Influence of Backbone Rigidity on the Thermotropic Behavior of Side-Chain Liquid Crystalline Polymers Synthesized by Ring-Opening Metathesis Polymerization

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ABSTRACT: The effect of backbone flexibility on the mesomorphic behavior of side-chain liquid crystalline polymers synthesized by ring-opening metathesis polymerization was investigated. The synthesis of norbornene and cyclobutene monomers containing a *p*-nitrostilbene moiety as the mesogenic group and polymerization of these monomers to produce side-chain liquid crystalline polymers with low polydispersities and defined molecular weights was accomplished. The relatively rigid poly(norbornene)s displayed enantiotropic nematic mesomorphism with glass transitions from 44 to 64 °C and isotropization temperatures between 108 and 121 °C, whereas the more flexible poly(butadiene)s showed enantiotropic smectic A mesomorphism with glass transition temperatures from 14 to 31 °C and isotropization temperatures between 74 and 111 °C. A diblock copolymer containing a 1:1 mixture of the poly(norbornene) and poly(butadiene) also exhibited a smectic A mesophase, clearly demonstrating the dominance of the poly(butadiene) backbone. The dependence of the degree of polymerization and flexible spacer length on the phase transitions of these systems was determined, demonstrating stabilization of the mesophase by both increasing molecular weight and flexible spacer length.

Introduction

Since their initial discovery in 1888 by Reinitzer,[1] liquid crystalline materials have been investigated intensely for their scientific and technological potentials. The ability of these anisotropic molecules to form supramolecular structures through self-organization prompted research to determine the criteria for the formation of liquid crystalline phases.[2,3] As information about these materials was accumulated, it was observed that increasing liquid crystalline order was found in many systems on passing from low molecular weight monomeric compounds to the corresponding polymeric materials.[4,5] Liquid crystalline polymers were divided into two major classes: (1) polymers containing the mesogenic group in the backbone (main-chain liquid crystalline polymers, MCLCPs) and (2) polymers with the mesogenic group on the side chains of the polymers (side-chain liquid crystalline polymers, SCLCPs), which were the focus of this study.

Finkelmann's and Ringsdorf's[6,7] discovery that the addition of a flexible spacer between the rigid mesogen and the polymer backbone greatly enhanced the observed liquid crystallinity in SCLCPs allowed for the systematic preparation of a wide variety of these materials. The flexible spacer enabled a partial decoupling of the motions of the polymer backbone and the mesogens, thus providing the mesogens with the ability to stack in organized domains.[6,7] Based on these initial results, SCLCPs have been synthesized utilizing various polymer backbones including poly(acrylate)s,[8−12] poly(methacrylate)s,[13,14] poly(siloxane)s,[15−18] and poly(phosphazene)s.[19−21] However, the methods of polymerization utilized for these systems, including free radical polymerization, hydrosilation, and ring-opening polymerization, were limited by the lack of control over polymer molecular weight and polydispersity (PDI). To control these properties, the application of living polymerization methods to these systems was necessary.[22] Recently, living cationic[23−25] and group transfer[24,26] polymerizations have been utilized for the production of SCLCPs with control over molecular weight and polydispersity.

Developments in ring-opening metathesis polymerization (ROMP)[27,28] have led to the ability to generate living polymerizations of strained cyclic olefins. The living ROMP of functionalized norbornenes bearing rigid biphenyl mesogens led to a series of new poly(norbornene) SCLCPs demonstrating enantiotropic nematic and smectic mesophases.[29−37] The effect of mesogen, degree of polymerization (DP), polydispersity, and flexible spacer length were investigated, which has given insight into the effects of these factors on the liquid crystallinity of the poly(norbornene)s.

The influence of backbone rigidity on SCLCP behavior was another feature of these polymeric systems of interest. To examine the role of the backbone rigidity on the liquid crystallinity of SCLCPs, a comparison of the fairly rigid poly(norbornene) backbone with a more flexible poly(butadiene) backbone was undertaken. The synthesis of substituted norbornenes and cyclobutenes bearing a *p*-nitrostilbene moiety as the mesogenic unit was accomplished. ROMP of these monomers with the highly functional group tolerant initiator $(PCy_3)_2Cl_2Ru{=}CHPh$ (**1**)[38,39] produced SCLCPs with poly(norbornene) and poly(cyclobutene) (equivalent to poly(butadiene)) backbones, respectively. The role of the backbone rigidity in effecting the liquid crystalline transitions and phase behavior of the resulting poly(norbornene)s and poly(butadiene)s was examined by differential scanning calorimetry (DSC) and polarized optical microscopy. The effect of the degree of polymerization and the flexible spacer length on the liquid crystallinity was determined as well, resulting in further insight into the effects of these properties in SCLCPs derived from ROMP.

Results and Discussion

Functionalized Mesogen Synthesis. 4-Hydroxy-4′-nitrostilbene (**2**) was synthesized in 50% yield by the

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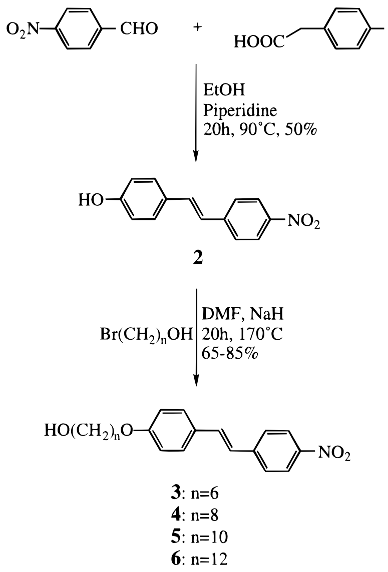
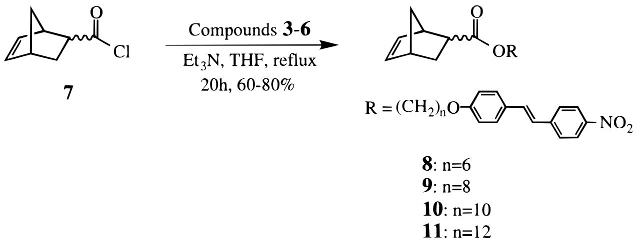
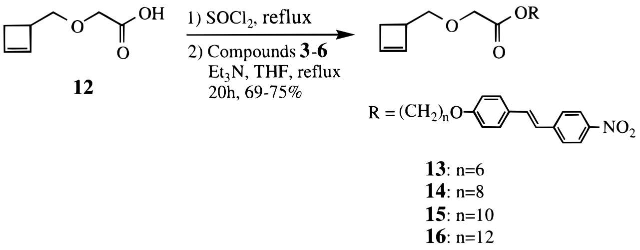
Scheme 1



Scheme 2



Scheme 3



Knoevenagel condensation[40] of *p*-nitrobenzaldehyde and *p*-hydroxyphenylacetic acid.[41] Alkylation of **2** with a series of bromo alcohols under basic conditions led to the desired hydroxy-functionalized mesogens **3**−**6** in 65−85% yield (Scheme 1).

Monomer Synthesis. Nobornene monomers **8**−**11** were synthesized in one step from the esterification of norborn-2-ene-5-carbonyl chloride (**7**)[42] with hydroxy-functionalized mesogens **3**−**6**. The reaction was carried out in tetrahydrofuran (THF) in the presence of triethylamine, resulting in monomers **8**−**11** in 60−80% yield after flash column chromatography (Scheme 2). Monomers **8**−**11** were crystalline solids exhibiting a single phase transition to the isotropic state.

Cyclobutene monomers **13**−**16** were synthesized in a two-step procedure by the initial conversion of [3-oxa-4-(2-cyclobutenyl)]butyric acid (**12**)[43] to the corresponding acid chloride with thionyl chloride ($SOCl_2$) and subsequent esterification with compounds **3**−**6** (Scheme 3). Monomers **13**−**16** were isolated in 69−75% yield after flash column chromatography, resulting in crystalline solids exhibiting only a single phase transition to the isotropic state.

Synthesis of Poly(norbornene) SCLCPs. Polymerization of the norbornene monomers **8**−**11** with initiator **1** was accomplished over 1 h at room temperature in CH_2Cl_2, as shown in Scheme 4. Polymerizations were quenched by treatment with an excess of ethyl vinyl ether to cleave the catalyst from the polymer chain. Precipitation of the reaction mixture in methanol resulted in poly(norbornene)s **17**−**20** as fluffy yellow solids in 90−99% isolated yields. The dependence of the flexible spacer length (*n*) using monomers **8**−**11** and the DP using monomer **9** at varying monomer-to-initiator ([M]/[I]) ratios were examined as shown in Table 1. The polymerizations resulted in materials with narrow PDI(s) between 1.08 and 1.11 and controlled molecular weights.

