 2 aromatic H ortho to OR), 7.01 (d, 2 aromatic H ortho to OR), 7.09 (d, 1 aromatic H ortho to  $\text{OOCNBE}$ ), 7.19 (dd, 1 aromatic H ortho to  $\text{OOCAr}$  and meta to  $\text{CH}_2$ ), 7.51 (d, 1 aromatic H ortho to  $\text{CH}_2$ ), 8.06 (d, 2 aromatic H meta to OR), 8.19 (d, 2 aromatic H meta to OR).

**Synthesis of 5-[[[2',5'-Bis[(4'-*n*-alkoxybenzoyl)oxy]benzyl]oxy]carbonyl]bicyclo[2.2.1]hept-2-ene (II-*n*, *n* = 1–6) by Phase-Transfer-Catalyzed Esterification of the Corresponding Benzyl Bromides.** Monomers II-*n* were prepared in 47–88% yield using the following procedure. A mixture of potassium bicyclo[2.2.1]hept-2-ene-5-carboxylate (2.2 g, 13 mmol), 2,5-bis[(4'-*n*-ethoxybenzoyl)oxy]benzyl bromide (5.8 g, 12 mmol), and TBAH (0.49 g, 1.4 mmol) in a mixture of THF (90 mL) and DMSO (5 mL) was stirred at 60 °C for 18.5 h and then poured into 400 mL of cold water. An oil separated which eventually solidified with further stirring. The precipitate was collected, dried, and recrystallized from a mixture of ethanol (150 mL) and toluene (5 mL) to yield 5.4 g (83%) of 5-[[[2',5'-bis[(4'-*n*-ethoxybenzoyl)oxy]benzyl]oxy]carbonyl]bicyclo[2.2.1]hept-2-ene. Monomer II-2 was purified for polymerization by repeated flash chromatography on basic activated  $\text{Al}_2\text{O}_3$  using THF as eluent until  $^1\text{H}$  NMR showed that the extraneous resonances at 6.85 and 7.77 ppm were absent, followed by recrystallization outside the drybox from toluene (20 mL) and then from ethanol (100 mL), and recrystallization in the drybox from a mixture of pentane (10 mL) and toluene (20 mL).

All monomers were similarly purified by flash chromatography on basic activated  $\text{Al}_2\text{O}_3$ ; 84:16 endo:exo. However, those monomers with *n* ≥ 4 were oily and extremely soluble and recrystallized with much more difficulty. Although the oils crystallized from ethanol only with stirring, it was possible to perform a final recrystallization from pentane/toluene without stirring.  $^1\text{H}$ -NMR resonances at 1.23 (d), 1.38 (m), 1.85 (m), 2.87 (s overlapped with m), and 3.15 (s) are due to the non-olefinic norbornene protons of both isomers; 5.83 (m) and 6.13 (m, olefinic methine of endo isomer), 6.04 (m) and 6.13 (m, olefinic methine of exo isomer). The resonances due to the mesogen are listed

below for each monomer except II-1, which were reported in the previous synthesis. II-2: 1.52 (t,  $\text{CH}_3$ , 6 H), 4.18 (q,  $\text{OCH}_2$ , 4 H), 5.14 (d) and 5.19 (d,  $\text{COOCH}_2\text{Ar}$ , 2 H), 7.04 (d, 4 aromatic H ortho to OR), 7.32 (m, 3 aromatic H of central ring), 8.21 (d, 4 aromatic H meta to OR). The  $^1\text{H}$ -NMR resonances due to the mesogens of monomers II-3 through II-6 are identical: 1.00 (t,  $\text{CH}_3$ , 6 H), 1.47 (m,  $[\text{CH}_2]_{n-3}$ , 2[*n* – 3] H), 1.86 (m,  $\text{OCH}_2\text{CH}_2$ , 4 H), 4.06 (t,  $\text{CH}_2$ , 4 H), 5.11 (d) and 5.16 (d,  $\text{COOCH}_2\text{Ar}$ , 2 H), 7.00 (d, 4 aromatic H ortho to OR), 7.31 (m, 3 aromatic H of central ring), 8.16 (d, 4 aromatic H meta to OR).

**Polymerizations.** In a typical procedure, a solution of 5,8-bis[(4'-methoxybenzoyl)oxy]-1,2,3,4-tetrahydronaphthalene (0.22 g, 0.47 mmol) in THF (4.8 g) was added dropwise over 2 min to a rapidly stirred yellow solution of  $\text{Mo}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{O}-t\text{-Bu})_2$  (5 mg, 9  $\mu\text{mol}$ ) in THF (0.51 g). After stirring at room temperature for an additional 2.5 h, the brownish orange solution was treated with benzaldehyde (3  $\mu\text{L}$ , 0.03 mmol) and stirred for 25 min. This solution was then taken outside the drybox and precipitated in hexanes (75 mL). The precipitate was collected, reprecipitated from THF (15 mL) into hexanes (75 mL), and dried *in vacuo* to yield 0.20 g (91%) of a white polymer;  $M_n = 20\,893$ ,  $M_w/M_n = 1.08$ .

**Fractionation of Poly(II-*n*).** Polymerizations of monomers II-*n* synthesized by the benzyl bromide route usually contained a small fraction of high molecular weight polymer in addition to the desired molecular weight polymer. This broadened the molecular weight distribution substantially and was removed by fractionation. For example, hexane was added dropwise to a solution of poly(II-2) (0.18 g,  $M_n = 20\,380$ ,  $M_w/M_n = 2.36$ ) dissolved in THF (100 mL) until a slight turbidity persisted (50 mL). The resulting solution was filtered through a 0.5- $\mu\text{m}$  filter, and the solvent was removed by rotary evaporation. The residue was dissolved in THF (10 mL) and precipitated in hexanes (60 mL), collected, and dried to yield 0.145 g of a white polymer;  $M_n = 17\,990$ ,  $M_w/M_n = 1.19$ .

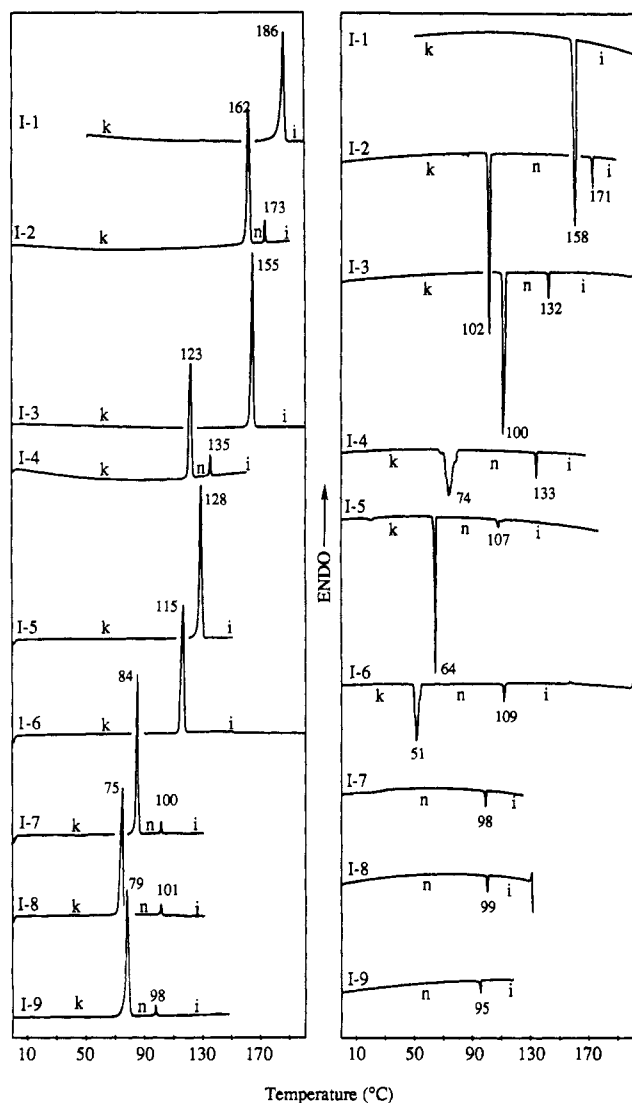
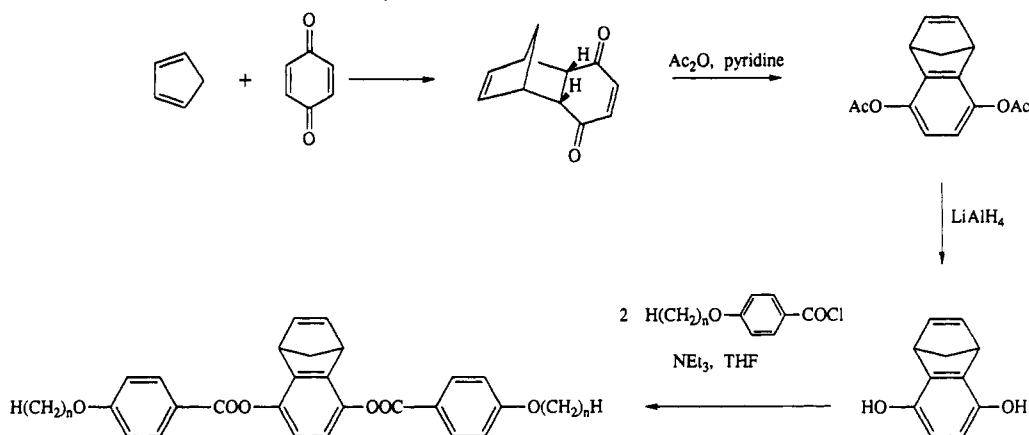
## Results and Discussion

