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Synthesis of ABA Triblock Copolymers via Ring Opening Metathesis Polymerization Using a Bimetallic Initiator: Influence of a Flexible Spacer in the Side Chain Liquid Crystalline Block

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ABSTRACT: A series of monomers with side chain liquid crystals (SCLCs) were synthesized for ring opening metathesis polymerization (ROMP). The liquid crystals (LCs) used were 4-hydroxybenzoic acid 4-methoxyphenyl ester (**MPOB**-H), which is known to exhibit a nematic liquid crystalline phase, and biphenyl-4-carboxylic acid 4-(1-butoxycarbonylethoxy)phenyl ester (**BPP4**-H), which is known to exhibit a smectic phase. The side chains differed in spacer length, spacer type, and the nature of the LC. Monomers were polymerized using a bimetallic ROMP initiator $[Mo(NAr)(OCMe_3)_2CH]_2C_6H_4$ (where Ar = 2,6-diisopropyl phenyl); both homopolymers and ABA type triblock copolymers, where the B block is the LC functional monomer, and A is methyltetracyclodocene (**MTD**) were prepared. The polymers gave unimodal peak distributions with polydispersities <1.22. Incorporation of a polyoxyethylene spacer decreased the glass transition temperature of the polymer block to −25 from +20 °C, the T_g when an alkyl spacer was used. Although no distinct LC phase was observed with the polyoxyethylene spacer when **MPOB** was used, when **BPP4** was attached via a polyoxyethylene spacer, a distinct liquid crystalline transition was observed. Polymers with an alkyl spacer exhibited liquid crystalline behavior and good phase segregation on the basis of differential scanning calorimetry and small-angle X-ray scattering studies.

Introduction

Block copolymers that contain a side chain liquid crystal (SCLC) block coupled to an amorphous block or blocks offer a unique combination of liquid crystalline and block copolymer properties.[1] This combination is a result of liquid crystal (LC) order confined within the microphase-segregated domains.[2,3] Phase-segregated triblock copolymers in particular are of significant interest because of potential applications as thermoplastic LC elastomers.[4,5] Incorporation of LC side chains within the soft domains of a phase-segregated thermoplastic elastomer (TPE) can produce liquid crystal thermoplastic elastomers (LCTPE) with interesting properties which can be altered and enhanced through processing, such as electromechanical properties, shape memory materials, or other mechanoresponsive elastomers.[3]

Ring opening metathesis polymerization (ROMP) has emerged as a powerful tool for preparing polymers with predictable molecular weights.[6−8] The living nature of some ROMP processes has been utilized successfully to prepare block copolymers.[9−14] Bicycloheptene-derived polymers are the most common polymers prepared via ROMP because of the relative ease in preparation, modification, and their often living characteristics.[6,8] In most cases, the block copolymers were obtained via sequential addition of monomers to monometallic initiators. Recently, we reported a series of bimetallic ROMP initiators with two initiation sites that allow symmetric ABA triblock copolymers to be synthesized through a two-step addition of monomer.[15]

We are particularly interested in ABA triblock copolymers where the A block is amorphous and the B block is a SCLC block with a glass transition temperature (T_g) well below room temperature. Successful synthesis of such triblock copolymers could yield a room-temperature LCTPE.[16−18] Monomers based on bicycloheptenes with SCLC containing nematic LC have been synthesized and polymerized and their properties have been studied.[19−24] The general architecture of these monomers consists of a polymerizable unit (a bicycloheptene in this case), a LC, and a spacer coupling the two. Generally, longer spacers lower the T_g of the polymer block, and influence the LC phase behavior and stability of nematic and smectic phases.[20] There is precedent for alkyl spacers in bicycloheptene-based monomers.[24] However, polyoxyethylene spacers have not been investigated in ROMP polymers despite their success in lowering the T_g of the polymer blocks in other systems.[25] In addition, triblock copolymers prepared by ROMP from monomers that contain polyoxyethylene spacers have not been reported in the literature. We present the synthesis of various bicycloheptene-based monomers with both alkyl and polyoxyethylene spacers and with 4-hydroxybenzoic acid 4-methoxyphenyl (**MPOB**-H) and biphenyl-4-carboxylic acid 4-(1-butoxycarbonylethoxy)-phenyl ester (**BPP4**−H) as the LCs. Thermal, optical and mechanical properties of these polymers, along with their morphologies are discussed in order to evaluate the possibilities of preparing a room-temperature TPE that contains a SCLC block.

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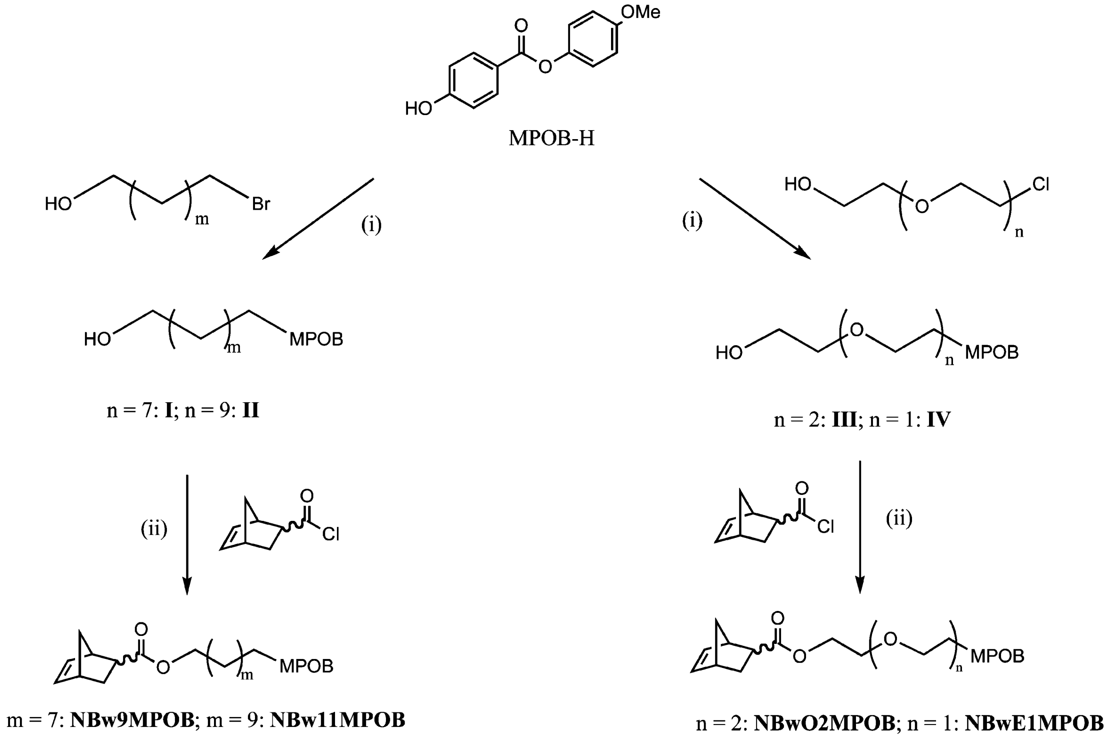
Scheme 1. Synthesis of Monomers NBw9MPOB, NBw11MPOB, NBwO2MPOB, and NBwO1MPOB[a]



[a] Key: (i) KI (catalytic), K_2CO_3, DMSO, 65 °C; (ii) Et_3N, THF, reflux.

Materials and Methods

All polymerizations were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox. 2-Norbornene-5-carboxylic acid chloride (exo:endo = 1:4),[26] 4-hydroxybenzoic acid 4-methoxyphenyl ester,[27] 4-hydroxybenzoic acid 4-(1-butoxycarbonylethoxy)phenyl ester,[25] bicyclo[2.2.1]hept-5-en-2-ylmethanol,[25] and $[Mo(NAr)(OCMe_3)_2CH]_2C_6H_4$[15] (where Ar = 2,6-diisopropylphenyl) were prepared as described in the literature. 1-Chloro-2-[2-(2-chloroethoxy)ethoxy]ethane and 2-[2-(2-chloroethoxy)ethoxy]ethanol were purchased from TCI America, and 11-bromoundecan-1-ol, 9-bromononan-1-ol and 2-(2-chloroethoxy)ethanol were purchased from Aldrich. These reagents were used as received.