Scheme 4

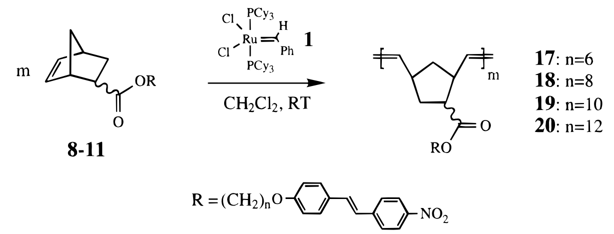


Table 1. Polymerization Results for Norbornenes 8−11

monomer	[M]/[I]	$\bar{M}_n$[a]	PDI[a]	phase transition[b] (°C) heating	phase transition[b] (°C) cooling
8	25	13 400	1.08	g64n121i	i117n60g
9	25	13 000	1.08	g52n117i	i114n48g
10	25	22 000	1.11	g50n108i	i104n46g
11	25	20 800	1.10	g44n108i	i106n40g
9	5	7 300	1.11	g46n108i	i107n43g
9	10	9 800	1.09	g50n114i	i111n46g
9	25	13 000	1.08	g52n117i	i114n48g
9	50	18 000	1.07	g51n118i	i116n50g
9	100	23 200	1.08	g49n121i	i118n44g

[a] Determined by gel permeation chromatography in CH_2Cl_2 relative to monodispersed polystyrene standards. [b] Analysis by differential scanning calorimetry with a scan rate of 10 °C/min.

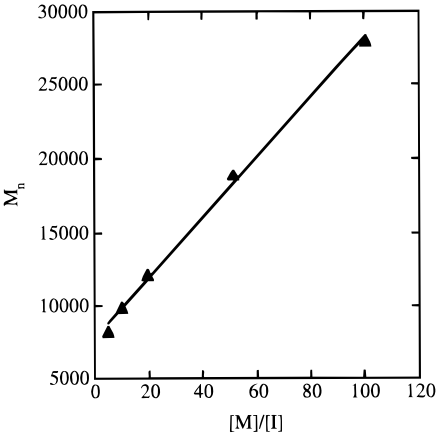


Figure 1. Dependence of the $\bar{M}_n$ on the [M]/[I] ratio for poly(norbornene) **18**. Molecular weights determined by gel permeation chromatography in CH_2Cl_2 relative to monodispersed polystyrene standards.

For a polymerization to be considered living, the monomer must be polymerized to completion in the absence of any chain transfer or chain termination reactions, and subsequent addition of monomer should lead to further polymerization of all chain ends.[22,44] The living nature of these polymerizations was examined using **9**. Compound **9** was polymerized at [M]/[I] ratios of 5-, 10-, 25-, 50-, and 100/1. As illustrated in Figure 1, a linear correlation was observed between the $\bar{M}_n$ and the [M]/[I], as one would expect for a living polymerization. Further experimental verification of the living nature of this polymerization was accomplished using

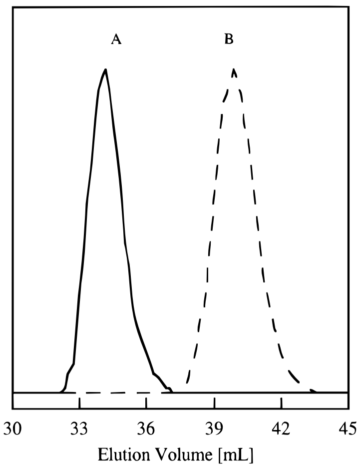
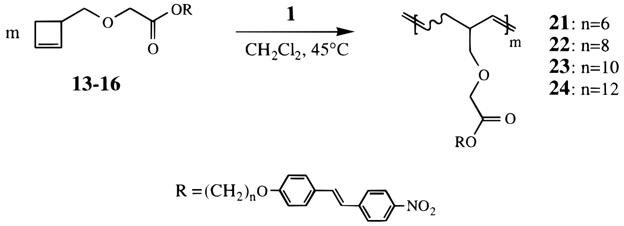


Figure 2. Sequential monomer addition experiment. Peak B resulted after the first monomer addition (23 equiv). Upon subsequent addition of excess monomer (660 equiv), a clean shift to peak A is observed. Molecular weights determined by gel permeation chromatography in CH_2Cl_2 relative to monodispersed polystyrene standards.

Scheme 5



a sequential monomer addition experiment. Compound **9** (23 equiv) was polymerized for 1 h until all the monomer was consumed, and an aliquot was removed for analysis by GPC. The polymerization was then allowed to sit for 3 h, and a second sample of **9** (660 equiv) was added to the polymerization mixture. The molecular weight for the final polymer shifted significantly relative to the polymer after the first polymerization, while the PDI increased only moderately from 1.08 to 1.10. The fact that no low molecular weight peaks were observed after the second polymerization clearly demonstrated the living character of this polymerization. Chain transfer, backbiting, and chain termination would all have produced polymers bearing inactive chain ends, which would have resulted in a broadening of the polydispersity or a bimodal distribution (Figure 2).

Synthesis of Poly(butadiene) SCLCPs. Polymerization of the cyclobutene monomers **13**–**16** was accomplished as shown in Scheme 5. These reactions were performed with initiator **1** in CH_2Cl_2 at 45 °C in a sealed vial for 24 h. Precipitation of the reaction mixture in acidic methanol (5% v/v of 1 N HCl/methanol) resulted in cleavage of the catalyst from the polymer chain, yielding polymers **21**–**24** as tacky yellow solids in 82–97% isolated yields. Cleavage with HCl was necessary because the propagating carbene in this system was unreactive with ethyl vinyl ether. Coordination of the ether–ester functionality to the propagating carbene produced a more inactive carbene, which propagated at a much slower rate than in the norbornene polymerizations and was stable to excess ethyl vinyl ether.[43] This resulted in the much longer reaction times required for this polymerization. As presented in Table 2, polymerizations of monomers **13**–**16** with differing flexible spacer lengths as well as polymerization of **14** at varying [M]/[I] ratios were accomplished.

Table 2. Polymerization Results for Cyclobutene Monomers 13–16

				phase transition[b] (°C)	
monomer	[M]/[I]	$\bar{M}_n$[a]	PDI[a]	heating	cooling
13	25	33 300	1.16	g31s104i	i91s18g
14	25	35 400	1.15	g25s104i	i95s13g
15	25	31 900	1.16	g23s111i	i97s10g
16	25	38 500	1.14	g21s108i	i99s11g
14	5	15 000	1.13	g23s74i	i61s10g
14	10	21 600	1.11	g21s86i	i78s9g
14	25	35 400	1.15	g25s104i	i95s13g
14	50	57000	1.27	g15s105i	i96s5g
14	100	89100	1.38	g14s107i	i98s5g

[a] Determined by gel permeation chromatography in CH_2Cl_2 relative to monodispersed polystyrene standards. [b] Analysis by differential scanning calorimetry with a scan rate of 10 °C/min.

Scheme 6

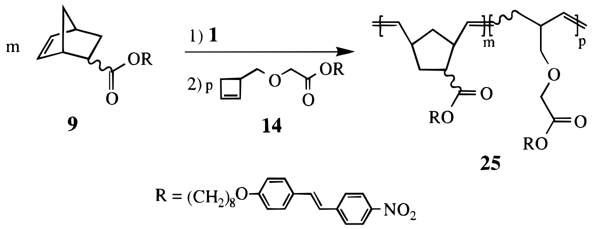


Table 3. DSC Analysis of the Block Copolymer 25

					phase transition[b] (°C)	
M_1	M_2	$[M_1]/[M2]/[I]$	$\bar{M}_n$[a]	PDI[a]	heating	cooling
9	**22**	27/28/1	12 800	1.12	g27s104i	i103s26g

[a] Determined by gel permeation chromatography in CH_2Cl_2 relative to monodispersed polystyrene standards. [b] Analysis by differential scanning calorimetry with a scan rate of 10 °C/min.

Control of the polymer molecular weight and low polydispersities of 1.11–1.38 were observed for these polymerizations. Despite the effective control over the polymer molecular weight, this polymerization was not living, which was especially evident in the broadening of the PDI as the [M]/[I] ratio was increased. This broadening was the result of a lower molecular weight tail in the GPC, consistent with chain termination processes during the polymerization. However, at low [M]/[I] ratios, apparently the polymerization was able to reach completion before significant decomposition occurred, thus resulting in the lower PDI(s). This catalyst decomposition was presumed to result from the extended reaction times and higher temperatures employed as compared to the conditions used in the norbornene polymerizations.[43]

Diblock Copolymer Synthesis. Based on the living polymerization of monomer **9**, though, the synthesis of a block copolymer was accomplished by sequential polymerization of monomer **9** followed by monomer **14** using initiator **1**. Polymerization of **9** was run for 1 h with a [M]/[I] ratio of 27/1 at room temperature, followed by the addition of **14** ([M]/[I] ratio of 28/1) and continued polymerization for 24 h (Scheme 6). Precipitation in acidic methanol resulted in polymer **25** as a fluffy yellow solid in 96% isolated yield. Although the polymerization of the second block was not living, the PDI of the resulting polymer was 1.12 (Table 3). ^1H and ^{13}C NMR results were consistent with a 1:1 mixture of a poly(butadiene) and a poly(norbornene) backbone.

