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# Correlation of Model Compounds and Laterally Attached Side-Chain Liquid Crystalline Polynorbornenes with a 1-Carbon Spacer

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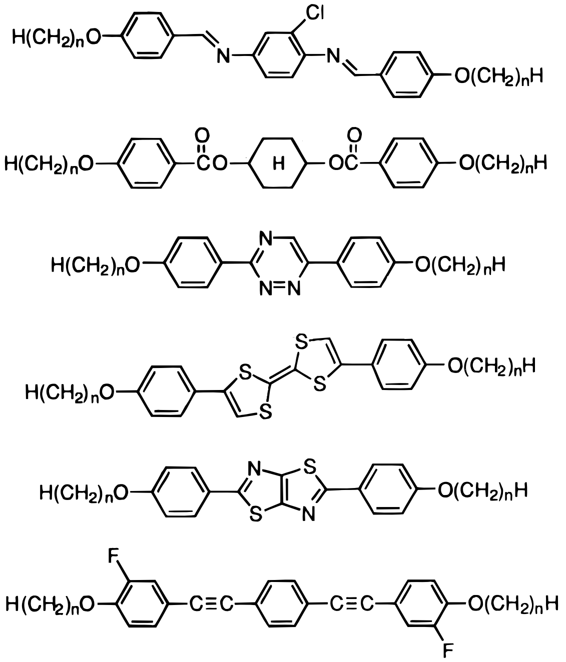
ABSTRACT: 1,4-Bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]toluenes mimic the thermotropic behavior of poly{5-[[[2′,5′-bis[(4′-*n*-alkoxybenzoyl)oxy]benzyl]oxy]carbonyl]bicyclo[2.2.1]hept-2-ene}s better than 1,4-bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzenes do. Polymers with approximately 50 repeat units and narrow polydispersity (pdi = 1.08−1.23) were prepared by ring-opening metathesis polymerization of 5-{[[2′,5′-bis[2-(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzyl]oxy]carbonyl}bicyclo[2.2.1]hept-2-enes in THF using $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}{}^iPr_2Ph)(O^tBu)_2$ as the initiator. All of the polymers exhibit an enantiotropic nematic mesophase in addition to the glass transition, and those with $n = 3-12$ slowly organize into a crystalline or $s_E$ phase that occurs over an extremely narrow temperature range. Whereas 1,4-bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzenes exhibit a k−$s_E$−$s_C$−n−i phase sequence when $n = 6-12$, all of the 1,4-bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]toluenes exhibit a nematic mesophase, and those with $n = 9-12$ also exhibit either a monotropic $s_C$ mesophase or an enantiotropic $s_C$ mesophase over a very narrow temperature range.

## Introduction

Since their discovery in the early 1970s,[1] hundreds of side-chain liquid crystalline polymers (SCLCPs) have been prepared.[2] However, their structure/property correlations are only now emerging through the study of well-defined SCLCPs prepared by controlled polymerizations in which a single structural variable is changed while all others remain constant.[3] Nevertheless, it is still difficult to design polymers with predetermined mesophases. Most SCLCPs exhibit either nematic (n) or smectic A ($s_A$) mesophases,[2] which have limited academic and/or practical interest. In contrast, polymers with ferroelectric mesophases such as chiral smectic C ($s_C$*) mesophases may be commercially important. For example, surface-stabilized ferroelectric liquid crystals are being developed as memory switching devices in flat panel displays because of their fast optical response.[4]

The extensive literature on low molar mass liquid crystals (LMMLCs) demonstrates that specific mesogens (specific chemical structures) tend to form specific mesophases that vary somewhat with the length of the flexible substituent(s).[3,5] We therefore expect that the type of mesogen, including the terminal substituents and the length of the spacer, should be the primary factor determining the specific mesophase exhibited by a given SCLCP. The nature of the polymer backbone, tacticity, polydispersity, etc. should then be secondary factors in enhancing, altering, or disrupting the natural ordering of the mesogenic side chains. The most obvious approach for obtaining SCLCPs with $s_C$* mesophases should therefore be to use mesogens that also exhibit this phase.