Monomer series I-*n* was synthesized in four steps as outlined in Scheme I. The first three steps involving the Diels–Alder addition of cyclopentadiene and benzoquinone, followed by aromatization of the resulting quinone using pyridine in the presence of acetic anhydride, and finally reduction to form 5,8-dihydroxy-1,4-dihydro-1,4-methanonaphthalene followed literature procedures and proceeded in good yields. The final esterification step also proceeded in high yields.

As reported previously for I-2,<sup>36</sup> all monomers of series I-*n* except the methoxy derivative form nematic mesophases. The DSC traces obtained on heating and on cooling are presented in Figure 1, and the thermal transitions are summarized in Table I. Lengthening the *n*-alkoxy substituents from methoxy to ethoxy depresses crystallization, such that a liquid crystalline mesophase is realized. The nematic mesophases of monomers I-2, I-4, I-7, I-8, and I-9 are enantiotropic, while those of monomers I-3, I-5, and I-6 are monotropic. The data obtained on heating are from equilibrated samples and represent samples crystallized either from solution or from the melt with short annealing times. That is, although these laterally substituted mesogens crystallize easily from the melt, crystallization is somewhat slower than the time scale of the DSC experiment. For this reason, either crystallization is incomplete on cooling or a glass is formed at or near 0 °C. However, even when the sample vitrifies as in the case of I-7, I-8, and I-9, the recrystallization exotherm observed on the next heating scan is much smaller than the melting endotherm, demonstrating that some recrystallization does take place on cooling.

Monomer series II was synthesized by either of the two routes outlined in Scheme II. The first route is based on that described previously for the synthesis of poly[[[2,5-bis[(4'-methoxybenzoyl)oxy]benzyl]oxy]acrylate],<sup>2,4</sup> ex-

**Scheme I**  
**Synthesis of Monomers I-n**



**Figure 1.** DSC equilibrium heating scans and cooling scans of monomers I-n.

cept that the conditions used for reduction of the benzaldehyde were modified. No explanation was given in the original paper for the low yield of this step (57%). Assuming that it was due to competing ester reduction,<sup>37</sup> we reduced the reaction time from 4 h to 30 min at 0 °C and changed the solvent system from 12:1 DMSO/H<sub>2</sub>O to 1:12 DMSO/THF since dipolar aprotic solvents enhance the reducing power of NaBH<sub>4</sub><sup>38</sup> and presumably decrease its selectivity. Some DMSO is required to solubilize the benzaldehyde. We found that under these conditions

**Table I**  
**Thermal Transitions and Thermodynamic Parameters of Monomers I-n<sup>a</sup>**

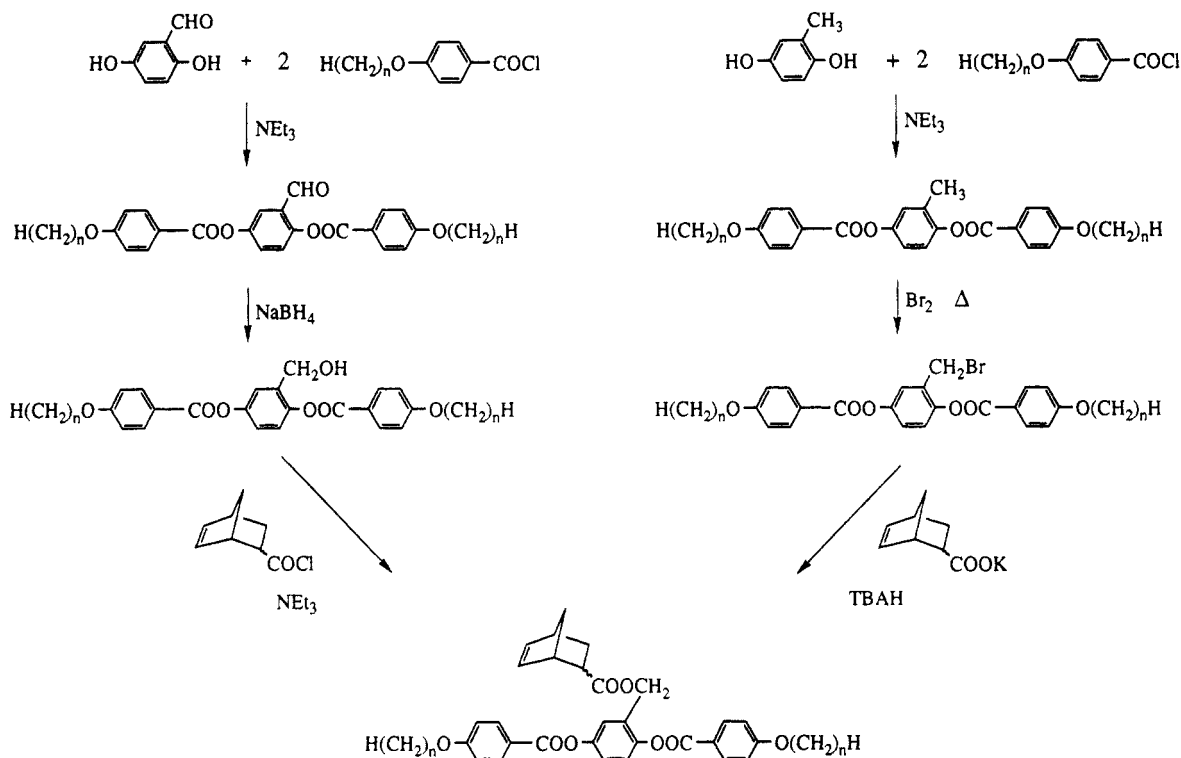
monomer	phase transitions, °C (corresponding $\Delta H$ , kJ/mol)	
	k	i
I-1	k 186.2 (38.4)	i 158.3 (36.1)
I-2	k 161.6 (43.3)	n 173.0 (2.95) i 170.6 (2.77) n 102.2 (25.4)
I-3	k 155.0 (44.8) [n 135.1 (2.17)]	i 132.4 (2.31) n 100.4 (33.9)
I-4	k 122.7 (35.9) n 135.1 (2.90)	i 132.7 (2.75) n 74.4 (28.6)
I-5	k 128.4 (47.6) [n 110.9 (2.04)]	i 107.4 (2.03) n 63.7 (20.6)
I-6	k 115.2 (48.8) [n 112.2 (2.48)]	i 108.8 (2.46) n 50.8 (29.5)
I-7	k 84.2 (43.8) n 100.3 (1.79)	i 97.9 (1.90)
I-8	k 74.8 (45.7) n 101.2 (1.97)	i 98.6 (2.28)
I-9	k 78.7 (54.8) n 97.7 (1.82)	i 94.8 (1.97)

<sup>a</sup> k = crystalline, n = nematic, i = isotropic; [monotropic]; 1st line obtained from equilibrium heating scan, 2nd line obtained on cooling.