Thermal Characterization of Poly(norbornene) SCLCPs. Analysis of the phase behavior of these polymers was accomplished using DSC and polarized optical microscopy. All heating and cooling scans were

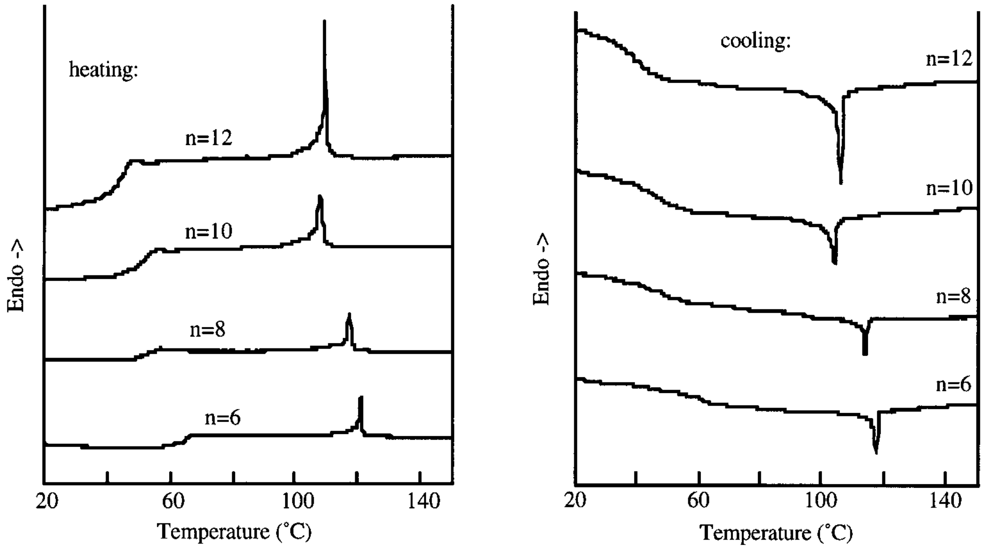


Figure 3. Normalized DSC thermograms for the poly(norbornene)s **17**–**20** of different flexible spacer length (*n*) with a scan rate of 10 °C/min.

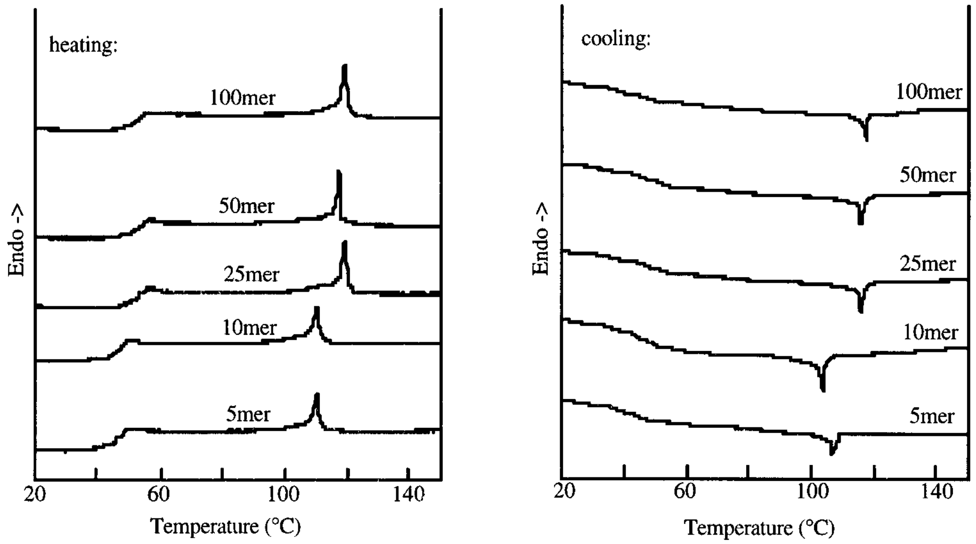


Figure 4. Normalized DSC thermograms for the poly(norbornene) **18** ($n = 8$) at different [M]/[I] obtained at a scan rate of 10 °C/min. The degree of polymerization shown is based solely on the initial [M]/[I] ratio employed.

completely reversible for each of the polymers. The second heating and first cooling scans were reported in all cases. Figure 3 shows the effect of the flexible spacer length on the phase transition temperatures. A decrease in the isotropization temperature from 121 to 108 °C was observed upon increasing the flexible spacer length, while the T_g decreased from 64 to 44 °C. The net result was an overall stabilization of the mesophase by 7 °C upon increasing the spacer length. Typically, upon increasing the flexible spacer length, the packing density of the chains is reduced, thus lowering the T_g. For most reported systems, the isotropization temperature is observed to be unaffected by an increase in the spacer length or to decrease only slightly compared to the significant decrease observed in the T_g, resulting in a stabilization of the mesophase.[29,36,45]

The effect of the DP on the phase transitions was also investigated for the polymerization of **9** (Figure 4). The isotropization temperature increased from 108 °C for the 5-mer to 121 °C for the 100-mer, yet the temperature was relatively invariant for DP >10–25. Similar independence of the isotropization temperature on the DP past a certain threshold has been found for other systems, including poly(siloxane)s (DP ~ 12),[15] poly(vinyl ether)s (DP ~ 10–20),[24,25] poly(acrylate)s (DP ~ 12–40),[8,9] poly(methacrylate)s (DP ~ 12),[26] and poly(norbornene)s (DP ~ 30–50).[29–31,33,35] The change in the T_g appeared to be independent of the DP, resulting in a range from 46 to 57 °C with no apparent trend. The result of increasing DP, therefore, was a stabilization of the mesophase by 10 °C.

Polarizing optical microscopy was used to identify the mesophases associated with the observed liquid crystalline transitions of the poly(norbornene)s **17**–**20**. For each polymer, a schlieren texture was observed upon cooling from the isotropic state, representative of a nematic mesophase.[46] These nematic mesophases were consistent with the results of previously studied SCLCP poly(norbornene)s[29–36] and corresponded to the lowest order of alignment of the mesogenic units. The schlieren texture presented in Figure 5a was obtained at 100 °C with a magnification of 50X. Larger domains were obtained through annealing at 115 °C as illustrated in Figure 5b.

Thermal Characterization of Poly(butadiene) SCLCPs. The phase transition temperatures for the poly(butadiene)s displayed many similarities to those of the poly(norbornene)s. The effect of flexible spacer

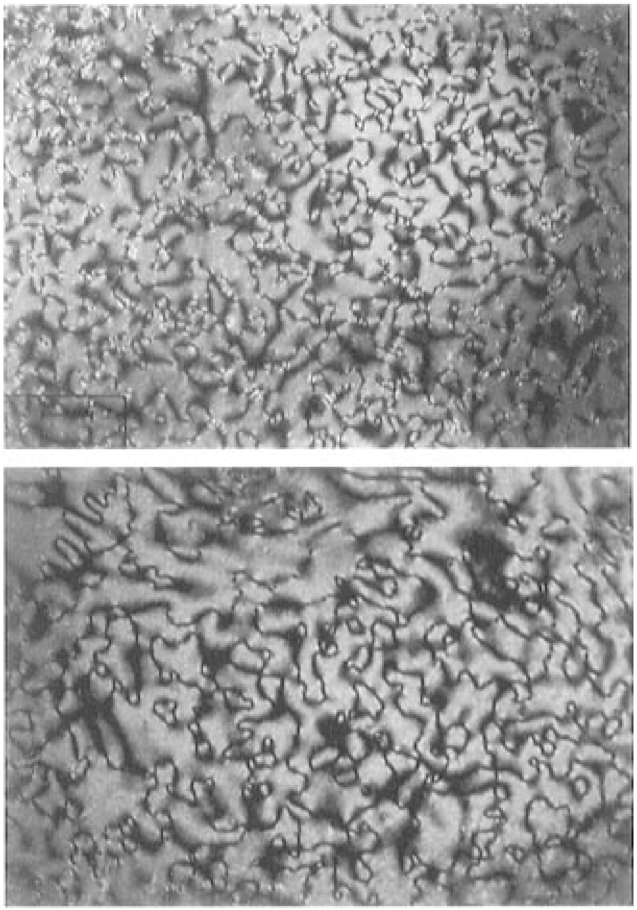


Figure 5. Polarizing optical micrographs (magnification 50X) of the nematic schlieren textures observed for poly(norbornene) **18** ($n = 8$, 10-mer) upon cooling from the isotropic state at (a, top) 100 °C and (b, bottom) at 115 °C after annealing for 15 min at 115 °C.

length was investigated, and, as observed in the poly(norbornene) systems, stabilization of the mesophase was observed upon increasing the spacer length (Figure 6). As the spacer length was increased, the isotropization temperature increased slightly from 104 to 108 °C, while the T_g decreased from 31 to 21 °C, resulting in a 14 °C stabilization of the mesophase.