NMR spectra were recorded on 500 or 300 MHz Varian spectrometers. ^1H NMR chemical shifts are reported in ppm vs residual protons in the deuterated solvents as follows: δ 7.27 $CDCl_3$; δ 7.16 C_6D_6; δ 2.50 $(CD_3)_2SO$. NMR chemical shifts are reported for the major isomer. The relative molecular weights were determined by gel permeation chromatography (GPC) at room temperature in THF (1 mL/min) or CH_2Cl_2 (1 mL/min) using a system equipped with two Jordi-Gel DVB mixed bed columns (250 mm length × 10 mm inner diameter) assembled in series. A Wyatt Technology mini Dawn light-scattering detector coupled with a Knauer differential refractometer was also employed for the purpose. The GPC columns were calibrated using polystyrene standards (Polymer Laboratories Ltd.). The polymer samples were cast from a concentrated toluene solution onto a Teflon-coated sheet, which was then air-dried for 24 h. A TA Instruments Q1000 differential scanning calorimeter (DSC) was used to determine the thermal transitions, which were read as the maxima and minima of the endothermic and exothermic peaks, respectively. All heating and cooling scans were performed at the rate of 5 °C/min. Glass transition temperatures (T_g) were read as the middle of the change in the heat capacity. A Zeiss Axioskop2 polarized light microscope with a Zeiss AxioCam HRc digital camera was used for the thermal transitions and to analyze the anisotropic textures. The samples were heated using a Linkam THMS 600 hot stage at the rate of 5 °C/min. A TA Instruments Q800 was used for dynamic mechanical analysis (DMA). The heating rate was maintained at 3 °C/min, and an oscillation amplitude of 25 μm and 0.02 MPa of tension at a frequency of 1 Hz were employed. Small-angle X-ray scattering data were collected with a Siemens 2-D SAXS detector. The X-rays were Cu Kα radiation with a wavelength of 0.1542 nm set at 40 kV and 0.66 mA. Silver behenate was used to calibrate the distance between the sample and the detector with a first-order scattering vector q of 1.076 nm^{-1} (with $q = (4\pi \sin \theta)/\lambda$, where 2θ is the scattering angle and λ is the wavelength).

Synthesis of Monomers. The synthesis of monomers **NBw9MPOB**, **NBw11MPOB**, **NBwO2MPOB**, and **NBwO1MPOB** is outlined in Scheme 1.

4-(11-Hydroxyundecyloxy)benzoic Acid 4-Methoxyphenyl Ester (II). 4-Hydroxybenzoic acid 4-methoxyphenyl ester (5.00 g, 2.05×10^{-2} mol) along with K_2CO_3 (5.67 g, 4.10×10^{-2} mol) and KI (100 mg) was dissolved in anhydrous DMSO (100 mL), and 11-bromoundecan-1-ol (5.14 g, 2.05×10^{-2} mol) was added to the mixture, which was then heated at 90 °C for 12 h. The reaction solution was cooled to room temperature and diluted with ethyl acetate (100 mL). The solution was washed with distilled water, and the organic fraction was dried over anhydrous $MgSO_4$. The volatiles were removed in vacuo, and the product was precipitated from diethyl ether as a white solid (7.10 g, 83%): ^1H NMR (C_6D_6, 300 MHz) δ 8.81 (d, 2, aromatic), 7.08 (d, 2, aromatic), 6.77 (d, 2, aromatic), 6.69 (d, 2, aromatic), 3.52 (t, 2, $CH_2OC_6H_4$), 3.37 (t, 2, CH_2OH), 3.24 (s, 3, OCH_3), 1.6−1.2 (m, 18, $(CH_2)_9$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.5, 163.6, 157.3, 144.6, 132.4, 122.7, 114.6, 114.4, 68.43, 63.15, 55.75, 32.93, 29.74, 29.68, 29.66, 29.58, 29.50, 29.24, 26.13, 25.90.

I, **III**, and **IV** were prepared using a method similar to that described for the preparation of **II**.

4-(9-Hydroxynonyloxy)benzoic Acid 4-Methoxyphenyl Ester (I). The yield was 76%: ^1H NMR (C_6D_6, 300 MHz) δ 8.81 (d, 2, aromatic), 7.08 (d, 2, aromatic), 6.77 (d, 2, aromatic), 6.69 (d, 2, aromatic), 3.52 (t, 2, CH_2OPh), 3.37 (t, 2, CH_2OH), 3.24 (s, 3, OCH_3), 1.6−1.2 (br m, 14, $(CH_2)_7$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.5, 163.4, 157.3, 144.6, 132.4, 122.5, 114.6, 114.4, 68.43, 63.15, 55.55, 32.93, 29.54, 29.68, 29.63, 29.58, 26.13, 25.90.

4-{2-[2-(2-Hydroxyethoxy)ethoxy]ethoxy}benzoic Acid 4-Methoxyphenyl Ester (III). The yield was 68%: ^1H NMR (C_6D_6, 300 MHz) δ 8.24 (d, 2, aromatic), 7.06 (d, 2, aromatic), 6.51 (d, 2, aromatic), 6.69 (d, 2, aromatic), 3.65 (t, 2, C*H*$_2$OC$_6$H$_4$), 3.42−3.34 (m, 10, C*H*$_2$C*H*$_2$O), 3.24 (s, 3, O*Me*); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 165.4, 163.2, 157.4, 144.7, 132.6, 132.5, 132.4, 122.3, 114.7, 114.5, 69.71, 69.69, 69.59, 69.56, 67.79, 63.33, 55.79.

4-[2-(2-Hydroxyethoxy)ethoxy]benzoic Acid 4-Methoxyphenyl Ester (IV). The yield was 70%: ^{1}H NMR (CDCl$_3$, 300 MHz) δ 8.15 (d, 2, aromatic), 7.12 (d, 2, aromatic), 6.97 (dd, 4, aromatic), 4.45 (t, 2, C*H*$_2$OPh), 3.85 (t, 2, C*H*$_2$OCH$_2$), 3.83 (s, 3, O*Me*), 3.80 (t, 2, HOC*H*$_2$), 3.71 (t, 2, C*H*$_2$OCH$_2$); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 165.4, 163.0, 157.3, 144.6, 132.4, 122.6, 114.6, 114.5, 72.79, 69.54, 67.70, 61.85, 55.73.

Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid 11-[4-(4-Methoxyphenoxycarbonyl)phenoxy]undecyl Ester (NBw11MPOB). Bicyclo[2.2.1]hept-5-ene-2-carbonyl chloride (1.90 g, 1.21 × 10^{-2} mol) was added dropwise to a refluxing solution of 4-(11-hydroxyundecyloxy)benzoic acid 4-methoxyphenyl ester (**II**) (5 g, 1.21 × 10^{-2} mol) and Et$_3$N (1.70 mL, 1.21 × 10^{-2} mol) in THF (40 mL), and the reaction was refluxed for 12 h. The reaction solution was cooled to room temperature and diluted with diethyl ether (50 mL). The reaction solution was washed with water and the organic layer was dried over anhydrous MgSO$_4$ and concentrated. The crude organic product was purified through column chromatography using silica as the static phase and hexanes:ethyl acetate (2:1) as the eluent. The product was obtained as a white solid (5.30 g, 80%): ^{1}H NMR (C$_6$D$_6$, 500 MHz) δ 8.26 (d, 2, aromatic), 7.03 (d, 2, aromatic), 6.68 (dd, 4, aromatic), 6.06 (s, 2, *H*C═C*H*), 4.0 (tt, 2, C*H*$_2$CO$_2$), 3.47 (t, 2, C*H*$_2$OPh), 3.19 (s, 3, OC*H*$_3$), 3.15 (s, 1, HCC*H*(CH$_2$)CH), 2.75 (quin, 1, C*H*CO$_2$), 2.59 (s, 1, HCCH(C*H*)CH$_2$)), 1.8−1.0 (m, 17, C*H*$_2$s and one bridging C*H*$_2$ of norbornene), (d, 1, one bridging C*H*$_2$ of norbornene, *J* = 8.1 Hz); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 174.9, 165.4, 163.5, 157.3, 144.6, 137.8, 132.5, 132.3, 122.6, 114.5, 114.3, 68.37, 64.41, 55.67, 49.73, 45.83, 43.50, 42.64, 29.63, 29.61, 29.48, 29.34, 29.27, 29.21, 28.79, 26.10, 26.06. HRMS (ESI): calcd for C$_{33}$H$_{42}$O$_6$ [M + Na], 557.2879; found, 557.2889.

NBw9MPOB, NBwO2MPOB, and **NBwO1MPOB** were all prepared in the same manner as described for **NBw11MPOB.**

Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid 9-[4-(4-Methoxyphenoxycarbonyl)phenoxy]nonyl Ester (NBw9MPOB). The yield was 86%: ^{1}H NMR (C$_6$D$_6$, 500 MHz) δ 8.26 (d, 2, aromatic), 7.03 (d, 2, aromatic), 6.68 (dd, 4, aromatic), 6.06 (s, 2, *H*C═C*H*), 4.0 (tt, 2, C*H*$_2$CO$_2$ (endo/exo)), 3.47 (t, 2, C*H*$_2$OPh), 3.19 (s, 3, OC*H*$_3$), 3.15 (s, 1, HCC*H*(CH$_2$)CH), 2.75 (quin, 1, C*H*CO$_2$), 2.59 (s, 1, HCC*H*(CH$_2$)CH$_2$)), 1.8−1.0 (m, 15, C*H*$_2$s and one bridging H of norbornene), (d, 1, one bridging *H* of norbornene, *J* = 8.1 Hz); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 175.0, 158.8, 158.4, 137.9, 133.6, 133.3, 132.5, 127.8, 114.9, 114.3, 68.16, 64.48, 55.44, 49.78, 45.88, 43.51, 42.69, 29.72, 29.67, 29.57, 29.47, 29.39, 29.32, 28.84, 26.23, 26.12. HRMS (ESI): calcd for C$_{31}$H$_{38}$O$_6$ [M + Na], 529.2561; found, 529.2541.

Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid 2-(2-{2-[4-(4-Methoxyphenoxycarbonyl)phenoxy]ethoxy}ethoxy)ethyl Ester (NBwO2MPOB). The yield was 78%: ^{1}H NMR (C$_6$D$_6$, 500 MHz) δ 8.24 (d, 2, aromatic), 7.06 (d, 2, aromatic), 6.51 (d, 2, aromatic), 6.69 (d, 2, aromatic) 6.10 (m, 2, *H*CC*H* (norbornene)), 4.1 (tt, 2, *H*CCH$_2$CHCO$_2$), 3.90 (q, 1, C*H*CO$_2$), 3.65 (t, 2, C*H*$_2$OC$_6$H$_4$), 3.47 (t, 2, C*H*$_2$CO$_2$), 3.42−3.34 (m, 10, C*H*$_2$C*H*$_2$O), 3.24 (s, 3, O*Me*), 3.19 (m, 1, CO$_2$HCC*H*), 2.6 (m, 1, CH$_2$C*H*) 1.04 (d, 1, *H* on bridging C), 0.93 (d, 1, *H* on bridging C, *J* = 7 Hz); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 174.9, 165.4, 163.2, 157.4, 144.7, 138.3, 138.1, 138.0, 135.9, 132.6, 132.5, 132.4, 122.3, 114.7, 114.5, 69.71, 69.69, 69.59, 69.56, 67.79, 63.33, 55.79, 49.79, 45.94, 43.42, 42.74, 29.45. HRMS (ESI): calcd for [M + Na], 519.1995; found, 519.1920.

Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid 2-{2-[4-(4-Methoxyphenoxycarbonyl)phenoxy]ethoxy}ethyl Ester (NBwO1MPOB). The yield was 70%: ^{1}H NMR (CDCl$_3$, 500 MHz) δ 8.14 (d, 2, aromatic), 7.12 (d, 2, aromatic), 7.00 (d, 2, aromatic), 6.11 (dd, 1, *H*C═CH), 5.94 (dd, 1, HC═C*H*), 4.23 (t, 2, COOC*H*$_2$), 3.92 (t, 2, CH$_2$C*H*$_2$O), 3.83 (s, 3, O*Me*), 3.76 (m, 2, C*H*$_2$OPh), 3.71 (m, 2, PhOCH$_2$C*H*$_2$), 2.80 (br s, 1 CH═CHC*H*), 2.39 (br s, 1, CH═CHC*H*), 1.80 (m, 1, C*H*CO$_2$), 1.42 (dd, 1, bridging *H* of norbornene), 1.24 (d, 2, C*H*$_2$CHCO$_2$), 0.45 (dd, 1, bridging *H* of norbornene); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 174.8, 165.3, 163.1, 157.3, 144.6, 137.8, 132.4, 132.3, 122.3, 122.1, 114.5, 114.4, 70.98, 70.65, 69.65, 69.37, 67.72, 63.33, 55.66, 49.68, 45.82, 43.29, 42.62, 29.33. HRMS (ESI): calcd for C$_{26}$H$_{28}$O$_7$ [M + Na], 475.1727; found, 475.1718.

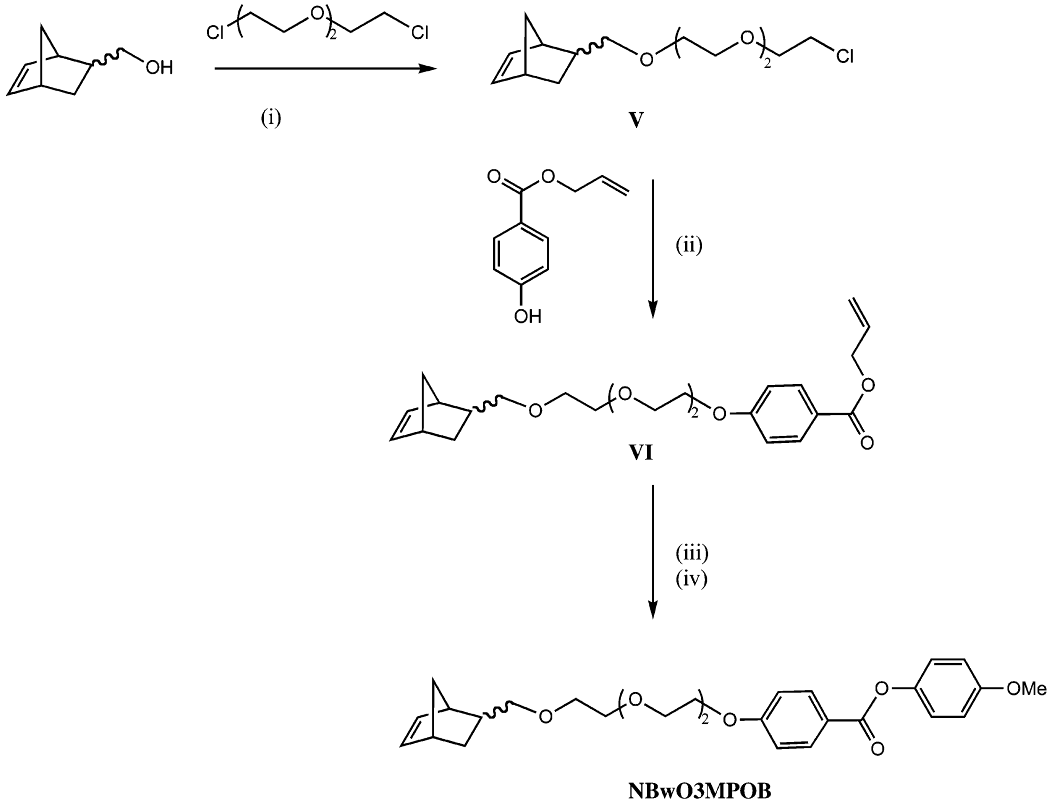
The synthesis of **NBwO3MPOB** is outlined in Scheme 2, the detailed experimental of which is described below.

5-{2-[2-(2-Chloroethoxy)ethoxy]ethoxymethyl}bicyclo[2.2.1]hept-2-ene (V). Bicyclo[2.2.1]hept-5-en-2-yl-methanol (5.0 g, 4.03 × 10^{-2}) dissolved in THF (20 mL) was added dropwise to a chilled (- 78 °C) suspension of NaH (610.8%, 1.60 g, 6.62 × 10^{-2}) in THF (20 mL). After the addition was complete, the reaction solution was brought to room temperature and stirred for 1 h. After effervescence ceased, the solution was transferred to a flask containing 1-chloro-2-[2-(2-chloroethoxy)ethoxy]ethane (15.1 g, 8.06 × 10^{-2} mol) dissolved in THF (20 mL). The reaction solution was stirred at room temperature for 3 h and then diluted with distilled water (50 mL). The mixture was extracted with diethyl ether (three aliquots of 100 mL). The organic layer was dried over anhydrous MgSO$_4$, and the volatiles were removed in vacuo. Purification by column chromatography using silica as the stationary phase and hexane:ethyl acetate (2:1) as eluent yielded the product as a light yellow oil (8.50 g, 77%): ^{1}H NMR (C$_6$D$_6$, 500 MHz) δ 6.08 (dd, 1, C*H*═CH), 5.98 (dd, 1, CH═C*H*), 3.43 (m, 6, C*H*$_2$OC*H*$_2$C*H*$_2$), 3.33 (m, 4, C*H*$_2$C*H*$_2$Cl), 3.16 (m, 4, OC*H*$_2$C*H*$_2$O), 2.68 (br s, 1, HC═CHC*H*), 2.68 (br s, 1, HC═CHC*H*), 2.37 (br s, 1, HC═CHC*H*), 1.68 (m, 1, C*H*CH$_2$O), 1.45 (dd, 1, bridging *H* on norbornene), 1.12 (m, 2, C*H*$_2$CHCH$_2$O), 0.45 (m, 1, bridging *H* norbornene); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 136.8, 132.2, 74.69, 71.09, 70.38, 70.32, 69.99, 69.95, 49.10, 43.65, 42.65, 41.91, 38.40, 28.84.