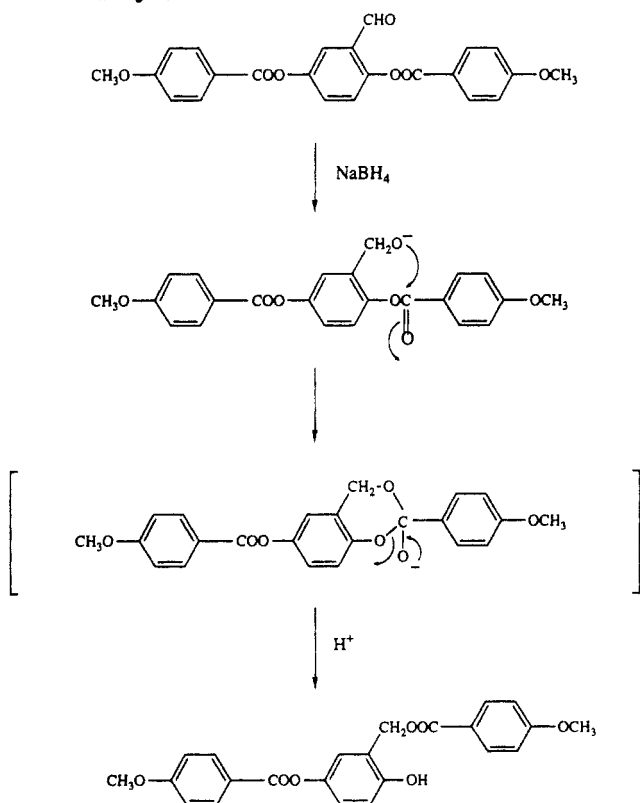
4-[(4'-methoxybenzoyl)oxy]benzaldehyde is selectively reduced to 4-[(4'-methoxybenzoyl)oxy]benzyl alcohol in 30 min at 0 °C. However, these conditions yielded only 37–68% 2,5-bis[(4'-methoxybenzoyl)oxy]benzyl alcohol. In addition, it was always possible to crystallize out 2-[(4'-methoxybenzoyl)oxy]methylene-4-[(4'-methoxybenzoyl)oxy]phenol as a second recrystallization fraction. Formation of this compound can be accounted for by rearrangement of the initial reduction product as shown in Scheme III. This rearrangement is strongly favored by the 6-membered endo-trig cyclic transition state<sup>39</sup> and by phenoxide being a better leaving group than alkoxide. The aldehyde reduction step evidently is not limited by ester reduction but rather by intramolecular transesterification, with the benzyl alcohol being the kinetic reduction product and the phenol being the thermodynamic product. Although Zhou et al. reported that the benzylic <sup>1</sup>H-NMR resonances appear as singlets at 2.14 ppm for both the benzyl alcohol and the corresponding acrylate,<sup>4</sup> this is inconsistent with typical spectral data for such groups.<sup>40</sup> The resonances reported in the Experimental Section of this paper at 4.69 and 5.16–5.36 ppm for the benzyl alcohol and benzyl esters, respectively, and 2.16 and 8.38 ppm for the corresponding OH protons are consistent with established values.

Monomers were prepared using both products of the reduction step in order to establish whether or not the

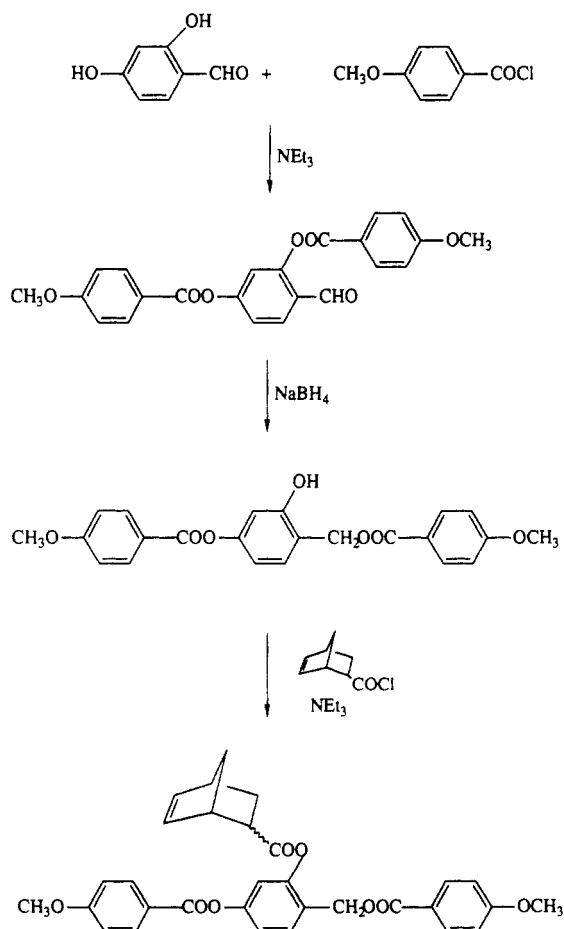
**Scheme II**  
**Two-Route Synthesis of Monomers II-*n***



**Scheme III**  
**Intramolecular Transesterification of the Initial Aldehyde Reduction Product of Monomer II-1**



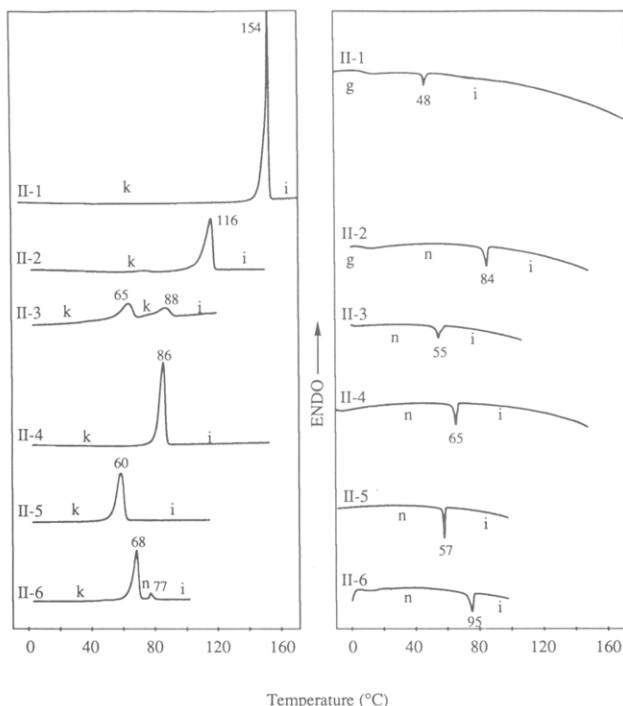
**Scheme IV**  
**Synthesis of Monomer IV-1**



benzyl ester unit is mesogenic. We also synthesized the corresponding para-substituted benzyl ester unit of monomer IV-1 by allowing the rearrangement step to go to completion during reduction of 2,4-bis[(4'-methoxybenzoyl)oxy]benzaldehyde (Scheme IV). The reaction medium rapidly becomes heterogeneous during reduction of the precursors of both II-1 and IV-1, which evidently slows the rearrangement step. When the products of reduction

remain in solution, such as when DMSO/EtOH is used as the solvent system, only the rearranged products are obtained. In addition, due to the increased solubility of the 2,5-bis[(4'-*n*-alkoxybenzoyl)oxy]benzaldehydes with