The dependence of the phase transitions on the DP of the polymerization of **14** was studied, as shown in Figure 7. A significant increase in the isotropization temperature from 74 to 107 °C was observed, but this temperature became relatively invariant at DP $>10-25$. The T_g varied between 23 and 14 °C with no consistent trend. The net stabilization of 33 °C of the mesophase for poly(butadiene)s was much larger than that observed for the poly(norbornene)s; however, the trend in stabilization of the mesophase upon increasing the DP was consistent for both polymer backbones. Interestingly, the peak widths significantly increased for poly(butadiene) **22** as the DP decreased. This broadening has been observed in other systems and presumably results from the higher sensitivity of low molecular weight polymers to the isotropization temperature compared to that of higher molecular weight polymers. If individual chains are assumed to act independently, broadening of the isotropization temperature at lower molecular weights would be expected.[29,47]

The most remarkable contrast in comparing the poly(butadiene) and poly(norbornene) backbones was revealed in the optical polarized microscopy. In contrast to the schlieren textures observed for the poly(norbornene)s, a bâtonnet texture was observed upon cooling just below the isotropic state. The bâtonnet texture has been well documented as evidence for a smectic A phase, which corresponds to a higher degree of alignment of the mesogenic units.[46,48] This texture has been typically observed as a kinetic effect upon cooling just below the isotropic state; upon further cooling, more pronounced textures representative of smectic A have been achieved.[46,48] This was also observed for the poly(butadiene)s. As shown in Figure 8, the growth of the final texture in Figure 8d from the initial bâtonnets in Figure 8a was observed upon slow cooling from the isotropic state. These observations were obtained for all the poly(butadiene)s **21**−**24**.

Thermal Characterization of the Diblock SCLCP. To elucidate which backbone would dominate the polymer phase behavior, a 1:1 diblock was synthesized containing both the poly(butadiene) and poly(norbornene) backbones. The DSC results for this diblock copolymer are presented in Table 3. As can be seen in Figure 9a, a texture typical of smectic A phase was observed, and, as for the poly(butadiene)s, a bâtonnet texture was observed just below the isotropic state (Figure 9b). The poly(butadiene) backbone dominated

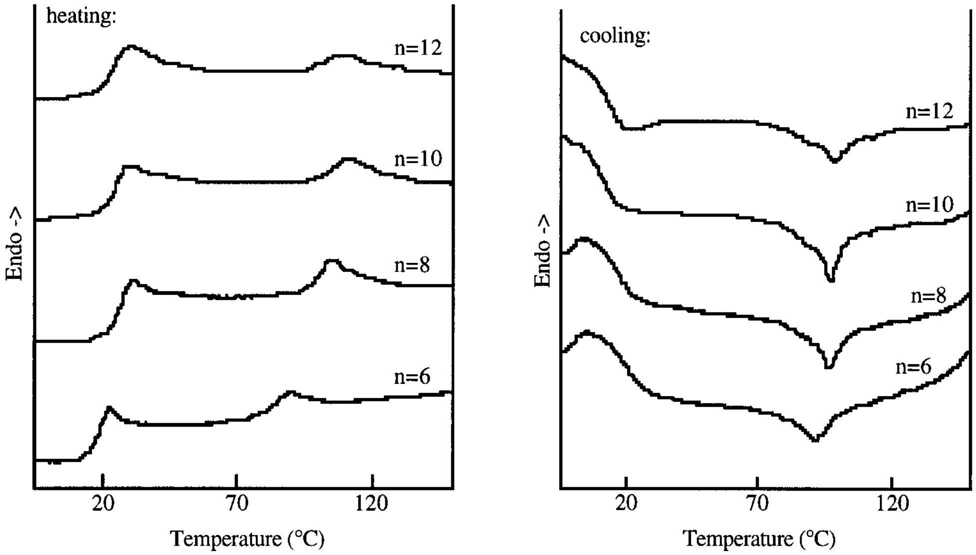


Figure 6. Normalized DSC thermograms for the poly(butadiene)s **21**−**24** of different flexible spacer lengths (n) with a scan rate of 10 °C/min.

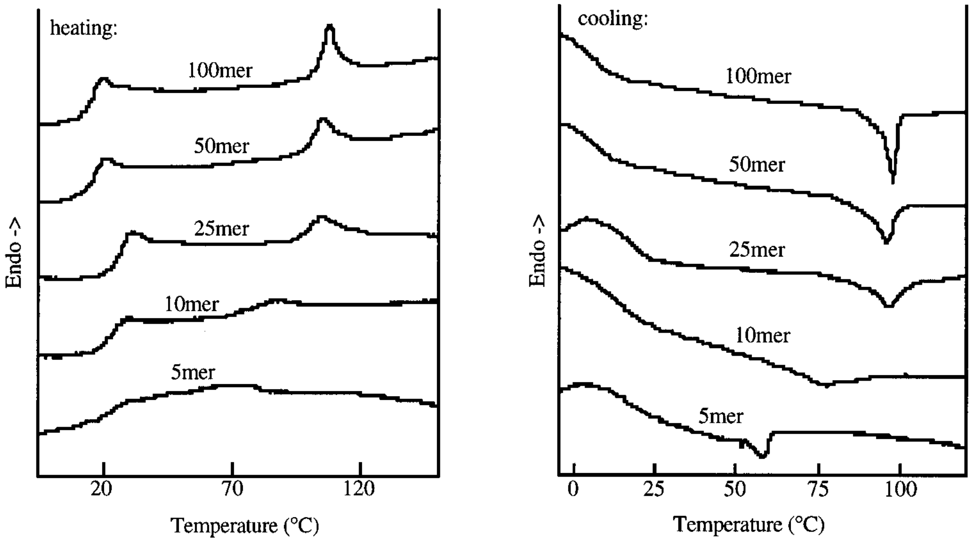


Figure 7. Normalized DSC thermograms for the poly(butadiene) **22** ($n = 8$) at different [M]/[I] obtained at a scan rate of 10 °C/min. The degree of polymerization shown is based solely on the initial [M]/[I] ratio employed.