4-(2-{2-[2-(Bicyclo[2.2.1]hept-5-en-2-ylmethoxy)ethoxy]ethoxy}ethoxy)benzoic Acid Vinyl Ester (VI). 4-Hydroxybenzoic acid allyl ester (1.95 g, 1.10 × 10^{-2} mol), K$_2$CO$_3$ (2.50 g, 1.82 × 10^{-2} mol), and 5-{2-[2-(2-chloroethoxy)ethoxy]ethoxy methyl}bicyclo-[2.2.1]hept-2-ene (2.50 g, 9.1 × 10^{-3} mol) were placed in a flask containing DMSO (50 mL) and the solution was heated at 90 °C for 12 h. The reaction solution was cooled to room temperature and distilled water (100 mL) was added to it. The solution was then extracted with diethyl ether (3 aliquots of 100 mL) and the organic fraction was dried over anhydrous MgSO$_4$. Removal of volatiles and column chromatography using silica as the stationary phase and hexane:ethyl acetate (2:1) as eluent yielded the product as a colorless oil (2.50 g, 70%): ^{1}H NMR (C$_6$D$_6$, 500 MHz) δ 8.14 (d, 2, aromatic), 6.69 (d, 2, aromatic), 6.02 (dd, 1, C*H*═CH), 5.96 (dd, 1, CH═C*H*), 5.80 (m, 1, C*H*═CH$_2$), 5.16, 4.98 (dd, 2, C*H*═CH), 4.64 (d, 2, C*H*$_2$CH), 3.64 (m, 6, C*H*$_2$OC*H*$_2$C*H*$_2$), 3.50 (m, 4, C*H*$_2$C*H*$_2$OPh), 3.41 (m, 4, OC*H*$_2$C*H*$_2$O), 2.61 (br s, 1, HC═CHC*H*), 2.68 (br s, 1, HC═CHC*H*), 2.37 (br s, 1, HC═CHC*H*), 1.68 (m, 1, C*H*CH$_2$O), 1.45 (dd, 1, bridging *H* on norbornene), 1.12 (m, 2, C*H*$_2$CHCH$_2$O), 0.45 (m, 1, bridging *H* norbornene); ^{13}C NMR (C$_6$D$_6$, 125 MHz) δ 166.0, 163.4, 137.5, 133.4, 132.4, 123.7, 118.0, 114.9, 75.57, 71.54, 71.44, 71.14, 69.96, 68.01, 65.56, 50.01, 44.75, 42.95, 39.58, 29.72.

4-(2-{2-[2-(Bicyclo[2.2.1]hept-5-en-2-ylmethoxy)ethoxy]ethoxy}ethoxy)benzoic Acid (VII). A solution of pyrrolidine (2.53 mL, 0.041 mol) dissolved in CH$_2$Cl$_2$ (25 mL) was added to an ice-cooled solution of 4-(2-{2-[2-(bicyclo[2.2.1]hept-5-en-2-ylmethoxy)ethoxy]ethoxy}ethoxy)benzoic acid vinyl ester (16.8 g, 0.039 mol), Pd(Ph$_3$P)$_4$ (1.13 g, 9.8 × 10^{-4} mol), and PPh$_3$ (0.511 g, 1.95 × 10^{-3} mol) in CH$_2$Cl$_2$ (150 mL). The resulting solution was stirred for 1 h at room temperature and then diluted with ethyl acetate. The volatiles were removed in vacuo to give a white solid product, which was used without further purification. Yield: 10.6 g, 70%. ^{1}H NMR (CDCl$_3$, 500 MHz) δ 8.02 (d, 2, aromatic), 6.94 (d, 2, aromatic), 6.20 (dd, 1, *H*C═CH), 5.96 (dd, 1, HC═C*H*) 4.78 (d, 2, C*H*$_2$CHCO$_2$−), 4.19−3.67 (m, 12, (C*H*$_2$C*H*$_2$)$_3$O), 3.22 (br s, 1, HCC*H*(CH$_2$)CH), 2.98 (quin, 1, C*H*CO$_2$−), 2.91 (br s, 1, HCC*H*(CH$_2$)CH$_2$)), 1.21 (d, 1, one bridging *H* of norbornene), 1.40 (d, 1, one bridging *H* of norbornene, *J* = 7.1 Hz).

Scheme 2. Synthesis of NBwO3MPOB[a]



[a] Key: (i) NaH, THF, dry ice acetone bath; (ii) K_2CO_3, DMSO, 65 °C; (iii) $Pd(PPh_3)_4$, PPh_3, pyrrolidine, CH_2Cl_2; (iv) DCC, DMAP, *p*-methoxyphenol, CH_2Cl_2.

4-Methoxyphenyl 4-(2-(2-((Bicyclo[2.2.1]hept-5-en-2-yl)methoxy)ethoxy)ethoxy)benzoate (NBO3MPOB). A solution of DCC (9.74 g, 0.04 mol) dissolved in CH_2Cl_2 (15 mL) was added to a stirred solution of bicyclo[2.2.1]hept-5-ene-2-carboxylic acid 2-{2-[2-(4-carboxyphenoxy)ethoxy]ethoxy}ethyl ester (9.2 g, 0.02 mol), DMAP (0.29 g, 2.3 × 10^{-3} mol) and *p*-methoxy phenol (3.07 g, 0.02 mol) in CH_2Cl_2 (30 mL) at room temperature. The mixture was stirred for 12 h. The precipitate that formed during that time was filtered off and the volatiles were removed in vacuo. The product was purified by column chromatography using silica as the stationary phase and ethyl acetate:hexanes (2:1) eluent. It was isolated as a yellow oil (10.6 g, 76%): ^1H NMR (C_6D_6, 500 MHz) δ 8.23 (d, 2, aromatic), 7.06 (d, 2, aromatic), 6.74 (d, 2, aromatic), 6.69 (d, 2, aromatic) 6.10 (m, 1, *H*C═CH), 5.92 (m, 1, CH═C*H*), 3.67 (t, 2, CH_2OC$_6$H$_4$), 3.42−3.34 (m, 10, (CH_2CH_2)$_3$O), 3.25 (s, 1, O*Me*), 2.62 (m, 1, CH$_2$C*H*), 2.36 (m, 1, CO$_2$*H*C), 1.68 (m, 1, CO$_2$*H*C), 1.45 (m, 1, *H* on bridging C of norbornene), 1.21 (CH_2-CHCO$_2$) 0.93 (d, 1, *H* on bridging C of norbornene); ^{13}C NMR (CDCl$_3$, 125 MHz) 174.94, 165.42, 163.15, 144.66, 138.28, 138.08, 137.97, 135.88, 132.58, 132.53, 132.40, 122.70, 114.65, 114.53, 69.71, 69.69, 69.59, 69.56, 67.79, 63.33, 55.79, 49.79, 46.56, 46.49, 45.94, 45.87, 43.42, 43.26, 43.24, 42.73, 29.45, 29.30, 21.25, 14.39. HRMS (ESI): calcd for $C_{35}H_{40}O_8$ [M + Na], 611.2615; found, 611.2639.

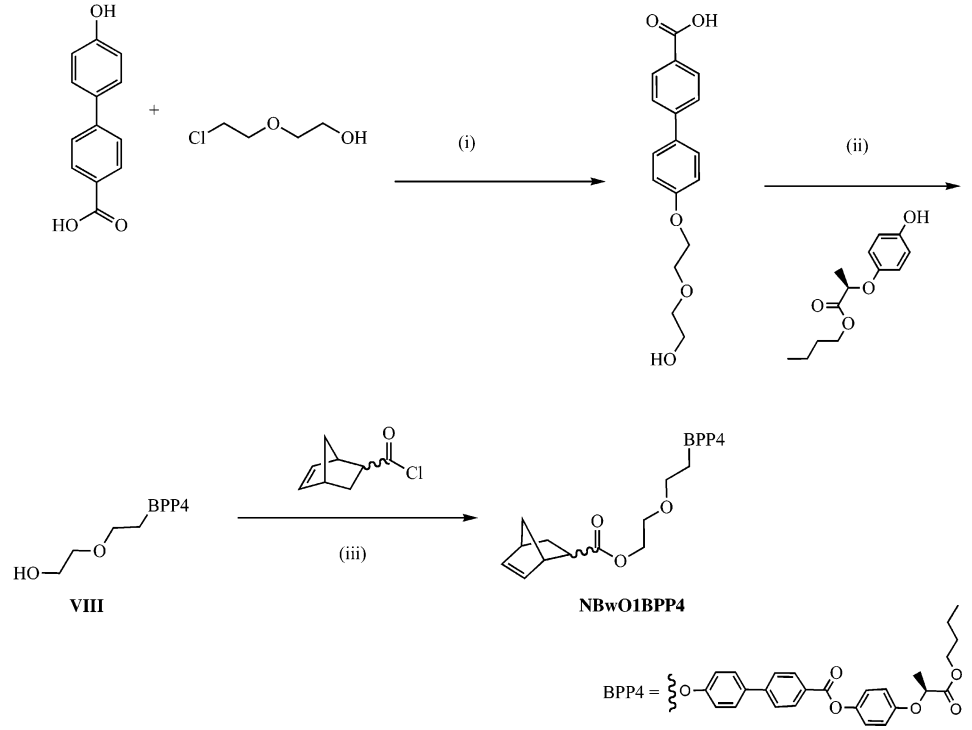
The synthesis of **NBwO1BPP4** is shown in Scheme 3 and described below.