**Chart 1. Typical Structures of Low Molar Mass Liquid Crystals That Form Smectic C Mesophases**



The literature on LMMLCs demonstrates that $s_C$ mesophases are common for extended mesogens that are symmetrically disubstituted with long *n*-alkoxy substituents.[5] Some examples of LMMLCs that form $s_C$ mesophases are shown in Chart 1 and include 2-chloro-*N*,*N*′-bis[4″-*n*-alkoxybenzylidene]phenylene-1,4-diamines ($n = 8, 10$),[5] *trans*-1,4-bis[4′-*n*-alkoxyphenyl]cylclohexane dicarboxylates ($n = 7, 8, 12, 14, 16$),[5] 3,6-bis[4′-*n*-alkoxyphenyl]-1,2,4-triazines ($n = 3-10$),[5] 2,6-bis[4′-*n*-alkoxyphenyl]-1,4,5,8-tetrathiafulvalenes ($n = 8, 10$),[5] 2,5-bis[4′-*n*-alkoxyphenyl]thiazolo[5,4-*d*]thiazoles ($n = 4-8$),[5] and 1,4-bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzenes ($n = 7-12$).[6] In addition, many of these compounds undergo a $s_C$−n transition before melting into the isotropic state,[5,6] which results in larger absolute values of spontaneous polarization, and presumably faster reorientation times, than systems exhibiting a $s_C$−$s_A$ phase sequence.[7]

Although attaching the mesogen terminally to the polymer backbone precludes its symmetrical disubstitution with long *n*-alkoxy groups, for most SCLCPs de-

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signed to exhibit $s_C$ (and/or $s_C$*) mesophases, not only are the SCLCPs based on mesogens containing only two aromatic rings but also these truncated mesogens are terminally attached.[8−10] If a $s_C$ mesophase is observed, it is usually monotropic and/or in the less desirable $s_C-s_A$ phase sequence,[8,9] although polymethacrylates containing azobenzene mesogens form $s_C$ mesophases more readily when the lengths of the spacer and *n*-alkoxy terminal substituent are identical.[11] Much more stable, enantiotropic $s_C$ mesophases have been achieved using more extended, albeit asymmetric, mesogens, terminally attached to the polymer backbone through long spacers.[12−14] However, most of these polymers also exhibit only the less desirable $s_C^*-s_A$ phase sequence.[13,14]

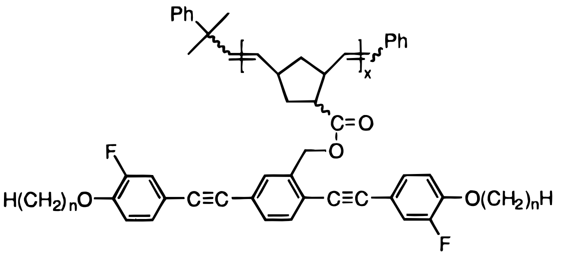
In contrast to terminal attachment, lateral attachment allows extended mesogens to be incorporated as side chains to a polymer backbone without disrupting their symmetrical disubstitution.[15] Although this lateral attachment is commonly believed to strongly favor formation of nematic mesophases,[16] or even prevent ordering into smectic layers,[17] most of these SCLCPs contain 1,4-bis[(4′-*n*-alkoxybenzoyl)oxy]benzene mesogens that show little tendency to organize into smectic layers.[5,15] However, we have recently demonstrated that polynorbornenes with laterally attached 1,4-bis-[(4′-*n*-alkoxybenzoyl)oxy]benzene mesogens can be forced to order into smectic layers by terminating their *n*-alkoxy substituents with immiscible fluorocarbon units.[18] This paper will describe the more obvious approach to designing SCLCPs with $s_C$ mesophases: incorporating mesogens that exhibit the desired $s_C-n$ phase sequence, namely 1,4-bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzenes.

In order to determine the effect of incorporating 1,4-bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzene mesogens into a laterally attached architecture without altering any other structural variables, we will use the poly{5-[[[2′,5′-bis[(4′′-*n*-alkoxybenzoyl)oxy]benzyl]oxy]carbonyl]bicyclo[2.2.1]hept-2-ene}s[19] shown in Chart 2 as a reference system for the title polymers. The reference polymers are the only well-defined laterally attached SCLCPs prepared to date; both the molecular weight dependence and the effect of the length of the *n*-alkoxy substituents are known. (In particular, the thermotropic behavior becomes independent of molecular weight at approximately 25 repeat units; therefore, the phase behavior will be representative of a *polymer* if the chains contain at least 25 repeat units.)