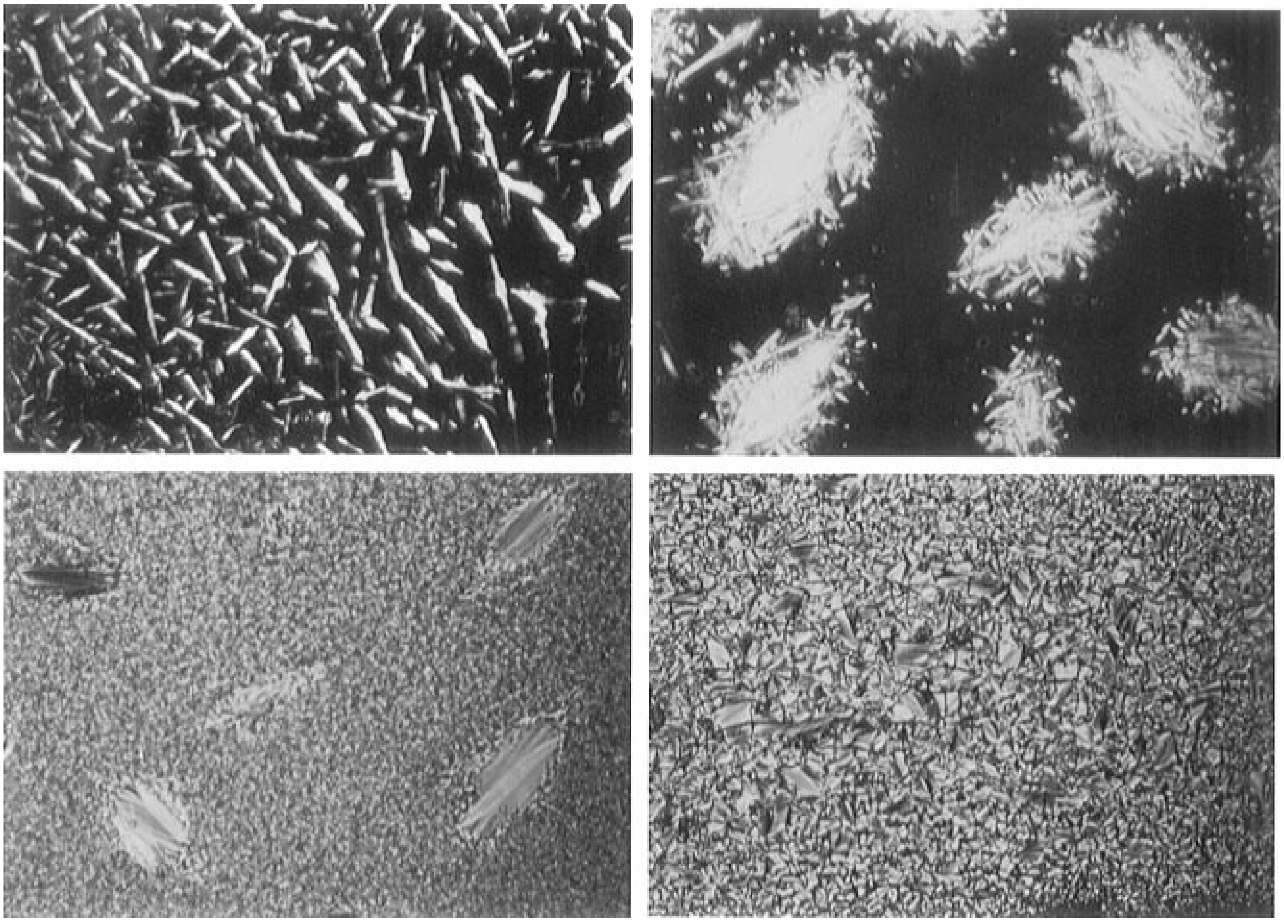


Figure 8. Polarizing optical micrographs (magnification 50X) of the smectic A textures observed for poly(butadiene) **24** ($n = 12$, 25-mer) upon cooling from the isotropic state at (a, top left) 118.8 °C, fine bâtonnets observed; (b, top right) 113.8 °C, bâtonnets of larger domains; (c, bottom left) 105.9 °C, bâtonnets transforming into new texture; and (d, bottom right) 100.0 °C, final texture typical for a smectic A mesophase (magnification 20×).

the phase behavior of the diblock copolymer **25** resulting in a smectic A mesophase instead of a nematic mesophase as observed for the poly(norbornene)s. Although diblock copolymers have been investigated containing an amorphous and a liquid crystalline block,[32,49,50] diblock copolymers containing two liquid crystalline blocks of differing phase behavior have not been investigated to our knowledge. An understanding of the factors that determine which phase will dominate the overall phase behavior of such block copolymers can only be acheived through further research in this area.

Conclusions

The synthesis and characterization of SCLCPs with both poly(norbornene) and poly(butadiene) backbones of controlled molecular weights and low polydispersities were achieved. Examination of the effect of the degree of polymerization and the length of the flexible spacer

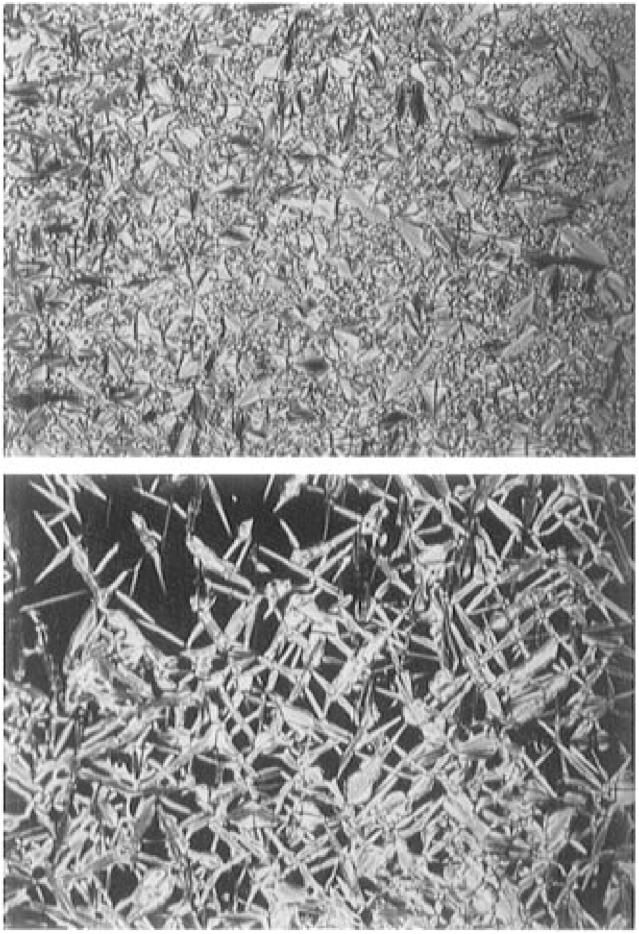


Figure 9. Polarizing optical micrographs (magnification 50×) of the smectic A textures observed for the diblock copolymer **25** upon cooling from the isotropic state at (a, top) 110.3 °C, final texture typical for smectic A mesophase, and (b, bottom) 111.0 °C, bâtonnet texture.

on the phase transitions was accomplished. Stabilization of the mesophase was observed with both increasing degree of polymerization and flexible spacer length. Despite similar isotropization temperatures for the poly(norbornene) and poly(butadiene) polymers, these polymers differed substantially in their phase behaviors. The SCLC polymers with the poly(norbornene) backbone exhibited textures typical of nematic mesophases, whereas the poly(butadiene)-based materials displayed textures representative of smectic A mesophases. This remarkable contrast appeared to result from the differing backbone rigidity for these two systems: the more flexible poly(butadiene) backbone allowed a higher order of alignment of the mesogenic units, resulting in a more ordered liquid crystalline phase. These results have prompted research on the development of living polymerizations of cyclobutenes and the use of the poly(butadiene) backbone with other mesogenic groups to further delineate the effect of this backbone on SCLCP mesomorphism.

Experimental Section

General. Argon was purified by passage through columns of BASF R-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). NMR spectra were recorded on a GE QE-300 Plus (300.1 MHz; 75.49 MHz ^{13}C) spectrometer. IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer. Gel permeation chromatographs were obtained on a HPLC system using an Altex Model 110A pump, a Rheodyne model 7125 injector with a 100 μL injection loop, two American Polymer Standards 10 μm mixed-bed columns, and a Knauer differential refractometer using CH_2Cl_2 as eluent at a 1.0 mL/min flow rate. Molecular weights and polydispersities were reported versus those of monodispersed polystyrene standards. Differential scanning calorimetry was carried out on a Perkin-Elmer DSC-7 with a scan rate of 10 °C/min. Polarizing optical microscopic observations of the textures were made using a Zeiss Axiophot polarizing microscope equipped with a Linkam THM 600 hot stage and a TMS 90 thermal control unit. All polarizing micrographs were taken with a 50-fold magnification unless noted otherwise.

Materials. CH_2Cl_2 was distilled from calcium hydride and degassed by repeated freeze−pump−thaw cycles. All other solvents were used without further purification unless otherwise noted. Furan, acryloyl chloride, sodium hydride, piperidine, *p*-hydroxybenzaldehyde, *p*-nitrophenylacetic acid, potassium carbonate, thionyl chloride, triethylamine, ethyl vinyl ether, and the series of bromo alcohols were purchased from Aldrich Chemical Co. and used without further purification. Catalyst **1** was graciously provided by Dr. Peter Schwab.

Preparation of 5-{([6-(4-[2-(4-Nitrophenyl)vinyl]phenoxy)-hexyl]oxy)carbonyl}bicyclo[2.2.1]hept-2-ene (8). A solution of **3** (3.75 g, 0.011 mol) and triethylamine (1.11 g, 0.011 mol) in THF (300 mL) was treated with a solution of **7** (1.56 g, 0.010 mol) in THF (10 mL) and stirred under reflux for 18 h. During this time, a white solid precipitated. The solution was filtered and the solvent evaporated under dynamic vacuum to obtain a yellow solid. The solid was purified by flash column chromatography (silica/CH_2Cl_2) to obtain 2.7 g (59%): ^{1}H NMR ($CDCl_3$) δ 8.15 (d, $J = 8.4$ Hz, 2H), 7.55 (d, $J = 8.4$ Hz, 2H), 7.45 (d, $J = 8.4$ Hz, 2H), 7.19 (d, $J = 16.3$ Hz, 1H), 6.95 (d, $J = 16.3$ Hz, 1H), 6.88 (d, $J = 8.4$ Hz, 2H), 6.16 (dd, $J_1 = 2.9$ Hz, $J_2 = 5.4$ Hz, 1H), 5.90 (dd, $J_1 = =2.9$ Hz, $J_2 = 5.4$ Hz, 1H), 4.04−3.95 (m, 4H), 3.18 (m, 1H), 2.93−2.89 (m, 2H), 1.89−1.23 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 174.5, 159.6, 146.1, 144.1, 137.5, 132.7, 132.1, 128.5, 128.2, 126.2, 123.9, 123.7, 114.6, 67.7, 63.9, 49.4, 45.5, 43.1, 42.3, 29.0, 28.9, 28.4, 25.5, 25.4; IR (thin film on a NaCl plate) 2943, 2807, 1727, 1630, 1590, 1571, 1514, 1467, 1391, 1340, 1271, 1254, 1175, 1108, 1065, 1022, 973, 957, 873, 842, 749, 714, 687, 536 cm^{-1}; HRMS (FAB) calcd for $C_{28}H_{31}NO_5$ (M)$^+$ 461.2202, found 461.2210.