4′-[2-(2-Hydroxyethoxy)ethoxy]biphenyl-4-carboxylic Acid 4-(1-Butoxycarbonylethoxy)phenyl Ester (VIII). A solution of DCC (5.12 g, 2.48 × 10^{-2} mol) dissolved in CH_2Cl_2 (20 mL) was added dropwise to the stirred solution of 4′-[2-(2-hydroxyethoxy)-ethoxy]biphenyl-4-carboxylic acid (3.0 g, 9.92 × 10^{-3} mol), 4-hydroxybenzoic acid 4-(1-butoxycarbonylethoxy)phenyl ester (2.36 g, 9.92 × 10^{-3} mol), and DMAP (303 mg, 2.48 × 10^{-3} mol) in CH_2Cl_2 (50 mL). The reaction was stirred for 12 h, during which time a white precipitate formed. The reaction solution was washed with water (3 × 20 mL aliquots) and the organic layer was dried over anhydrous MgSO$_4$. The volatiles were removed in vacuo, and the residue was purified by column chromatography with silica as the stationary phase and ethyl acetate:hexanes (1:2) as eluent. The product was isolated as a white solid (2.9 g, 56%): ^1H NMR (DMSO, 500 MHz) δ 8.14 (d, 2, aromatic), 7.86 (d, 2, aromatic), 7.74 (d, 2, aromatic), 7.21 (d, 2, aromatic), 7.09 (d, 2, aromatic), 6.95 (d, 2, aromatic), 5.01 (q, 1, C*H*CH$_3$), 4.16 (m, 2, CH_2OPh), 3.77 (m, 2, CH_2OH), 3.52 (m, 4, CH_2OCH_2), 1.71 (m, 2, CO$_2$CH_2), 1.61 (m, 2, CH_2CH$_3$), 1.53 (d, 3, CH_3CH), 1.25 (m, OCH$_2$CH_2-CH$_2$CH$_3$), 0.86 (t, 3, CH$_2$CH_3).

4′-{2-[2-(Bicyclo[2.2.1]hept-5-ene-2-carbonyloxy)ethoxy]ethoxy}biphenyl-4-carboxylic Acid 4-(1-Butoxycarbonylethoxy)-phenyl Ester (NBwO1BPP4). Bicyclo[2.2.1]hept-5-ene-2-carbonyl chloride (600 mg, 3.82 × 10^{-3} mol) was added dropwise to the refluxing solution of 4′-[2-(2-hydroxyethoxy)ethoxy]biphenyl-4-carboxylic acid 4-(1-butoxycarbonylethoxy)phenyl ester (2 g, 3.82 × 10^{-3}) and Et$_3$N (532 μL, 3.82 × 10^{-3}) in THF (40 mL) and the reaction solution was refluxed for 12 h. The reaction solution was cooled to room temperature, and washed with distilled water (3 × 20 mL aliquots). The organic fraction was dried over anhydrous MgSO$_4$. The volaties were removed in vacuo, and the crude product was purified through column chromatography with silica as a stationary phase and hexanes:ethyl acetate (2:1) as the eluent. The product was obtained as a colorless oil (1.54 g, 65%): ^1H NMR (CDCl$_3$, 500 MHz) δ 8.22 (d, 2, aromatic), 7.69 (d, 2, aromatic), 7.61 (d, 2, aromatic), 7.13 (d, 2, aromatic), 7.04 (d, 2, aromactic), 6.93 (d, 2, aromatic), 6.18 (dd, 1, CH═C*H*), 5.95 (dd, 1, C*H*═CH), 4.75 (q, 1, OC*H*CH$_3$), 4.31−4.17 (m, 5, OCH_3 + norbornene CH_2), 3.90 (t, 2H, CH_2O), 3.78 (t, 2H, CH_2CH$_2$O), 3.23 (br s, 1H, norbornene), 2.98 (tt, 1H, C*H*CO$_2$), 2.91 (br s, 1H, norbornene), 1.90 (d, 1H, bridging norbornene), 1.64 (d, 3H, CHCH_3); ^{13}C NMR (CDCl$_3$, 125 MHz) 172.08, 165.46, 160.43, 156.33, 146.40, 146.08, 137.55, 132.97, 131.40, 129.1, 128.68, 127.2, 123.47, 116.35, 115.58, 70.98, 70.65, 69.65, 69.37, 67.72, 63.33, 55.66, 49.68, 45.82, 43.29, 42.62, 39.51, 35.50, 33.15, 31.10, 30.41, 30.01, 29.38, 26.80, 19.52, 18.97, 14.03.

The homopolymers were prepared in a manner similar to that described for **NBw11MPOB**. A solution of **NBw11MPOB** (286

Scheme 3. Synthesis of NBwO1BPP4[a]



[a] Key: (i) NaOH, EtOH, reflux; (ii) DCC, DMAP, CH_2Cl_2; (iii) Et_3N, THF, reflux.

mg, 0.534 mmol) dissolved in THF (2 mL) was added in one portion to a solution of $[Mo(NAr)(OCMe_3)_2CH]_2C_6H_4$ (5 mg, 5.34×10^{-3} mmol) (where Ar = 2,6-diisopropyl phenyl) in THF (10 mL), and the solution was stirred at room temperature for 1 h. The polymerization was quenched through addition of benzaldehyde (100 μL). After 1 h, the polymer was precipitated out from methanol and filtered off as a white powder (280 mg, 98%).

Homopolymers containing the polyoxyethylene spacer were gluelike, which made isolation by precipitation from methanol impossible. Therefore, these polymers were isolated by passing them through a layer of silica to remove the metal byproducts. Removal of the volatile components in vacuo yielded the polymer as a glassy mass.

The triblock copolymers were prepared in the manner described for poly-**MTD$_{100}$NBw11MPOB$_{200}$MTD$_{100}$**. **NBw11MPOB** (572 mg, 1.07 mmol) dissolved in THF (2 mL) was added in one portion to a stirred solution of $[Mo(NAr)(OCMe_3)_2CH]_2C_6H_4$ (5 mg, 5.34×10^{-3} mmol) (where Ar = 2,6-diisopropyl phenyl) in THF (10 mL), and the solution was stirred at room temperature for 1 h. Methyltetracyclododecene (**MTD)** (180 mg, 1.07 mmol) dissolved in THF (2 mL) was added in one portion, and the resulting solution was stirred at room temperature. After 1 h, the reaction was quenched through the addition of benzaldehyde (100 μL) and the solution was stirred at room temperature for 1 h. The polymer was then precipitated from methanol as a white solid (738 mg, 98%).

The triblock copolymers containing polyoxyethylene spacers were precipitated from hexanes.

Results and Discussion

Monomer Synthesis and Polymerization. A series of five monomers with the LC **MPOB** (Scheme 1 and Scheme 2), and one monomer with the LC **BPP4** (Scheme 3) have been synthesized.

Monomers **NBw9MPOB, NBw11MPOB, NBwO2MPOB**, and **NBwO1MPOB** were synthesized as shown in Scheme 1 by reacting the appropriate reagent (9-bromononan-1-ol for **NBw9MPOB**, 11-bromoundecan-1-ol for **NBw11MPOB,** 2-[2-(2-chloroethoxy)ethoxy]ethanol for **NBwO2MPOB**, and 2-(2-chloroethoxy)ethanol for **NBwO1MPOB**) with 4-hydroxybenzoic acid 4-methoxyphenyl ester (**MPOB-**H) followed by esterification of the terminal alcohol with 5-norbornene-2-carboxylic acid chloride. **NBwO3MPOB** was synthesized by reacting 1-chloro-2-[2-(2-chloroethoxy)ethoxy]ethane with *p*-phenol allyl ester, followed by alkylation at the terminal chloro position, and deprotection of the allyl group for coupling with *p*-methoxyphenol (Scheme 2). Finally, **NBwO1BPP4** was synthesized by alkylating 4′-hydroxy-biphenyl-4-carboxylic acid with 2-(2-chloroethoxy)ethanol followed by coupling with 2-(4-hydroxyphenoxy)-propionic acid butyl ester, and finally esterification of the alcohol with 5-norbornene-2-carboxylic acid chloride (Scheme 3). All the monomers displayed endo:exo = 4:1 isomeric distribution in $CDCl_3$.