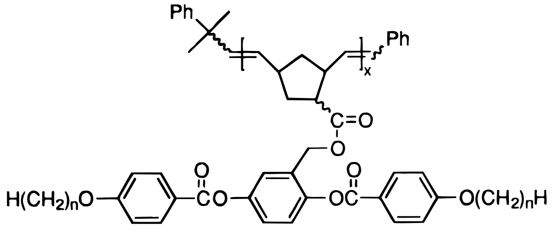
However, short spacers generally preclude smectic layering.[3] In addition, the mesogen density appears to have a pronounced effect on the phase(s) formed by liquid crystalline polynorbornenes. For example, polynorbornenes with one terminally attached *p*-cyanobiphenyl mesogen per repeat unit form only nematic mesophases,[20] whereas the corresponding polynorbornenes[21] with two mesogens per repeat unit form $s_A$ mesophases if the spacer contains at least eight carbons. This paper will therefore be the first paper in a systematic study of SCLCPs laterally attached with 1,4-bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzene mesogens designed to exhibit the $s_C-n$ phase sequence. Once we have determined the effect of changing only the laterally attached mesogen from one that normally forms only a nematic mesophase to one that exhibits a $s_C-n$ phase sequence, we will determine the effect of using a long spacer, and if necessary, the effect of doubling the mesogen density along the polynorbornene backbone.

**Chart 2. Comparison of SCLCPs with Laterally Attached Mesogens (Title Polymer System) That Exhibit $s_C-n$ Phase Sequences to a Well-Defined SCLCP with Laterally Attached Mesogens (Reference Polymer System) That Tend To Form Only Nematic Mesophases and to Potential Model Compounds**

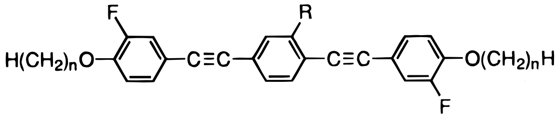
**Title Polymer System:**



**Reference Polymer System:**



**Model Compounds (R = -H, -CH3):**

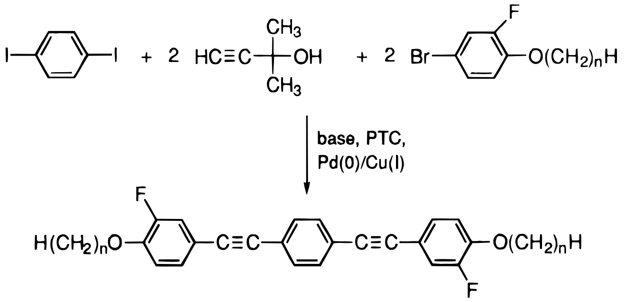


If the mesogen and its substituents are the primary factors determining the specific mesophase(s) exhibited by a given SCLCP, then the thermotropic behavior of the SCLCP should be predictable by comparison to an appropriate model compound. (Not surprisingly, the monomers themselves, which contain olefin end groups and/or cyclic units that are very different from the chemical structure of the polymer backbone, are the least appropriate model compounds for the resulting SCLCPs.[3]) Therefore, this paper will also compare the thermotropic behavior of both 1,4-bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzenes (R = H model compounds) and 2,5-bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]-toluenes (R = $CH_3$ model compounds) to that of the title polymers (Chart 2) in order to determine whether or not the alkyl substituent is necessary for low molar mass liquid crystals to mimic the thermotropic behavior of laterally attached SCLCPs.

## Results and Discussion

**Synthesis and Thermotropic Behavior of 1,4-Bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzenes (R = H Model Compounds).** As reported previously,[6] the symmetrically difluorinated 1,4-bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzenes with $n$ = 7−12 exhibit a $k-s_E-s_C-n-i$ phase sequence. In order to determine the minimum length of the *n*-alkoxy substituents necessary for $s_C$ mesophase formation, we completed the synthesis and characterization of the series with $n$ = 1−6 by the same one-pot, phase-transfer, Pd(0)/Cu(I)-catalyzed, three-step coupling of 1,4-diiodobenzene with 2-methyl-3-butyn-2-ol and the appropriate 1-bromo-3-fluoro-(4-*n*-alkoxy)benzene described previously.[6] Only the final product was isolated and purified. Although the overall yields appear to be

**Table 1. Thermal Transitions and Thermodynamic Parameters of 1,4-Bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzenes (R = H Model Compounds)**[a]



| *n* | Phase Transitions, °C (ΔH, kJ/mol) | |
|---|---|---|
| | Heating | Cooling |
| 1 | k 191 (41.2) n 250 (1.06) i | i 246 (0.88) n 168 (31.6) k |
| 2 | k 167 (6.81) k 186 (31.5) n 258 (1.60) i | i 252 (1.28) n 165 (10.6) k 143 (1.27) k |
| 3 | k 134 (25.0) k 177 (31.8) n 225 (1.24) i | i 222 (1.44) n 154 (26.9) k 18 (2.56) k |
| 4 | k 83 (5.74) k 166 (30.9) n 225 (1.54) i | i 223 (1.83) n 154 (28.5) k 70 (7.16) k |
| 5 | k 120 (8.02) k 150 (28.4) [$s_C$ [b] ] n 204 (1.37) i | i 201 (1.38) n 140 (2.33) $s_C$ 137 (25.7) k 117 (8.60) k |
| 6 | k 113 (2.15) k 127 (9.13) $s_E$ 132 (12.3) $s_C$ 147 (1.79) n 197 (1.30) i | i 196 (1.52) n 145 (1.89) $s_C$ 128 (16.2) $s_E$ 108 (10.7) k |

[a] k = crystalline, $s_E$ = smectic E, $s_C$ = smectic C, n = nematic, i = isotropic, [monotropic]. [b] Crystallizes too fast to detect $s_C$−n transition on heating by DSC or microscopy.

rather low (31−62%), they correspond to an average 68−85% yield for each of the three (coupling, deprotection, coupling) steps.