Preparation of 5-{([8-(4-[2-(4-Nitrophenyl)vinyl]phenoxy)octyl]oxy)carbonyl}bicyclo[2.2.1]hept-2-ene (9). Compound **9** was synthesized in analogy to the procedure described above using **4** (6 g, 0.016 mol) and **7** (2.52 g, 0.016 mol) in THF to yield 5.3 g (68%): ^{1}H NMR ($CDCl_3$) δ 8.19 (d, $J = 8.4$ Hz, 2H), 7.58 (d, $J = 8.4$ Hz, 2H), 7.47 (d, $J = 8.4$ Hz, 2H), 7.21 (d, $J = 16.2$ Hz, 1H), 6.98 (d, $J = 16.2$ Hz, 1H), 6.90 (d, $J = 8.4$ Hz, 2H), 6.17 (dd, $J_1 = =3.0$ Hz, $J_2 = 5.6$ Hz, 1H), 5.90 (dd, $J_1 = 3.0$ Hz, $J_2 = 5.6$ Hz, 1H), 4.03−3.95 (m, 4H), 3.19 (m, 1H), 2.96−2.89 (m, 2H), 1.89−1.24 (m, 14H); ^{13}C NMR ($CDCl_3$) δ 174.5, 159.8, 146.3, 144.3, 137.7, 132.9, 132.3, 128.7, 128.4, 126.4, 124.1, 123.9, 114.8, 68.0, 64.2, 49.59, 45.7, 43.3, 42.5, 29.2, 29.1, 28.6, 25.9; IR (thin film on a NaCl plate) 2932, 2854, 1715, 1633, 1590, 1574, 1514, 1474, 1392, 1338, 1308, 1271, 1255, 1176, 1108, 1030, 980, 952, 913, 876, 843, 824, 798, 749, 715, 686, 583, 531 cm^{-1}; HRMS (FAB) calcd for $C_{30}H_{35}NO_5$ (M)$^+$ 489.2515, found 489.2531.

Preparation of 5-{([10-(4-[2-(4-Nitrophenyl)vinyl]phenoxy)decyl]oxy)carbonyl}bicyclo[2.2.1]hept-2-ene (10). Compound **10** was synthesized in analogy to the procedure described above using **5** (5 g, 0.013 mol) and **7** (2 g, 0.013 mol) in THF to give 4.5 g (68%): ^{1}H NMR ($CDCl_3$) δ 8.19 (d, $J = 8.4$ Hz, 2H), 7.58 (d, $J = 8.4$ Hz, 2H), 7.48 (d, $J = 8.4$ Hz, 2H), 7.21 (d, $J = 16.2$ Hz, 1H), 6.99 (d, $J = 16.2$ Hz, 1H), 6.91 (d, $J = 8.4$ Hz, 2H), 6.19 (dd, $J_1 = 3.0$ Hz, $J_2 = 5.6$ Hz, 1H), 5.94 (dd, $J_1 = 3.0$ Hz, $J_2 = 5.6$ Hz, 1H), 4.09−3.96 (m, 4H), 3.22 (m, 1H), 2.98−2.91 (m, 2H), 1.95−1.27 (m, 18H); ^{13}C NMR ($CDCl_3$) δ 174.6, 159.6, 146.1, 144.1, 137.5, 132.8, 132.1, 128.5, 128.2, 126.2, 123.9, 123.6, 114.6, 67.9, 64.1, 49.4, 45.5, 43.1, 42.3, 29.2, 29.1, 29.0, 28.4, 25.8, 25.7; IR (thin film on a NaCl plate) 2935, 2851, 1810, 1718, 1630, 1591, 1574, 1519, 1474, 1423, 1389, 1339, 1299, 1271, 1250, 1176, 1108, 1066, 1042, 1025, 980, 952, 913, 876, 843, 824, 797, 748, 716, 686, 671, 583, 530 cm^{-1}; HRMS (FAB) calcd for $C_{32}H_{39}NO_5$ (M)$^+$ 517.2749, found 517.2791.

Preparation of 5-{([12-(4-[2-(4-nitrophenyl)vinyl]phenoxy)dodecyl]oxy)carbonyl}bicyclo[2.2.1]hept-2-ene (11). Compound **11** was synthesized according to the procedure described above using **6** (3 g, 0.007 mol) and **7** (1.2 g, 0.0075 mol) in THF to give 3.1 g (81%): ^{1}H NMR ($CDCl_3$) δ 8.19 (d, $J = 8.7$ Hz, 2H), 7.58 (d, $J = 8.7$ Hz, 2H), 7.47 (d, $J = 8.7$ Hz, 2H), 7.22 (d, $J = 16.2$ Hz, 1H), 6.99 (d, $J = 16.2$ Hz, 1H), 6.90 (d, $J = 8.7$ Hz, 2H), 6.18 (dd, $J_1 = 3.0$ Hz, $J_2 = 5.4$ Hz, 1H), 5.91 (dd, $J_1 = 3.0$ Hz, $J_2 = 5.4$ Hz, 1H), 4.07−3.96 (m, 4H), 3.19 (m, 1H), 2.96−2.88 (m, 2H), 1.88−1.27 (m, 22H); ^{13}C NMR ($CDCl_3$) δ 174.6, 159.7, 146.1, 144.1, 137.5, 132.8, 132.1, 128.5, 128.2, 126.2, 123.9, 123.6, 114.6, 67.9, 64.1, 49.4, 45.5, 43.1, 42.3, 29.3, 29.2, 29.0, 28.5, 25.8, 25.7; IR (thin film on a NaCl plate) 2916, 2851, 1717, 1590, 1574, 1518, 1474, 1389, 1339, 1270, 1246, 1176, 1109, 1040, 980, 953, 913, 875, 843, 824, 795, 748, 716, 686, 671, 530 cm^{-1}; HRMS (FAB) calcd for $C_{34}H_{43}NO_5$ (M)$^+$ 545.3141, found 545.3152.

Preparation of 6-(4-[2-(4-Nitrophenyl)vinyl]phenoxy)hexyl [3-Oxa-4-(2-cyclobutenyl)]butyrate (13). [3-Oxa-4-(2-cyclobutenyl)]butyric acid (**12**)[43] (2.4 g, 0.017 mol) was combined with thionyl chloride (6.0 g, 0.050 mol) in a 25 mL round-bottom flask. This mixture was then heated to reflux for 1.5 h, at which point gas evolution had ceased. The flask was then concentrated *in vacuo*. The resulting orange oil was then added over 5 min to a solution of **3** (4.0 g, 0.012 mol) and triethylamine (1.88 g, 0.019 mol) in THF (200 mL). The reaction was then heated to reflux under argon overnight. A solution of saturated K_2CO_3 (75 mL) was added, and the organic layer was separated and dried over $MgSO_4$. Following concentration *in vacuo*, the yellow solid was purified by flash column chromatography (silica/15% ethyl acetate, hexanes) to give 4.26 g (75%): ^{1}H NMR ($CDCl_3$) δ 8.18 (d, $J = 9.0$ Hz, 2H), 7.57 (d, $J = 9.0$ Hz, 2H), 7.46 (d, $J = 9.0$ Hz, 2H), 7.18 (d, $J = 16.2$ Hz, 1H), 6.93 (d, $J = 16.2$ Hz, 1H), 6.89 (d, $J = 9.0$ Hz, 2H), 6.07 (dd, $J_1 = 3.0$ Hz, $J_2 = 10.5$ Hz, 2H), 4.16 (t, $J = 6.6$ Hz, 2H), 4.08 (s, 2H), 3.97 (t, $J = 6.6$ Hz, 2H), 3.60 (d, $J = 6.9$ Hz, 2H), 3.11 (m, 1H), 2.6 (dd, $J_1 = 4.2$ Hz, $J_2 = 13.8$ Hz, 1H), 2.2 (d, $J = 13.8$ Hz, 1H), 1.90−1.33 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 170.6, 159.8, 146.5, 144.3, 137.9, 137.1, 133.0, 128.9, 128.4, 126.4, 124.1, 124.0, 114.9, 75.3, 68.5, 67.9, 64.6, 43.3, 34.3, 29.1, 28.5, 25.6; IR (thin film on a NaCl plate) 3055, 2943, 2866, 1742, 1605, 1588, 1570, 1512, 1474, 1339, 1272, 1252, 1205, 1176, 1135, 1110, 1011, 969, 956, 844, 750, 718, 670 cm^{-1}; HRMS (FAB) calcd for $C_{34}H_{43}NO_5$ (M)$^+$ 465.2151, found 465.2130.