The monomers were polymerized by the bimetallic ROMP initiator $[Mo(NAr)(OCMe_3)_2CH]_2C_6H_4$ (where Ar = 2,6-diisopropyl phenyl) in THF at room temperature to yield polymers in >95 % yields. The synthesis and living nature of this bimetallic ROMP initiator was recently reported.[15] In all cases, methyltetracyclododecene (**MTD**) was used as the glassy outer block for the synthesis of ABA type triblock copolymers. In triblock copolymers, the percentage of the liquid crystalline block of the polymer was maintained between 70 and 80%. Benzaldehyde was used to quench the polymerization in a Wittig like fashion to give benzylidene-capped polymers, which were isolated in >95% yields. Gel permeation chromatography (GPC) studies on the triblock copolymers displayed an unimodal peak distribution (see Supporting Information) and relatively low polydispersities (Table 1). Lack of any homopolymer components in the GPC traces of the triblock copolymers indicates quantitative reactivation of the bimetallic initiator for the second step of polymerization yielding ABA triblock copolymers. In another experiment to determine the end group of the polymers, a polymer chain prepared using the bimetallic initiator was quenched with ferrocenecarboxaldehyde. MALDI−TOF analysis on the polymer revealed that there were in fact two ferrocenyl moieties (one on each side) and not just one.[15] This result also

Table 1. Gel Permeation Chromatography Data of Homopolymers and Triblock Copolymers in THF or CH_2Cl_2 Calculated vs Polystyrene Standard

polymers[c]	M(theory) ($\times 10^3$)	M_n(found) ($\times 10^3$)[d]	PDI
NBw9MPOB$_{100}$[a]	50	66	<1.10
NBw11MPOB$_{100}$[a]	53	110	<1.10
NBwO2MPOB$_{100}$[a]	49	130	<1.10
NBwO3MPOB$_{100}$[b]	59	120	<1.10
NBwO1MPOB$_{100}$[b]	45	93	<1.10
NBwO1BPP4$_{100}$[b]	57	100	<1.10
MTD$_{100}$NBw9MPOB$_{200}$MTD$_{100}$[a]	130	390	1.20
MTD$_{100}$NBw11MPOB$_{200}$MTD$_{100}$[a]	140	400	1.18
MTD$_{100}$NBwO2MPOB$_{200}$MTD$_{100}$[a]	130	350	<1.10
MTD$_{100}$NBwO3MPOB$_{200}$MTD$_{100}$[b]	150	380	<1.10
MTD$_{100}$NBwO1MPOB$_{200}$MTD$_{100}$[b]	120	300	1.18
MTD$_{100}$NBwO1BPP4$_{200}$MTD$_{100}$[b]	15	4 2	1.21

[a] In THF. [b] In CH_2Cl_2. [c] Refer to Schemes 1, 2 and 3. [d] M_n calculated vs polystyrene standards.

supports that there is virtually quantitative reactivation of the bimetallic initiator for the second step of polymerization. The ability of these bimetallic ROMP initiators to synthesize polymers with predictable molecular weight has been verified by MALDI−TOF analysis, where the calculated molecular weight matched the theoretical molecular weight.[15] It should also be noted that, for the GPC data, the theoretical average molecular weight was significantly smaller than the calculated molecular weight in all cases as they were calculated vs the polystyrene standards.

Thermal Studies. Differential scanning calorimetry (DSC) was used in order to determine the glass transition temperatures (T_g) and LC transitions of homopolymers (**NBw9MPOB$_{100}$**, **NBw11MPOB$_{100}$**, and **MTD**) and triblock copolymers (**MTD$_{100}$NBw9MPOB$_{200}$MTD$_{100}$** and **MTD$_{100}$NBw11MPOB$_{200}$MTD$_{100}$**), which are reported in Figure 1 and Table 2. A distinct T_g was observed for the MTD homopolymer at 210 °C. The first and subsequent DSC heating scans were essentially identical and all heating and cooling scans showed good reversibility. Thermal studies on the triblock copolymers revealed T_gs that were consistent with those of the respective homopolymers, which is indicative of good phase segregation (Figure 1). **MTD$_{100}$NBw9MPOB$_{200}$MTD$_{100}$** exhibited two distinct T_gs at 20 and 200 °C, which corresponds with the homopolymer T_gs. Similarly, **MTD$_{100}$NBw11MPOB$_{200}$MTD$_{100}$** displayed two T_gs at 15 and 200 °C, also consistent with their respective homopolymers. The appearance of both glass transitions at temperatures very similar to those of their respective homopolymers is indicative of a well phase-segregated morphology. A slight broadening of nematic to isotropic LC transitions was observed for the triblock copolymers in comparison to the corresponding homopolymers. We ascribe such broadening of the transitions to the interaction of the LC phase with the inter-material dividing surface (IMDS) of the **MTD** block.

The DSC scans for monomers **NBw9MPOB** and **NBw11MPOB** displayed sharp nematic to isotropic liquid crystalline transitions at 60 and 70 °C, respectively (Figure 1 and Table 2). In the **NBw11MPOB** homopolymer, a liquid crystalline phase transition was observed at 75 °C, which is an increase of 5 °C with respect to its monomer. Similarly, **NBw9MPOB** homopolymer displayed a liquid crystalline transition 20 °C above the transition in the monomer. Polarized optical microscopy (POM) further confirmed the LC transitions of the homopolymers as well as the triblock copolymers. POM data was in good agreement with DSC data for homopolymers and triblock copolymers containing **NBw9MPOB** (Figure 2) and **NBw11MPOB** (Figure 3).

Small-angle X-ray scattering (SAXS) studies were performed on triblock copolymers containing **NBw9MPOB** and **NBw11MPOB** monomers to investigate the morphology of the block copolymer and liquid crystalline mesophases.(Figure 4). Both

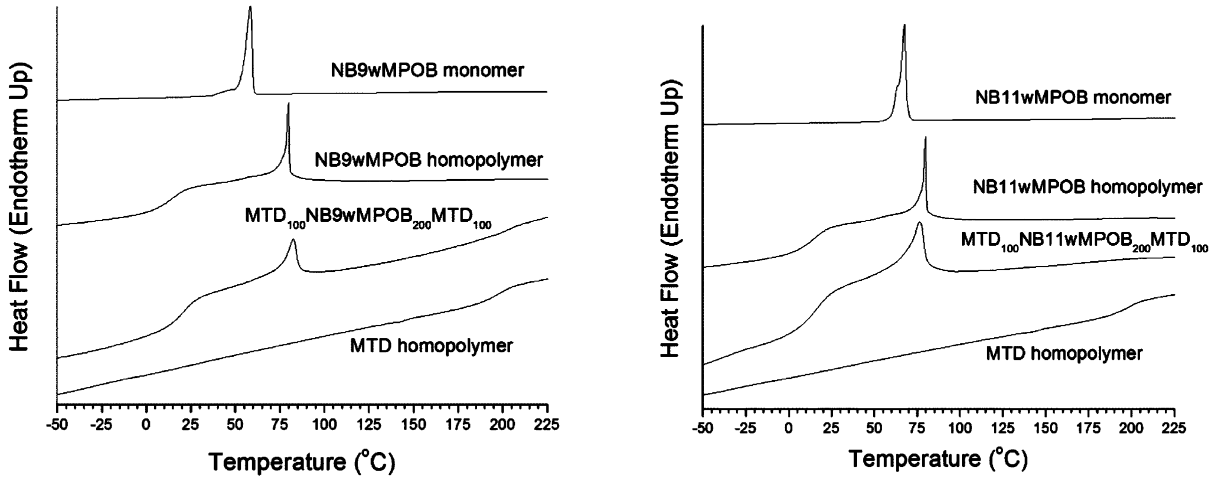
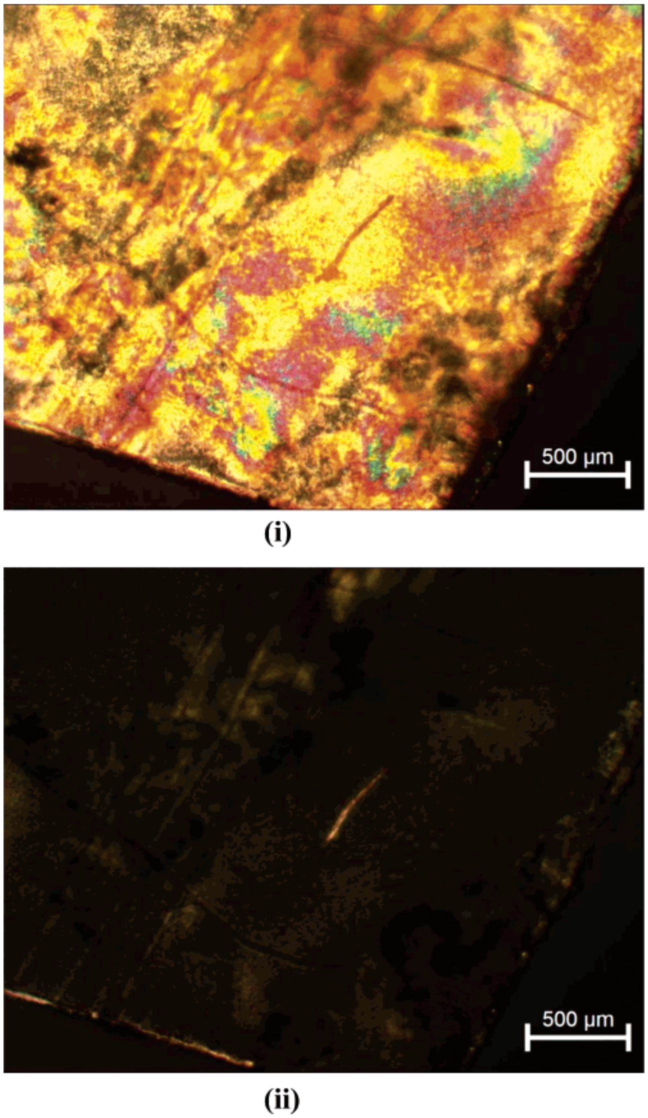


Figure 1. Differential scanning calorimetry scans of monomer (top), homopolymer, triblock copolymer and methyltetracyclododecene homopolymer (bottom).