**Figure 2.** DSC equilibrium heating scans and cooling scans of monomers II-*n*.

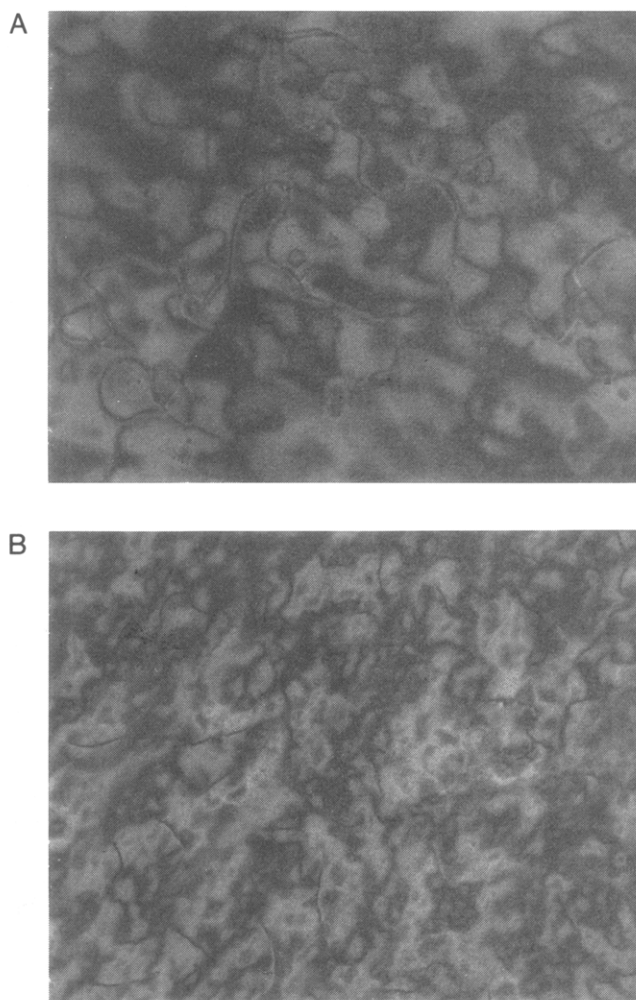
longer *n*-alkoxy substituents, rearrangement to the phenol predominates, and the two products are not easily separated by fractional recrystallization. We therefore established the alternative synthetic route outlined in Scheme II for the synthesis of monomers II-*n* with *n* ≥ 2. It has the advantage that larger quantities of monomer can be synthesized, both because all steps proceed in high yield and because the hydroquinone reagent is available in much larger quantities at lower prices than 2,5-dihydroxybenzaldehyde. In this case, the mesogen is functionalized by bromination under free-radical conditions, followed by solid-liquid phase-transfer-catalyzed esterification of the resulting benzyl bromide. Since the potassium bicyclo[2.2.1]hept-2-ene-5-carboxylate was prepared starting with the bicyclo[2.2.1]hept-2-ene-5-carboxyl chloride used in the first route, monomers with the same ratio of endo and exo isomers (86:14) were obtained in either case.

The DSC traces obtained on heating and on cooling monomers II-*n* are presented in Figure 2, and the thermal transitions are summarized in Table II. Again, the heating scans are primarily from the first run, representing samples crystallized from solution. Compared to monomers I-*n*, these compounds crystallize with much more difficulty, as is to be expected because of the less symmetric and more bulky lateral substituents and because of the presence of isomers. With the exception of II-1, which forms an isotropic glass, nematic glasses are obtained in most cases upon cooling from the isotropic melt. However, polarized optical microscopy of II-1 demonstrates that some crystallites also are forming above  $T_g$ , which may be the source of the small exotherm seen in the DSC cooling scan (Figure 2). Only II-6 forms an enantiotropic nematic mesophase and crystallizes on cooling at approximately 0 °C. Monomers II-1, II-2, and II-4 recrystallize on heating above the glass transition. Neither monomers II-3 nor II-5 recrystallize easily from the melt. Representative polarized optical micrographs showing the nematic textures of I-7 and II-6 are presented in Figure 3. Monomers III-1 and IV-1 are not mesomorphic and form isotropic glasses upon cooling the melt of solution-crystallized samples.

**Table II**  
**Thermal Transitions and Thermodynamic Parameters of Monomers II-*n*<sup>a</sup>**

monomer	phase transitions, °C (corresponding $\Delta H$ , kJ/mol)	
	1st line	2nd line
II-1	k 153.6 (50.2) i	i 10.4 g
II-2	k 115.5 (32.3) [n 86.9 (1.29)] i	i 84.1 (1.66) n 7.4 g
II-3	k 65.2 (14.2) k 88.3 (10.6) [n 54.3 (1.37)] i	i 54.8 (1.23) n
II-4	k 86.5 (39.2) [n 67.8 (1.63)] i	i 64.7 (1.69) n
II-5	k 59.9 (31.0) [n 60.3 (1.31)] i	i 57.2 (1.37) n
II-6	k 68.3 (24.3) n 77.4 (1.65) i	i 74.4 (1.93) n

<sup>a</sup> g = glass, k = crystalline, n = nematic, i = isotropic; [monotropic]; 1st line obtained from equilibrium heating scan, 2nd line obtained on cooling.



**Figure 3.** Polarized optical micrographs (magnification 160X) of the threaded marbled nematic textures observed on cooling (A) monomer I-7, 77.4 °C, and (B) monomer II-6, 75.6 °C.

The results of the ring-opening metathesis polymerization of monomers I-IV are summarized in Tables III and IV. Benzylidene-terminated polymers of varying molecular weights were obtained by reacting the appropriate molar ratio of monomer and Mo(CHMe<sub>2</sub>Ph)(NAr)-(O-*t*-Bu)<sub>2</sub> initiator, followed by termination with benzaldehyde. Although the polymerizations were quantitative, the polymers became more soluble as the length of the *n*-alkoxy substituents increased. Most of the polymers precipitated better from hexane than from methanol.

**Table III**  
**Polymerization of Monomers I-*n* and Characterization of the Resulting Polymers<sup>a</sup>**

monomer	[M] <sub>0</sub> /[I] <sub>0</sub>	yield (%)	GPC			DSC: <i>T</i> <sub>g</sub> , °C	TGA	
			<i>M</i> <sub>n</sub>	<i>M</i> <sub>w</sub> / <i>M</i> <sub>n</sub>	<i>X</i> <sub>n</sub>		dec temp, °C	% wt loss
I-1	40	99	12 371	1.06	28	186		
I-1	69	90	29 203	1.16	66	196	371–423	61.7
I-1	101	94	33 296	1.21	75	195		
I-2	51	95	20 893	1.08	44	179	376–426	61.9
I-3	51	93	16 996	1.06	35	161	377–429	65.2
I-4	51	86	39 642	1.19	72		385–429	66.3
I-5	51	93	27 158	1.10	49		383–433	69.6
I-6	51	93	36 951	1.13	51		385–433	70.2
I-7	50	89	33 828	1.09	50		396–437	71.8
I-8	51	95	23 098	1.15	36		388–438	71.5
I-9	52	95	40 352	1.13	60		391–437	72.5

<sup>a</sup> Reaction time 2.5–3.5 h.

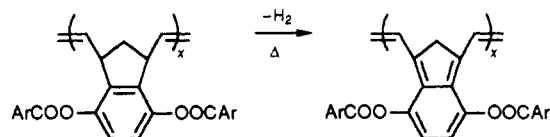
However, poly(I-*n*) polymers with *n* ≥ 7 were almost completely soluble in hexanes and therefore were precipitated in methanol.