Preparation of 8-(4-[2-(4-Nitrophenyl)vinyl]phenoxy)octyl [3-Oxa-4-(2-cyclobutenyl)]butyrate (14). Compound **14** was synthesized from **12** (1.98 g, 0.014 mol) and **4** (3.5 g, 0.0095 mol) as above to yield 3.42 g (73% yield): ^{1}H NMR ($CDCl_3$) δ 8.18 (d, $J = 9.0$ Hz, 2H), 7.54 (d, $J = 9.0$ Hz, 2H), 7.44 (d, $J = 9.0$ Hz, 2H), 7.19 (d, $J = 16.2$ Hz, 1H), 6.95 (d, $J = 16.2$ Hz, 1H), 6.87 (d, $J = 9.0$ Hz, 2H), 6.07 (dd, $J_1 = 2.7$ Hz, $J_2 = 9.3$ Hz, 2H), 4.13 (t, $J = 6.6$ Hz, 2H), 4.07 (s, 2H), 3.95 (t, $J = 6.6$ Hz, 2H), 3.58 (d, $J = 6.9$ Hz, 2H), 3.12 (m, 1H), 2.65 (dd, $J_1 = 4.8$ Hz, $J_2 =13.8$ Hz, 1H), 2.22 (d, $J = 13.8$ Hz, 1H), 1.81−1.33 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 170.6, 159.8, 146.4, 144.3, 137.9, 137.0, 133.0, 128.8, 128.4, 126.4, 124.1, 123.9, 114.9, 75.2, 68.5, 68.0, 64.8, 43.3, 34.3, 29.2, 29.1, 28.5, 25.9, 25.8; IR (thin film on a NaCl plate) 3028, 2921, 2854, 1743, 1587, 1573, 1513, 1470, 1423, 1339, 1270, 1245, 1208, 1176, 1135, 1115, 1024, 968, 954, 841, 748, 665, cm^{-1}; HRMS (FAB) calcd for $C_{34}H_{43}NO_5$ (M)$^+$ 493.2464, found 493.2449.

Preparation of 10-(4-[2-(4-Nitrophenyl)vinyl]phenoxy)decyl [3-Oxa-4-(2-cyclobutenyl)]butyrate (15). Compound **15** was synthesized from **12** (0.79 g, 0.006 mol) and **5** (1.5 g, 0.004 mol) as above to yield 1.40 g (71% yield): ^{1}H NMR ($CDCl_3$) δ 8.18 (d, $J = 9.0$ Hz, 2H), 7.57 (d, $J = 9.0$ Hz, 2H), 7.45 (d, $J = 9.0$ Hz, 2H), 7.20 (d, $J = 16.2$ Hz, 1H), 6.93 (d, $J = 16.2$ Hz, 1H), 6.89 (d, $J = 9.0$ Hz, 2H), 6.07 (dd, $J_1 = 3.0$ Hz, $J_2 = 10.5$ Hz, 2H), 4.13 (t, $J = 6.6$ Hz, 2H), 4.07 (s, 2H), 3.97 (t, $J = 6.6$ Hz, 2H), 3.60 (d, $J = 7.2$ Hz, 2H), 3.12 (m, 1H), 2.67 (dd, $J_1 = 4.2$ Hz, $J_2 = 13.5$ Hz, 1H), 2.22 (d, $J = 13.5$ Hz, 1H), 1.85−1.05 (m, 16H); ^{13}C NMR ($CDCl_3$) δ 170.6, 159.9, 146.5, 144.3, 137.9, 137.0, 133.0, 128.8, 128.4, 126.4, 124.1, 123.9, 114.9, 75.3, 68.6, 68.2, 64.9, 43.3, 34.3, 29.4, 29.3, 29.2, 29.1, 28.6, 26.0, 25.8; IR (thin film on a NaCl plate) 3056, 2923, 2852, 1747, 1589, 1572, 1513, 1477, 1467, 1438, 1340, 1270, 1245, 1214, 1176, 1135, 1111, 1041, 1020, 979, 954, 842, 748, 716, 687, 702, 671 cm^{-1}; HRMS (FAB) calcd for $C_{34}H_{43}NO_5$ (M)$^+$ 521.2777, found 521.2768.

Preparation of 12-(4-[2-(4-Nitrophenyl)vinyl]phenoxy)dodecyl [3-Oxa-4-(2-cyclobutenyl)]butyrate (16). Compound **16** was synthesized from **12** (0.84 g, 0.006 mol) and **6** (1.7 g, 0.004 mol) as above to yield 1.52 g (69% yield): ^{1}H NMR ($CDCl_3$) δ 8.18 (d, $J = 9.0$ Hz, 2H), 7.57 (d, $J = 9.0$ Hz, 2H), 7.46 (d, $J = 9.0$ Hz, 2H), 7.19 (d, $J = 16.2$ Hz, 1H), 6.93 (d, $J = 16.2$ Hz, 1H), 6.89 (d, $J = 9.0$ Hz, 2H), 6.07 (dd, $J_1 = 3.0$ Hz, $J_2 = 9.9$ Hz, 2H), 4.13 (t, $J = 6.6$ Hz, 2H), 4.07 (s, 2H), 3.97 (t, $J = 6.6$ Hz, 2H), 3.58 (d, $J = 6.6$ Hz, 2H), 3.13 (m, 1H), 2.6 (dd, $J_1 = 4.5$ Hz, $J_2 = 14.1$ Hz, 1H), 2.2 (d, $J = 14.1$ Hz, 1H), 1.90−1.33 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 170.6, 159.9, 146.5, 144.4, 138.0, 137.0, 133.0, 128.8, 128.4, 126.4, 124.1, 124.0, 115.0, 75.3, 68.5, 68.2, 64.9, 43.3, 34.4, 29.5, 29.3, 29.3, 29.2, 28.6, 26.0, 25.8; IR (thin film on a NaCl plate) 3043, 2921, 2851, 1750, 1606, 1589, 1573, 1514, 1469, 1424, 1340, 1271, 1250, 1206, 1179, 1134, 1110, 1032, 972, 953, 839, 824, 749, 699, 686 cm^{-1}; HRMS (FAB) calcd for $C_{34}H_{43}NO_5$ (M)$^+$ 550.3169, found 550.3194.

General Polymerization Procedure for the Norbornene Monomers 8−11. Under an inert atmosphere, the catalyst and the monomer were weighed into vials and dissolved in CH_2Cl_2 (~1 mL of CH_2Cl_2 for every 100 mg of monomer). The reaction was initiated by adding the catalyst solution to the vigorously stirred monomer solution. The reaction mixture was allowed to stir under argon for 1 h. The reaction mixture was terminated by adding a small amount of ethyl vinyl ether and poured into methanol (~50 mL) to precipitate the polymer. The resulting yellow polymer was purified by dissolving in CH_2Cl_2, reprecipitating from methanol several times, and drying *in vacuo*. Isolated yields ranged from 85 to 99% (100% by ^{1}H NMR).

Polymer 17: ^{1}H NMR ($CDCl_3$) δ 8.15 (bd, 2H), 7.54 (bd, 2H), 7.43 (bd, 2H), 7.17 (bd, 1H), 6.95 (bd, 1H), 6.87 (bd, 2H), 5.38 (bs, 1H), 5.28 (bs, 1H), 3.94 (bs, 2H), 2.85−2.74 (bm, 2H), 2.40 (bs, 1H), 1.75 (bs, 2H), 1.40 (bs, 2H), 1.25 (bs 4H); ^{13}C NMR ($CDCl_3$) δ 174.2, 159.6, 146.3, 144.0, 132.7, 134.3−129.4 (backbone C-olefin), 128.7, 128.1, 126.2, 123.8, 114.7, 67.7, 63.8, 49.4−35.6 (backbone C-alkyl), 28.8, 28.4, 25.6, 25.5; IR (thin film on a NaCl plate) 3422, 2941, 2860, 1723, 1632, 1588, 1511, 1339, 1252, 1174, 1109, 968, 842, 749, 688, 533 cm^{-1}.

Polymer 18: ^{1}H NMR ($CDCl_3$) δ 8.14 (bd, 2H), 7.53 (bd, 2H), 7.42 (bd, 2H), 7.16 (bd, 1H), 6.94 (bd, 1H), 6.86 (bd, 2H), 5.37 (bs, 1H), 5.28 (bs, 1H), 3.92 (bs, 2H), 2.84−2.72 (bm, 2H), 2.39 (bs, 1H), 1.74 (bs, 2H), 1.41 (bs, 2H), 1.31 (bs 8H); ^{13}C NMR ($CDCl_3$) δ 174.2, 159.6, 146.3, 144.0, 132.7, 134.3−129.4 (backbone C-olefin), 128.7, 128.1, 126.2, 124.1, 114.7, 67.9, 63.9, 48.1−35.6 (backbone C-alkyl), 29.0, 28.5, 25.7; IR (thin film on a NaCl plate) 2934, 2855, 1723, 1631, 1606, 1588, 1511, 1472, 1393, 1338, 1303, 1253, 1174, 1109, 1025, 967, 873, 841, 750, 688, 668, 533 cm^{-1}.