Table 2. Differential Scanning Calorimetry Data on Polymers Synthesized

LC monomer[a]	monomer		homopolymer heating	homopolymer cooling	triblock copolymers heating	triblock copolymers cooling
NBw9MPOB	N 60 I	I 60 N	G_{LC} 20 N 80 I	I 80 N 20 G_{LC}	G_{LC} 20 N 80 G_H 200 I	I 200 G_H 80 N 20 G_{LC}
NBw11MPOB	N 70 I	I 70 N	G_{LC} 15 N 75 I	I 75 N 15 G_{LC}	G_{LC} 15 N 75 G_H 200 I	I 200 G_H 75 N 15 G_{LC}
NBwO2MPOB			G_{LC} − 25	−25 G_{LC}	G_{LC} − 25	−25 G_{LC}
NBwO3MPOB			G_{LC} − 25	−25 G_{LC}	G_{LC} − 25	−25 G_{LC}
NBwO1MPOB[b]			G_{LC} − 25	−25 G_{LC}	G_{LC} − 25	−25 G_{LC}
NBwO1BPP4	N 60 I	I 60 N	G_{LC} 25 S_C* 60 I	I 60 S_C* 25 G_{LC}	G_{LC} 25 S_C* 182−190 I	I 180−190 S_C* 25 G_{LC}

[a] Refer to Schemes 2 and 3.



(i)

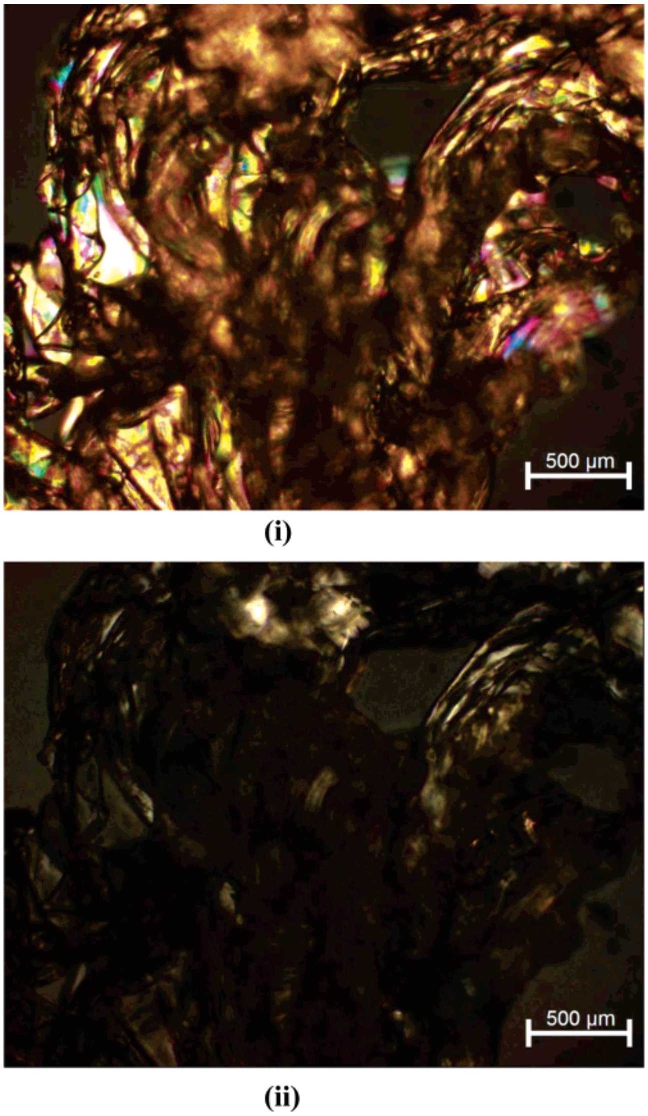
(ii)

Figure 2. Polarized optical micrographs of the polymers containing NBw9MPOB observed on heating (i) triblock copolymer at 60 °C and (ii) triblock copolymer at the isotropic state at 100 °C

polymers exhibited a scattering peak at approximately 40 nm, which is characteristic of the block copolymer domain spacing of phase-segregated polymers. In both triblock copolymers, a weak second-order peak at $\sqrt{7}$ nm is observed, which is typically indicative of hexagonal cylindrical phase morphology of the block copolymer. As the second-order peak is not well-defined, it is concluded that a disordered cylindrical morphology is being observed.

It was concluded from the DSC studies that the polymers are well phase-segregated as the glass transitions temperatures of the block copolymer are very similar to those of the respective homopolymers. However, due to the high T_g of the **MTD** block, annealing could not take place at sufficiently high temperatures to allow for the block copolymer to reach its equilibrium conformation without degrading the polymer, resulting in the lack of long range ordering, and thus the disordered cylindrical morphology is observed.

Dynamic mechanical analysis (DMA) studies on the triblock copolymers containing **NBw9MPOB** and **NBw11MPOB** confirmed the T_gs of the center liquid crystalline blocks (Figure 5). Oscillations of 25 μm were applied to films of the samples in tension at a frequency of 1 Hz and heated from −20 °C at a rate of 3 °C/min. The T_gs of the liquid crystalline polymers were observed near 35 °C for the polymers containing **NBw9MPOB** and **NBw11MPOB**. It should be noted that it is typical to observe thermal transitions at higher temperatures (by 10−20 °C) with DMA as compared to other techniques such as DSC. Two elastic plateaus were observed for each sample; the first precedes a "glassy" transition and lies below the T_g of liquid crystalline polymer block, while the second indicates a rubber



(i)

(ii)

Figure 3. Polarized optical micrographs of the polymers containing NBw11MPOB observed on heating (i) triblock copolymer at 60 °C; (iv) triblock copolymer at the isotropic state 100 °C.

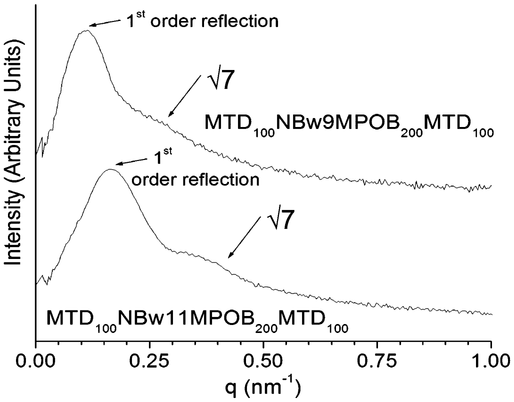


Figure 4. Small-angle X-ray diffraction of triblock copolymers containing 9 (NBw9MPOB) and 11 (NBw11MPOB) alkyl spacers.