The GPC traces of poly(I-*n*) and poly(II-*n*) used to establish their thermotropic behavior are presented in Figure 4. As demonstrated in Table III, we attempted to polymerize monomers I-*n* primarily with 50 repeat units. The molecular weights determined by GPC analysis using polystyrene standards correspond fairly well to the theoretical values, and fairly narrow polydispersities were obtained. Using approximately 50 equiv of monomer I-*n* per 1 equiv of initiator resulted in polymers with 35–72 repeat units. This demonstrates that it is possible to control the molecular weight of mesogenic norbornene monomers containing phenyl benzoate units by ROMP; the variation in the observed versus theoretical molecular weights is primarily due to errors in weighting only a few milligrams of initiator. Although not exact, we previously found that the GPC-determined molecular weights (versus polystyrene) of conventional SCLCPs prepared by ROMP also correspond to the theoretical values.<sup>25,26</sup>

Monomers II-1, III-1, and IV-1 prepared by esterification of bicyclo[2.2.1]hept-2-ene-5-carboxyl chloride with the appropriate alcohol also polymerize cleanly. However, monomers II-*n* prepared by phase-transfer-catalyzed esterification of the corresponding 2,5-bis[(4'-*n*-alkoxybenzoyl)oxy]benzyl bromide generally yielded polymers with a small amount of a double molecular weight peak and/or a small amount of a much higher molecular weight fraction, even after extensive purification of the monomers. In all cases, thin-layer chromatography (TLC) of the monomers showed a single spot in all solvent systems. As stated in the Experimental Section, the <sup>1</sup>H-NMR spectra of the benzyl bromides contained two minor, unidentified singlets at 6.85 and 7.77 ppm which may be due to an aryl bromide and ArCHBr<sub>2</sub>. These impurities could be removed by passing the monomers through basic activated Al<sub>2</sub>O<sub>3</sub>. However, the fact that these monomers still could not be polymerized cleanly demonstrates that this alternative route for the synthesis of monomers II-*n* is not ideal when they are to be used for ROMP. Nevertheless, it did enable us to determine the thermotropic behavior of the desired polymers with narrow molecular weight distributions. Although the high molecular weight fraction substantially broadened the original polymers' polydispersities, it was easily removed in all cases by a single fractional precipitation. We also removed a minor double molecular weight shoulder (original *M*<sub>w</sub>/*M*<sub>n</sub> = 1.26) from the 100-mer of poly(II-1), which in this case is associated with insufficient degassing of the solvent used for polymerization.

The expanded DSC traces obtained on heating poly(I-*n*) are presented in Figure 5. With the exception of the baseline noise, these thermograms are quite featureless. Only poly(I-1) exhibits a well-defined *T*<sub>g</sub> and what appears to be an ordering exotherm on the first heating scan. Poly(I-2) and poly(I-3) also appear to undergo a glass transition or softening point. The softening points of the polymers with longer *n*-alkoxy substituents are not detected, and in no case is an isotropization endotherm observed. Polarized optical microscopy indicates that poly(I-1) is birefringent at temperatures above the exotherm. However, the sample simultaneously begins to darken at this temperature, indicating that some sort of decomposition takes place. It also becomes increasingly difficult to shear the film as would be expected if oxidative cross-linking occurred.

Heating the poly(I-*n*) samples to approximately 300 °C in the DSC results in soluble red glasses. Figure 6 shows the UV/vis spectra of poly(I-1) before and after DSC analysis. The relative intensity of the absorbances at 248 and 296 nm reverses, and new resonances appear at 350, 368, and 390 nm, as well as an absorption tail at longer wavelengths. In addition, the absorbances at 248 and 296 nm develop fine structure. The absorption pattern at 350–390 nm is typical of sequences of conjugated double bonds<sup>41</sup> and may be accounted for by loss of hydrogen at the allylic/benzylic positions of the polymer backbone.



However, the cyclopentadiene ring of the resulting non-aromatic repeat unit should immediately undergo a facile [1,5] sigmatropic rearrangement<sup>42</sup> to a vinylidene repeat unit containing an aromatic ring. Maximum conjugation would occur for this system by [1,5] sigmatropic rearrangements of two adjacent repeat units as shown below. The UV/vis absorption pattern at 350–390 nm shown in Figure 6 is in fact nearly identical to that of cinnamylidenindene in the same region.<sup>43</sup>

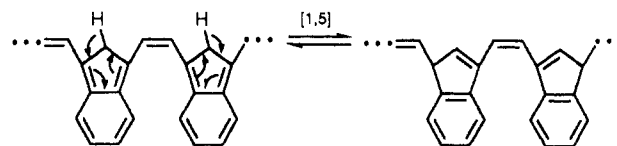


Table III also includes the TGA analysis of poly(I-*n*), and a typical TGA scan is presented in Figure 7 for poly(I-1). All poly(I-*n*) samples are stable up to approximately 370 °C and then decompose in one step with 60–72% weight loss. Loss of H<sub>2</sub> cannot be detected, since it corresponds to only 0.30–0.46% weight loss.

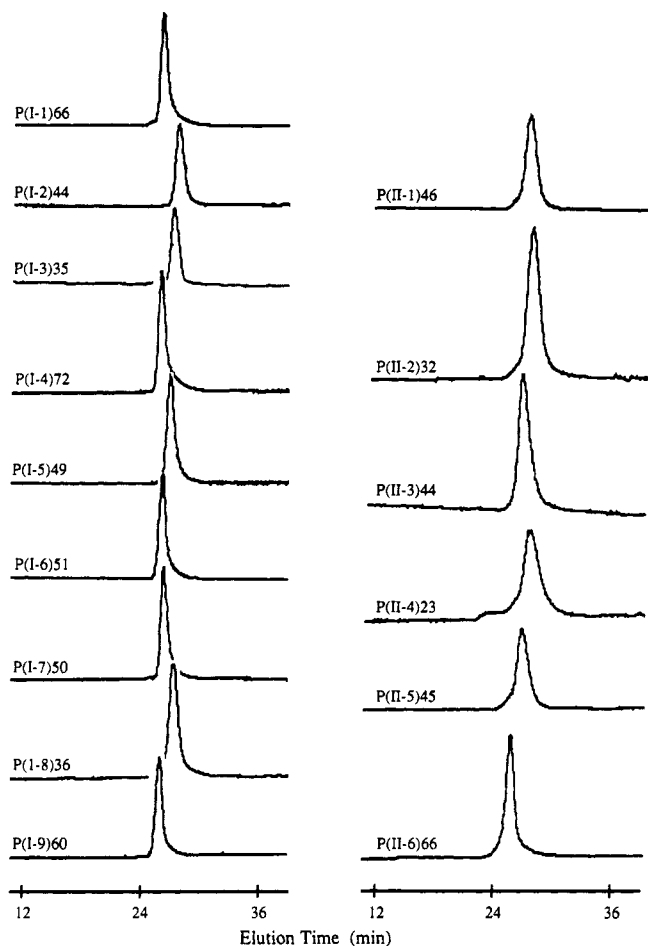
Previous studies on laterally substituted SCLCPs have demonstrated that both the glass transition and isotropization temperatures decrease as the length of the *n*-alkoxy substituent increases.<sup>3,5,12</sup> Polarized optical microscopy confirms that the glass transition or softening point of poly(I-*n*) decreases as *n* increases. Although neither transition is detected by DSC for the entire series, it becomes possible to prepare films for microscopic analysis at increasingly lower temperatures with longer *n*-alkoxy substituents. For example, it is possible to prepare a colorless, fluid film of poly(I-7) at 165 °C that is anisotropic between crossed polarizers. Only the edges of the polymer film darken at this temperature. Since the film is prepared by shearing and since it is not possible to heat through an isotropic transition in order to relieve the alignment, the



**Table IV**  
**Polymerization of Monomers II-*n*, III-1, and IV-1 and Characterization of the Resulting Polymers<sup>a</sup>**