Polymer 19: ^{1}H NMR ($CDCl_3$) δ 8.15 (bd, 2H), 7.53 (bd, 2H), 7.43 (bd, 2H), 7.17 (bd, 1H), 6.94 (bd, 1H), 6.87 (bd, 2H), 5.37 (bs, 1H), 5.28 (bs, 1H), 3.93 (bs, 2H), 2.87−2.74 (bm, 2H), 2.40 (bs, 1H), 1.75 (bs, 2H), 1.40 (bs, 2H), 1.27 (bs 12H); ^{13}C NMR ($CDCl_3$) δ 174.3, 159.7, 146.3, 144.0, 132.7, 134.3−129.3 (backbone C-olefin), 128.6, 128.1, 126.2, 123.8, 114.7, 67.9, 64.0, 48.1−35.6 (backbone C-alkyl), 29.3, 29.1, 29.0, 28.5, 25.8; IR (thin film on a NaCl plate) 2927, 2854, 1725, 1633, 1588, 1512, 1470, 1393, 1338, 1253, 1174, 1109, 1022, 967, 841, 750, 688, 666, 534 cm^{-1}.

Polymer 20: ^{1}H NMR ($CDCl_3$) δ 8.15 (bd, 2H), 7.54 (bd, 2H), 7.43 (bd, 2H), 7.17 (bd, 1H), 6.95 (bd, 1H), 6.87 (bd, 2H), 5.36 (bs, 1H), 5.28 (bs, 1H), 3.94 (bs, 2H), 2.85−2.75 (bm, 2H), 2.41 (bs, 1H), 1.75 (bs, 2H), 1.42 (bs, 2H), 1.25 (bs 16H); ^{13}C NMR ($CDCl_3$) δ 174.2, 159.7, 146.3, 144.1, 132.7, 134.3−129.3 (backbone C-olefin), 128.6, 128.1, 126.2, 123.8, 114.7, 68.0, 64.0, 49.5−35.6 (backbone C-alkyl), 29.3, 29.1, 29.0, 28.5, 25.8; IR (thin film on a NaCl plate) 3023, 2925, 2853, 1725, 1630, 1606, 1589, 1512, 1467, 1393, 1339, 1303, 1254, 1175, 1109, 1023, 967, 871, 841, 750, 688, 668, 581, 534 cm^{-1}.

General Polymerization Procedure for the Cyclobutene Monomers 13−16. Under an inert atmosphere, the catalyst and the monomer were weighed into vials and dissolved in CH_2Cl_2 such that the overall [M] was 0.3 M. The reaction was initiated by adding the catalyst solution to the vigorously stirred monomer solution. The reaction mixture was allowed to stir under argon for 24 h at 45 °C. The reaction mixture was poured into methanol (~150 mL) containing 1 N HCl (5% v/v) to precipitate the polymer, and this was left to stir for 30 min. The polymer was then redissolved in CH_2Cl_2 and reprecipitated into methanol (~150 mL). The polymer was then isolated by filtration and dried *in vacuo*. Isolated yields ranged from 82 to 98% (100% by ^1H NMR).

Polymer 21: ^1H NMR ($CDCl_3$) δ 8.12 (bs, 2H), 7.51 (bs, 2H), 7.41 (bs, 2H), 7.38−6.75 (bm, 4H), 5.51−5.13 (bm, 2H), 4.21−3.80 (bm, 6H), 3.51 (bs, 2H), 2.70 (bs, 1H), 2.44−1.26 (bm, 10H); ^{13}C NMR ($CDCl_3$) δ 170.4, 159.8, 146.9, 144.2, 132.9, 132.6−131.1 (backbone C-olefin), 128.9, 128.4, 126.4, 124.1, 114.9, 74.8, 68.5, 67.9, 64.5, 42.8−35.2 (backbone C-alkyl), 29.1, 28.6, 25.7; IR (thin film on a NaCl plate) 2933, 2856, 1751, 1628, 1589, 1512, 1473, 1341, 1254, 1197, 1175, 1139, 1110, 1022, 967, 842, 749, cm^{-1}.

Polymer 22: ^1H NMR ($CDCl_3$) δ 8.15 (bd, 2H), 7.56 (bd, 2H), 7.43 (bd, 2H), 7.39−6.75 (bm, 4H), 5.51−5.12 (bm, 2H), 4.19−3.82 (bm, 6H), 3.51 (bs, 2H), 2.73 (bs, 1H), 2.43−1.07 (bm, 14H); ^{13}C NMR ($CDCl_3$) δ 170.4, 159.8, 146.5, 144.3, 132.9, 132.5−131.3 (backbone C-olefin), 128.9, 128.4, 126.4, 124.0, 114.9, 74.8, 68.5, 68.1, 64.7, 42.8−35.1 (backbone C-alkyl), 29.7, 29.2, 29.1, 28.6, 26.0, 25.8; IR (thin film on a NaCl plate) 2928, 2854, 1751, 1589, 1511, 1474, 1341, 1253, 1196, 1175, 1139, 1110, 1026, 967, 841, 749, 717 cm^{-1}.

Polymer 23: ^1H NMR ($CDCl_3$) δ 8.19 (bd, 2H), 7.57 (bd, 2H), 7.45 (bd, 2H), 7.38−6.78 (bm, 4H), 5.59−5.17 (bm, 2H), 4.24−3.87 (bm, 6H), 3.56 (bs, 2H), 2.73 (bs, 1H), 2.45−1.13 (bm, 18H); ^{13}C NMR ($CDCl_3$) δ 170.4, 159.9, 146.6, 144.3, 133.0, 132.5−131.6 (backbone C-olefin), 128.9, 128.4, 126.4, 124.1, 115.0, 74.9, 68.6, 68.2, 64.7, 42.9−35.2 (backbone C-alkyl), 29.5, 29.4, 29.3, 29.3, 29.2, 28.7, 26.0, 25.9; IR (thin film on a NaCl plate) 2927, 2854, 1753, 1630, 1589, 1513, 1468, 1394, 1342, 1254, 1196, 1175, 1140, 1110, 1031, 967, 842, 749, 718, 688 cm^{-1}.

Polymer 24: ^1H NMR ($CDCl_3$) δ 8.15 (bd, 2H), 7.54 (bd, 2H), 7.44 (bd, 2H), 7.35−6.78 (bm, 4H), 5.54−5.14 (bm, 2H), 4.19−3.84 (bm, 6H), 3.53 (bs, 2H), 2.85 (bs, 1H), 2.42−1.01 (bm, 22H); ^{13}C NMR ($CDCl_3$) δ 170.4, 159.9, 146.6, 144.3, 133.0, 132.4−131.5 (backbone C-olefin), 128.9, 128.4, 126.4, 124.0, 115.0, 74.8, 68.5, 68.2, 64.7, 42.8−35.2 (backbone C-alkyl), 29.5, 29.4, 29.3, 28.7, 26.0, 25.9; IR (thin film on a NaCl plate) 2924, 2852, 1752, 1589, 1512, 1467, 1341, 1303, 1254, 1196, 1175, 1140, 1109, 1025, 966, 872, 841, 749, 718, 687 cm^{-1}.

Preparation of the Block Copolymer 25. **9** (150 mg, 3.07×10^{-4} mol) was polymerized with initiator **1** (9.3 mg, 1.13×10^{-5} mol) in analogy to the procedure outlined above for the norbornene monomers. After 1 h, **14** (150 mg, 3.22×10^{-4} mol) in CH_2Cl_2 (1 mL) was added via a gas-tight syringe. The vial was sealed and the mixture stirred for 24 h at 45 °C. The solution was then poured into methanol (100 mL) containing 1 N HCl 5% (v/v). The yellow precipitate was filtered and reprecipitated several times to give **25** in 96% (288 mg) yield: ^1H NMR ($CDCl_3$) δ 8.13 (bs), 7.52 (bs), 7.42 (bs), 7.15 (bd), 6.93 (bd), 6.85 (bs), 5.36 (bs), 4.08 (bs), 4.01 (bs), 3.92 (bs), 3.38 (bs), 3.16 (bs), 2.84 (bs), 2.71 (bs), 2.34 (bs), 1.94 (bs), 1.73 (bs), 1.54 (bs), 1.40 (bs), 1.30 (bs); ^{13}C NMR ($CDCl_3$) δ 174.2, 174.2, 159.6, 146.2, 144.0, 132.7, 134.3−129.4 (backbone C-olefin), 128.6, 128.1, 126.2, 123.8, 114.7, 74.5, 68.3, 67.9, 64.4, 63.9, 49.5−34.9 (backbone C-alkyl), 29.0, 28.9, 28.5, 28.4, 25.7, 25.5.

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Supporting Information Available: Experimental procedures for the syntheses of compounds **2**−**7** (3 pages). Ordering information is given on any current masthead page.

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