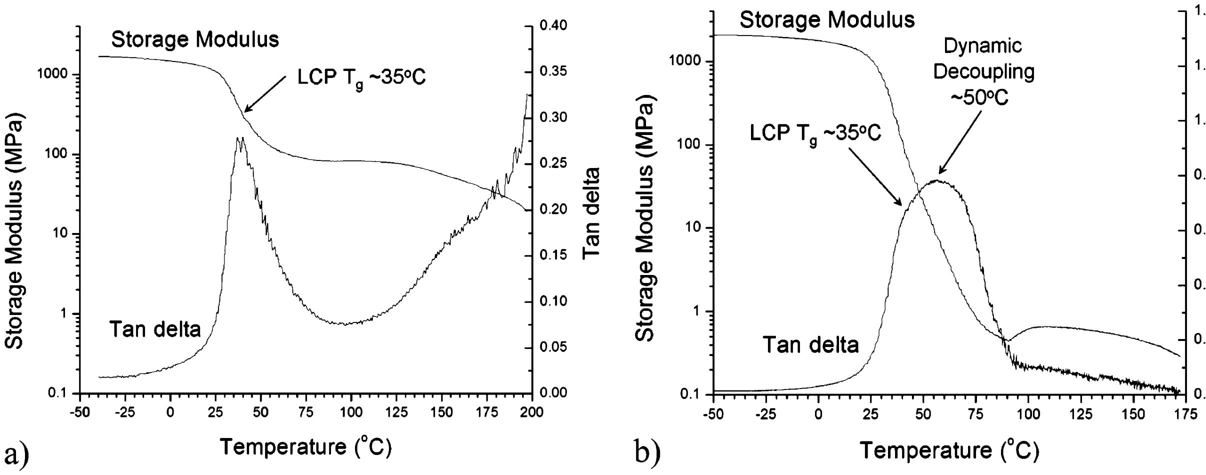


Figure 5. Dynamic mechanical analysis of triblock copolymer containing (a) 9 (NBw9MPOB) and (b) 11 (NBw11MPOB) alkyl spacers.

elasticity plateau of the triblock copolymer and exists between the T_g of the LCP and the MTD blocks. In the case of the triblock copolymer **MTD$_{100}$NBw9MPOB$_{200}$MTD$_{100}$**, the elastic plateau persisted up to 200 °C, indicating rubberlike elasticity. Additionally, the **MTD$_{100}$NBw11MPOB$_{200}$MTD$_{100}$** triblock copolymer shows a broader transition in the DMA, which is believed to be a superposition of the LCP T_g and the dynamic decoupling of the nematic mesogen from the polymer backbone. This second transition results in an elastic plateau of **MTD$_{100}$NBw11MPOB$_{200}$MTD$_{100}$** that is nearly two orders lower than that of **MTD$_{100}$NBw9MPOB$_{200}$MTD$_{100}$**. It is thought that the dynamic decoupling of the polymer backbone from the nematic mesogen allows the backbone to move more independently of the attached mesogen. Thus, the polymer with the longer spacer has a lower modulus, as the polymer backbone with the shorter spacer is supported by the stronger interaction with the nematic mesogen.

Further characterization to quantify the elastic nature of these triblock copolymers will be reported separately along with deformation studies.

There was no significant difference in the T_gs of the homopolymers obtained by increasing the spacer length by two alkyl units (**NBw9MPOB** vs **NBw11MPOB)** (Figure 1). It is apparent that increasing the alkyl spacer was not a viable means to obtaining a T_g, lower than 0 °C, as the inverse relationship between the T_g and the number of methylene units in the alkyl spacer seems to level out after 10 or 11 methylene units.[19] In addition, increasing the spacer length decouples the LC moiety from the polymer backbone, decreasing the influence of the LC on the polymer backbone and lowering the rigid rod aspect ratio and overall stability of the LC, which are important for the proposed applications of these triblock copolymers. Therefore, a new type of spacer that could lower the T_g of the polymer, maintain LC stability at room and higher temperatures, and give significant coupling between the LC and the polymer backbone was required.

Polymers such as polyoxyethylene [$(-CH_2-CH_2-O-)_n$] that have relatively flexible chains because of easy rotation about main chain bonds have been reported to have low values of T_g.[25] We chose to investigate the influence of polyoxyethylene spacers in the T_g of the resulting polymers. The first series of polymers prepared containing polyoxyethylene spacers were **NBwO2MPOB$_{100}$** and **NBwO3MPOB$_{100}$** (Scheme 1 and Scheme 2), with ester and ether functional moieties, respectively, that connected the polymer backbone and spacers. DSC studies on the homopolymers of these monomers yielded a T_g of −25 °C in both cases (Table 2), showing no difference between the two connecting moieties in terms of their T_gs. Unfortunately, neither a distinct nematic to isotropic phase transition, nor birefringence between the temperature range of 30 and 200 °C were observed for either of these homopolymers. The lack of a clear LC transition is due to the destabilization of the LC phase by the polyoxyethylene spacer; in such cases, the LC clearing point effectively falls below such that it overlaps with the T_g of the polymer backbone, rendering it impossible to detect. The lowering of the LC transition phase temperature has been observed in other systems when a polyoxythylene spacer was employed, but the lack of any direct evidence in our system did not allow us to confirm the same. A monomer with a shorter polyoxyethylene spacer, **NBwO1MPOB** (Scheme 2), was synthesized to examine its effect on the LC phase transition. A T_g of −25 °C was also observed for the homopolymer of **NBwO1MPOB** based on DSC studies, with a weak LC clearing transition near the T_g (−15 °C). This was a first direct evidence of a polyoxyethylene spacer lowering the LC transition phase in our system. A more distinct LC clearing transition was observed when **BPP4**, which has shown stable, high-temperature smectic phases in various systems, was used with the polyoxyethylene spacer. **NBwO1BPP4$_{100}$** (Scheme 3) exhibited a T_g of the LC block of 25 °C with another broad transition at ∼60 °C. We assign this broad transition to be the smectic to isotropic phase transition. It was noticed that introduction of the **BPP4** side chain (**NBwO1BPP4$_{100}$)** elevated the T_g of the polymer backbone in comparison to **MPOB** (**NBwO1MPOB$_{100}$**) by 50 °C (−25 to +25 °C). Compared to the alkyl spacer, incorporation of polyoxyethylene spacers decreased the smectic to isotropic phase transition by 80 °C in the BPP4 system (T_{iso} with alkyl spacer = 140 °C[28] and T_{iso} polyoxyethylene spacer = 60 °C), which is consistent with the lowering of the LC transition phase due to polyoxyethylene spacers. The DSC studies on the triblock copolymer containing **NBwO1BPP4** resulted in a T_g for the liquid crystalline block at the same temperature range as its homopolymer (25 °C), suggesting phase segregation, but the smectic to isotropic transition was not prominent. This observation can be explained by considering interactions between IMDS of the **MTD** block and the LC phase block, as observed for the alkyl spacers. In summary, use of polyoxyethylene spacers in the monomers lowered the T_g's of their polymers along with the LC transitions, which were broad and overlapped with the T_g of the polymer backbone for **NBwO2MPOB** and **NBwO3MPOB**. Such overlap was distinct in the case of homopolymers of **NBwO1MPOB** and **NBw-**

O1BPP4. The LC transitions in the triblock copolymer were further broadened due to the stabilization of **MTD** block by the ordering of the LCs.

In the polyoxyethylene spacer system, birefringence was not observed for the homopolymers **NBwO2MPOB**, **NBwO3MPOB**, and **NBwO1MPOB** in the temperature range between 30 and 200 °C as determined by POM. Homopolymer of **NBwO1BPP4** revealed birefringence until 60 °C, which coincides with the LC transition as determined by DSC studies. In all triblock copolymers containing polyoxyethylene spacer, birefringence was observed over a broad temperature range without any distinct isotropization point, which is attributed to IMDS of the **MTD** block stabilizing the LC phases.

The DSC scans of monomer **NBwO1BPP4** revealed a LC transition at 60 °C, which is also supported by the observation of birefringence at the same temperature. Because of the lack of distinct LC transitions in bicycloheptene-based monomers containing polyoxyethylene spacer, further mechanical and diffraction studies were not successful.

Conclusion

A series of monomers for ROMP with SCLCs that vary in spacer length, spacer type, and LC have been synthesized. These monomers were polymerized using a molybdenum bimetallic ROMP initiator to yield homopolymers and ABA triblock copolymers with **MTD** as the A block in high yields and with low polydispersities. Triblock copolymers with alkyl spacers connecting the polymer backbone and the LC showed good phase separation as verified by DSC and SAXS studies. Incorporation of polyoxyethylene spacers in the monomers resulted in polymers with lower T_gs in comparison to the related alkyl spacers; however, absence of a sharp nematic to isotropic phase change did not allow for further characterization of these polymers. The presence of a distinct LC transition in the homopolymer of **NBwO1BPP4** showed the possibility of using polyoxyethylene spacers with **BPP4** LCs. We are currently exploring this possibility in a different polymer backbone. SAXS studies on triblock copolymers consisting of **NBw9MPOB** and **NBw11MPOB** revealed phase segregation of the polymers. Presence of a higher order peak in both triblock copolymers suggested hexagonal cylindrical morphology of the block copolymer domains in each case. The lack of long range order is ascribed to the high melting temperature of the **MTD** block, which inhibits the attainment of an equilibrium morphology. DMA studies of the triblocks containing **NBw9MPOB** and **NBw11MPOB** showed an elastic plateau above the liquid crystalline polymer T_g suggestive of rubber elasticity in these samples. This finding was encouraging mainly because this shows the possibility for similar materials to be used as TPEs.

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Supporting Information Available: GPC traces of **NBw9MPOB**$_{100}$, **MTD**$_{100}$**NBw9MPOB**$_{200}$**MTD**$_{100}$, **NBw11MPOB**$_{100}$, **MTD**$_{100}$**NBw9MPOB**$_{200}$**MTD**$_{100}$, **NBwO3MPOB**$_{100}$, and **MTD**$_{100}$-**NBwO3MPOB**$_{200}$**MTD**$_{100}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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