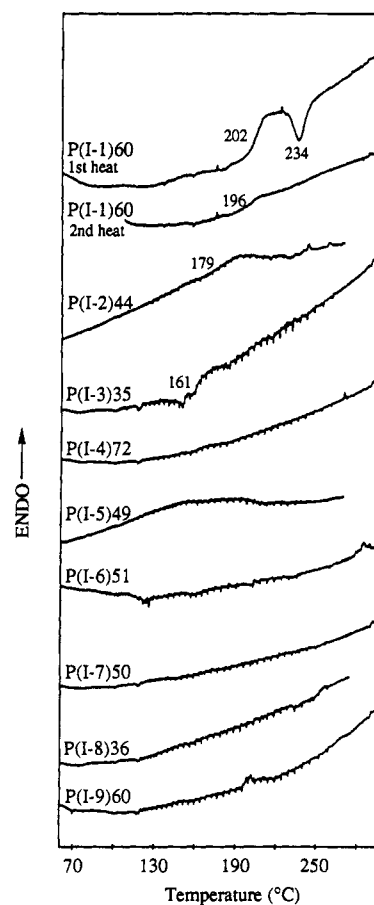
monomer	method <sup>b</sup>	[M] <sub>0</sub> /[I] <sub>0</sub>	time (h)	yield (%)	GPC			phase transitions, °C (enthalpy changes, kJ/mru)	
					<i>M<sub>n</sub></i>	<i>M<sub>w</sub></i> / <i>M<sub>n</sub></i>	<i>X<sub>n</sub></i>	heating	cooling
II-1	A	3.8	0.5	91	2 670	1.16	5.1	g 79.2 n 131.4 (1.80) i	i 128.0 (1.82) n 76.2 g
II-1	A	10.1	0.5	89	4 292	1.27	8.1	g 85.3 n 145.3 (2.36) i	i 142.7 (2.19) n 83.0 g
II-1	B	9.7	0.5	91	4 320	1.20	8.2	g 89.6 n 145.9 (2.16) i	i 142.1 (2.19) n 84.4 g
II-1	A	19.5	1.5	91	7 221	1.12	13.7	g 91.4 n 155.2 (2.39) i	i 152.0 (2.14) n 90.8 g
II-1	B	19.5	2.0	94	7 707	1.18	14.6	g 93.9 n 156.4 (2.88) i	i 153.6 (2.43) n 88.0 g
II-1	B	49.6	0.5	91	20 773 <sup>c</sup>	1.13 <sup>c</sup>	39.3 <sup>c</sup>	g 96.9 n 162.6 (2.76) i	i 158.9 (2.46) n 90.7 g
II-1	A	30.7	2.5	93	24 051	1.13	45.5	g 97.7 n 163.5 (2.76) i	i 159.7 (2.44) n 93.3 g
II-1	A	68.6	2.5	96	52 631 <sup>c</sup>	1.16 <sup>c</sup>	99.6 <sup>c</sup>	g 97.1 n 162.5 (2.63) i	i 159.3 (2.46) n 91.8 g
II-2	B	39.0	2.5	89	20 380	2.36	36.6		
					17 990 <sup>c</sup>	1.19 <sup>c</sup>	32.3 <sup>c</sup>	g 92.5 n 172.2 (3.96) i	i 168.3 (3.49) n 87.4 g
II-3	B	45.3	2.0	87	39 378	2.74	67.4		
					25 826 <sup>c</sup>	1.24 <sup>c</sup>	44.2 <sup>c</sup>	g 83.0 n 140.2 (2.88) i	i 137.9 (2.43) n 77.1 g
II-4	B	4.7	0.5	89	5 178	1.16	8.4	g 62.8 n 122.8 (3.04) i	i 120.1 (2.77) n 56.6 g
II-4	B	39.2	3.0	86	14 316	1.17	23.4	g 73.4 n 138.5 (3.57) i	i 133.3 (3.36) n 67.4 g
II-5	B	50.8	2.0	72	34 050	2.20	53.1		
					28 748 <sup>c</sup>	1.18 <sup>c</sup>	44.9 <sup>c</sup>	g 60.3 n 123.2 (3.14) i	i 119.8 (2.76) n 56.0 g
II-6	B	52.4	2.0	78	55 780	2.36	87.1		
					44 082 <sup>c</sup>	1.24 <sup>c</sup>	65.9 <sup>c</sup>	g 55.6 n 126.1 (3.72) i	i 121.9 (3.63) n 49.5 g
III-1	A	30.2	2.5	95	15 198	1.20	28.8	g 77.5 i	i 65.7 g
III-1	A	50.7	2.5	97	21 235	1.14	40.2	g 78.9 i	i 71.3 g
IV-1	A	51.2	2.5	96	20 528	1.15	38.8	g 81.4 i	i 75.5 g
IV-1	A	158.6	2.0	92	89 008	1.20	168.4	g 84.1 i	i 79.3 g

<sup>a</sup> g = glassy, n = nematic, i = isotropic. <sup>b</sup> Method A = reaction with NBE(COCl); Method B = PTC reaction with NBE(COOK). <sup>c</sup> Fractionated polymer; *M<sub>n</sub>* and *M<sub>w</sub>*/*M<sub>n</sub>* of the original polymer polymer listed on the previous line.



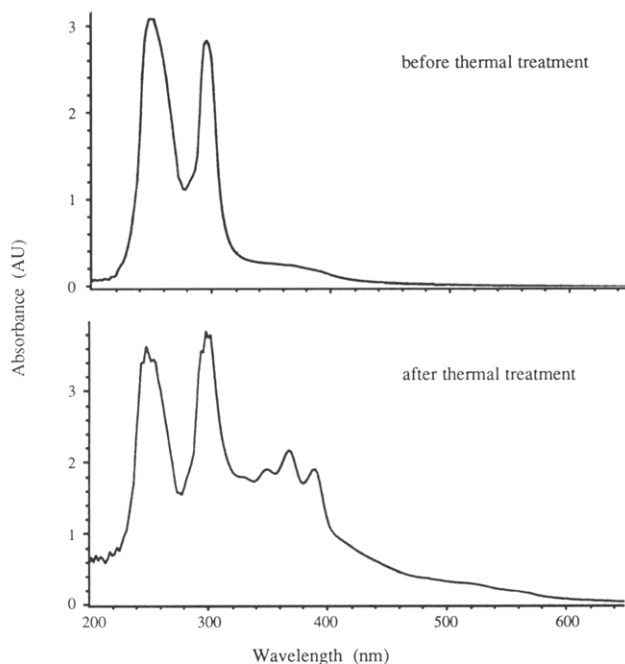
**Figure 4.** Gel permeation chromatograms of poly(I-*n*) and poly(II-*n*) with the designated degrees of polymerization.

representative nematic texture of poly(I-8) shown in Figure 8A is homogeneous with only a few schlieren threads. Therefore, poly(I-*n*) with *n* ≥ 7 form nematic mesophases; poly(I-*n*) with *n* < 7 also evidently form nematic mesophases, but the fluid nature of the phase is masked by simultaneous decomposition and apparently oxidative cross-linking at elevated temperatures. DSC, TGA, optical

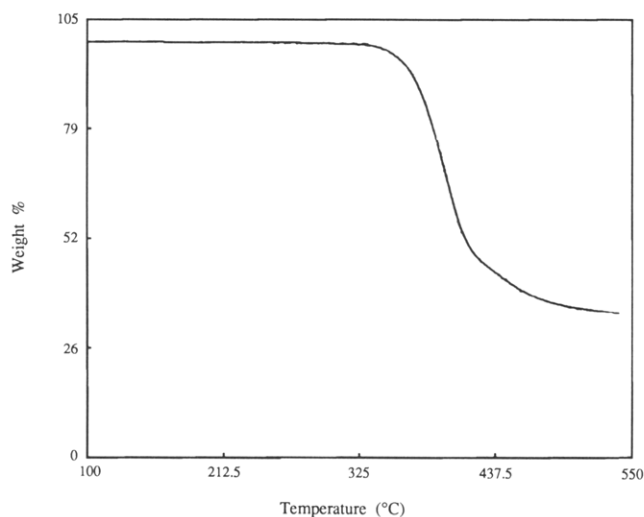


**Figure 5.** DSC heating scans of poly(I-*n*) with the designated degrees of polymerization.

microscopy, and UV/vis spectroscopic analyses are consistent with loss of hydrogen at elevated temperatures to form conjugated sequences involving indene repeat units. We do not know at this time if it is possible to obtain polymers with fully rearranged backbones; heating poly(I-*n*) at 300 °C for extended periods of time yields insoluble material, presumably due to oxidative cross-linking.



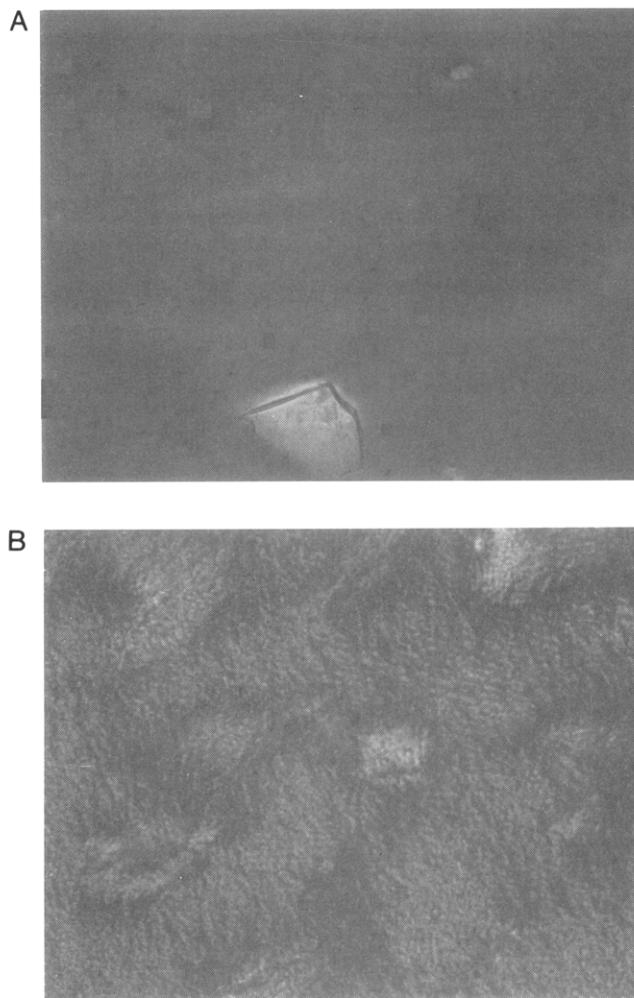
**Figure 6.** UV/vis spectra of poly(I-1)66 before and after heating to 300 °C in the DSC.



**Figure 7.** TGA scan of poly(I-1)66 under nitrogen, 5 °C/min.

The poly(II-*n*) series was prepared in order to determine the effect of molecular weight on the thermotropic behavior of laterally attached SCLCPs. The transition temperatures of poly(II-*n*) are lower than those of poly(I-*n*) due to the use of a short spacer between the polymer and mesogenic units and due to the polymers' regioirregularity. Since the mesogen is asymmetric, head-to-head, head-to-tail, and tail-to-tail sequences of endo- and exo-substituted repeat units are possible, as well as the presence of both *cis* and *trans* double bonds. Figures 9–12 and Table IV confirm that poly(II-*n*) displays both a glass and a first-order transition. The textures observed by polarized optical microscopy and the small enthalpy changes are characteristic of nematic mesophases. Poly(II-*n*) (*n* = 1–6) displays only an enantiotropic nematic mesophase over the entire range of molecular weights and *n*-alkoxy substituent lengths. Figure 8B presents a representative polarized optical micrograph showing the schlieren nematic texture of poly(II-1).

The DSC traces obtained on heating and on cooling poly(II-1) with degrees of polymerization of 5–100 are presented in Figure 9, and the thermal transitions are



**Figure 8.** Polarized optical micrographs (magnification 160X) of the nematic textures of (A) poly(I-8)36, homogeneous, 165 °C, and (B) poly(II-1)39, 159.7 °C.

summarized in Table IV. The second and subsequent heating scans are identical, as are all cooling scans. These polymers undergo an ordering exotherm at the glass transition temperature on the first heating scan, indicating that they are disordered in solution. As shown in Figure 9, the isotropization endotherms are extremely sharp. Although the transitions of some samples are sharper than others, the variation in peak width cannot be assigned either to changes in molecular weight or to the route used to synthesize the monomer. In general, the change in enthalpy of the nematic–isotropic transition is also relatively independent of molecular weight, except at the shortest chain length.

The phase-transition temperatures of poly(II-1) obtained on heating are plotted in Figure 10 as a function of the chain length determined by GPC. Both the glass transition and isotropization temperatures become independent of molecular weight at approximately 25 repeat units. This is comparable to our previous results on conventional SCLCPs with polynorbornene backbones.<sup>25,26</sup> In order to compare the thermotropic behavior of poly(II-*n*) samples with different *n*-alkoxy chain lengths, it is therefore necessary to compare polymers with at least 25 repeat units.

The DSC traces obtained on heating and on cooling poly(II-*n*) with *n* = 1–6 and at least 23 repeat units are presented in Figure 11. The isotropization transitions are sharp in all cases. The corresponding transition temperatures obtained on heating are plotted in Figure 12 as a

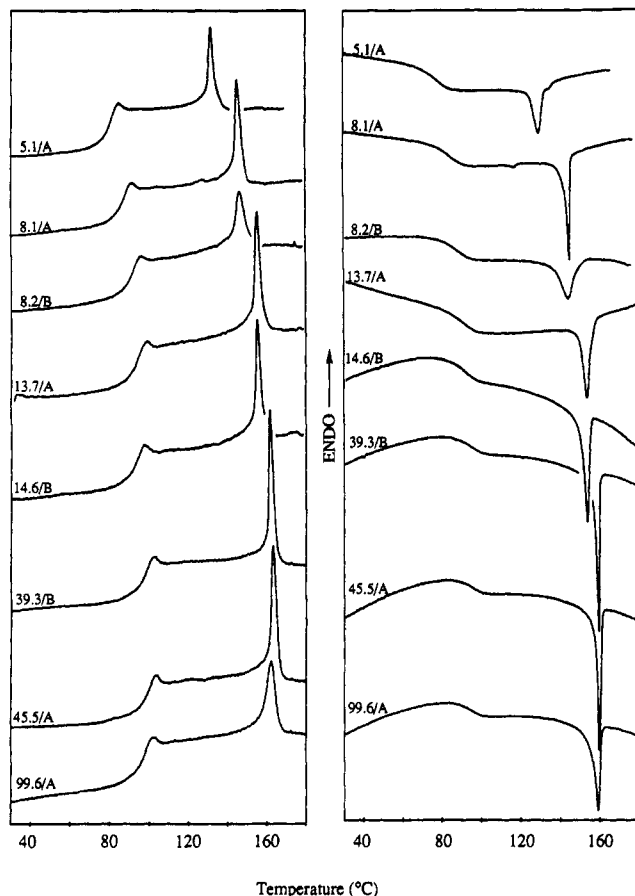


Figure 9. DSC heating and cooling scans of poly(II-1) with the designated degrees of polymerization and the designated method used to synthesize the monomer (corresponds to Table IV).

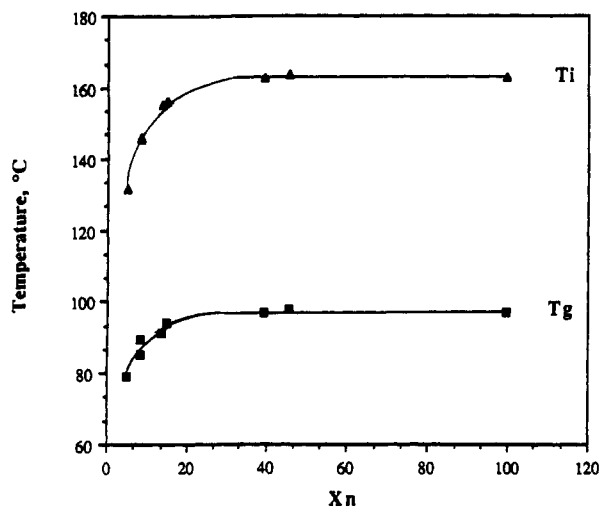


Figure 10. Dependence of the phase transitions of poly(II-1) on the GPC-determined degrees of polymerization.

function of the number of methylenic units in the  $n$ -alkoxy substituents. Again,  $T_g$  decreases as the length of the  $n$ -alkoxy substituent increases. The isotropization temperatures also generally decrease with increasing  $n$ , but with an odd-even alternation. As with other laterally attached SCLCPs based on the same mesogen,<sup>3,5</sup> the even-membered substituents display the higher isotropization temperatures. Therefore, the temperature window of the nematic mesophase broadens as the length of the  $n$ -alkoxy substituent increases, with the even-membered substituents having broader and more stable nemesophases than the odd-membered substituents.

With a glass transition of 38–40 °C, the polynorbornene backbone is less flexible than the polyacrylate backbone

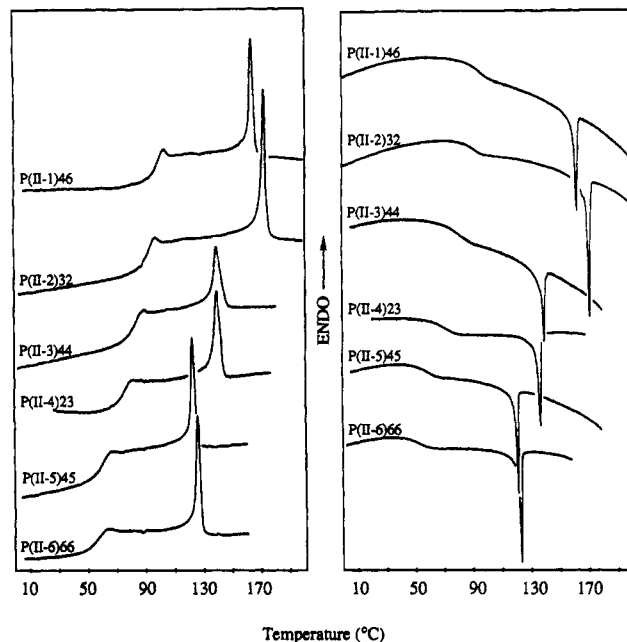


Figure 11. DSC heating and cooling scans of poly(II- $n$ ) with the designated degrees of polymerization.

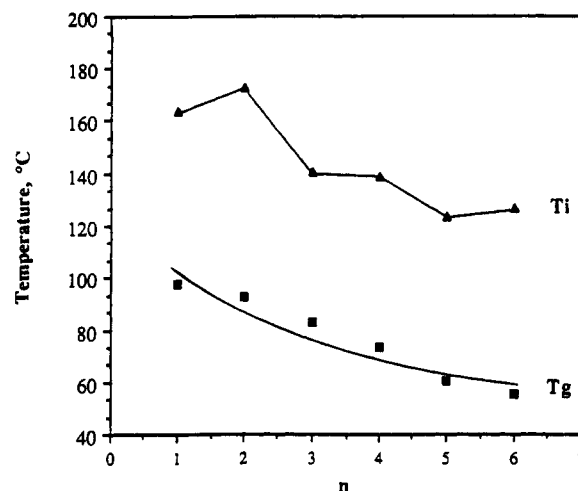


Figure 12. Dependence of the phase transitions of poly(II- $n$ ) on the number of methylenic units in the  $n$ -alkoxy substituents.

(polymethacrylate  $T_g = 10$  °C<sup>44</sup>). The poly(II- $n$ ) series presented in this paper are direct analogs of the poly-[[[2,5-bis[(4'- $n$ -alkoxybenzoyl)oxy]benzyl]oxy]acrylate]s ( $n = 1, 2, 4$ ) reported by Zhou et al.<sup>4</sup> Surprisingly, the length of the  $n$ -alkoxy substituent had very little effect on the transition temperatures of the polyacrylates. The methoxy derivative displays a  $T_g$  at 103 °C and isotropization at 160 °C, which is nearly identical to poly(II-1) ( $g$  97 n 163 i). This indicates that the polymer backbone has very little effect on the thermotropic behavior of laterally attached SCLCPs with identical mesogens, spacers, and substituents. Similar results were obtained with laterally attached polyacrylates, poly(chloroacrylates), and polymethacrylates based on the same mesogen but with a long spacer.<sup>5</sup>

Poly(II-1), poly(III-1), and poly(IV-1) are constitutional isomers. Their thermal transitions are summarized in Table IV. The mesogen of poly(II-1) is a symmetric bis(benzoate) phenyl unit which is connected to the polymer backbone through a  $\text{CH}_2\text{OOC}$  spacer. In contrast, a mixed phenyl ester/benzyl ester unit is connected to the poly(III-1) and poly(IV-1) backbones through an  $\text{OOC}$  spacer. Not surprisingly, poly(III-1) with the kinked "mesogen" is amorphous. However, its constitutional isomer with

the analogous linear mixed "mesogen" is also amorphous. Compared to the phenyl benzoate unit which has double-bond character at the O-CO link, the benzyl ester unit is flexible and evidently not linear enough to induce mesomorphic behavior in even poly(IV-1). The  $T_g$  of poly(IV-1) is slightly higher than that of poly(III-1).

## Conclusions

Ring-opening metathesis polymerization can be used to polymerize norbornene derivatives containing 2,5-bis[(4'-*n*-alkoxybenzoyloxy)] mesogens to give polymers with controllable molecular weight and fairly narrow polydispersity. Enantiotropic nematic mesophases are obtained from these laterally attached SCLCPs, even when the mesogen is fused to the polymer backbone. The phase behavior becomes independent of molecular weight at approximately 25 repeat units, and the transition temperatures decrease with increasing length of the *n*-alkoxy substituents. Polymers with an even number of methylenic units in the substituents display higher isotropization temperatures and more stable mesophases than polymers with odd-membered substituents. The polymer backbone has little effect on the transition temperatures of laterally attached SCLCPs displaying nematic mesophases, even when the chemical structures of the backbones are substantially different, as with polynorbornenes versus polyacrylates. This result is consistent with the proposal that mesogens jacket the extended polymer chain.

**Acknowledgment.** R.R.S. thanks the Office of Naval Research for support.

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**Registry No.** I-1, 143903-14-4; I-1 (homopolymer), 143903-42-8; I-2, 143903-15-5; I-2 (homopolymer), 143903-43-9; I-3, 143903-16-6; I-3 (homopolymer), 143903-44-0; I-4, 143903-17-7; I-4 (homopolymer), 143903-45-1; I-5, 143903-18-8; I-5 (homopolymer), 143903-46-2; I-6, 143903-19-9; I-6 (homopolymer), 143903-47-3; I-7, 143903-20-2; I-7 (homopolymer), 143903-48-4; I-8, 143903-21-3; I-8 (homopolymer), 143903-49-5; I-9, 143903-22-4; I-9 (homopolymer), 143903-50-8; II-1, 143903-30-4; II-1 (homopolymer), 143903-51-9; II-1 aldehyde base, 105252-90-2; II-1 toluene base, 51933-65-4; II-1  $\alpha$ -bromotolyl base, 143903-26-8; II-1  $\alpha$ -hydroxytolyl base, 105252-91-3; II-2, 143903-33-7; II-2 (homopolymer), 143903-52-0; II-2 toluene base, 76387-03-6; II-2  $\alpha$ -bromotolyl base, 143903-27-9; II-3, 143903-34-8; II-3 (homopolymer), 143903-53-1; II-3 toluene base, 76387-02-5; II-3  $\alpha$ -bromotolyl base, 143903-28-0; II-4, 143903-35-9; II-4 (homopolymer), 143903-54-2; II-4 toluene base, 66786-95-6; II-4  $\alpha$ -bromotolyl base, 143903-29-1; II-5, 143903-36-0; II-5 (homopolymer), 143903-55-3; II-5 toluene base, 76387-01-4; II-5  $\alpha$ -bromotolyl base, 143923-64-2; II-6, 143903-37-1; II-6 (homopolymer), 143903-56-4; II-6 toluene base, 26314-54-5; II-6  $\alpha$ -bromotolyl base, 143923-65-3; III-1, 143903-31-5; III-1 (homopolymer), 143903-57-5; III-1 free alcohol, 143903-24-6; IV-1, 143903-32-6; IV-1 (homopolymer), 143903-58-6; IV-1 free alcohol, 143903-25-7; 4-MeOC<sub>6</sub>H<sub>4</sub>COCl, 100-07-2; 2,5-(OH)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CHO, 1194-98-5; 2,4-(MeOC<sub>6</sub>H<sub>4</sub>-*p*-CO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CHO, 143903-23-5; 5,8-dihydroxy-1,2,3,4-tetrahydronaphthalene, 13623-10-4; bicyclo[2.2.1]hept-2-ene-5-carboxyl chloride, 27063-48-5; potassium bicyclo[2.2.1]hept-2-ene-5-carboxylate, 53551-88-5.