The thermal transitions obtained both on heating and on cooling the R = H model compounds are summarized in Table 1. (Those compounds with isotropization transitions over 220 °C decompose slightly with repeated heating.) The data obtained on heating are from samples that are at thermodynamic equilibrium and represent samples crystallized from solution and/or from the melt. In most cases, these compounds crystallize from the melt to the most thermodynamically stable phase within the time scale of the differential scanning calorimetry (DSC) experiment, without further annealing. Only the $n = 6$ derivative exhibits an enantiotropic $s_C$ mesophase; that of the $n = 5$ derivative is monotropic. The $n = 6$ derivative is also the shortest member of the series to exhibit an enantiotropic $s_E$ mesophase. Since the $s_C$−n phase sequence is exhibited when $n = 6-12$, the corresponding SCLCPs with $n = 6-12$ should also exhibit a $s_C$ mesophase if the 1,4-bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzenes are appropriate model compounds.

**Synthesis and Thermotropic Behavior of Monomers.** The norbornene monomers with laterally attached 1,4-bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzene mesogens were synthesized by the route outlined in Scheme 1, in which methyl anthranilate was used to prepare a 1,4-diiodobenzene functionalized at the 2-position. Methyl anthranilate was first iodinated *para* to the amine group by using benzyltrimethylammonium dichloroiodate under conditions similar to those used to iodinate phenols substituted with electron-withdrawing groups;[22] this route is milder and more selective than the traditional iodination of anthranilic acid using iodine monochloride in hydrochloric acid.[23] Methyl 2-amino-5-iodobenzoate was then converted to the triazene via a diazonium salt,[24] which was then reacted with methyl iodide under the pressurized[25] conditions optimized by Moore et al.[26] The ester group of the resulting methyl 2,5-diiodobenzoate was selectively reduced using lithium triethylborohydride[27] to produce 2,5-diiodobenzyl alcohol. The benzyl alcohol was subsequently esterified with bicyclo[2.2.1]hept-2-ene-5-carboxyl chloride to produce a 1,4-diiodobenzene functionalized at the 2-position with a polymerizable norbornene group. The final monomers were prepared by coupling this aryl diiodide with 2 equiv of a preformed 1-(3′-fluoro-4′-*n*-alkoxyphenyl)acetylene according to a literature[28] procedure using a catalytic amount of cuprous iodide in the presence of triphenylphosphine; palladium catalysts were avoided to prevent Pd(II)-catalyzed addition polymerization of the norbornene ring.[29]

Table 2 summarizes the thermotropic behavior of the 5-{[[2′,5′-bis[2-(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzyl]oxy]carbonyl}bicyclo[2.2.1]hept-2-enes. These monomers frequently crystallize differently from the melt than from solution. For example, the solution-crystallized monomer with $n = 2$ displays two melting endotherms at 90 and 100 °C (total $\Delta H_m = 32.0$ kJ/mol), whereas the melt-crystallized monomer displays two melting endotherms at 86 and 90 °C (total $\Delta H_m = 21.6$ kJ/mol). The solution-crystallized monomer with $n = 3$ also displays two melting endotherms at 53 and 73 °C (total $\Delta H_m = 24.1$ kJ/mol), although the melt-crystallized monomer displays a single melting endotherm at 67 °C ($\Delta H_m = 18.5$ kJ/mol). All of the monomers crystallize from the melt with extreme difficulty and never crystallize by 0 °C during the DSC cooling scans at 10 °C/min. Although they crystallize after sitting at room temperature for several days or several months, they do not crystallize within 30 min at elevated temperatures. (However, monomers with $n = 1-3$, $11-12$ exhibit an additional transition at low temperature due to nucleation of small crystallites.) The crystalline melting temperatures and corresponding changes in enthalpy presented in Table 2 are therefore

**Scheme 1. Synthesis of the 5-{[[2′,5′-Bis[2-(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzyl]oxy]carbonyl}bicyclo[2.2.1]hept-2-ene Monomers**

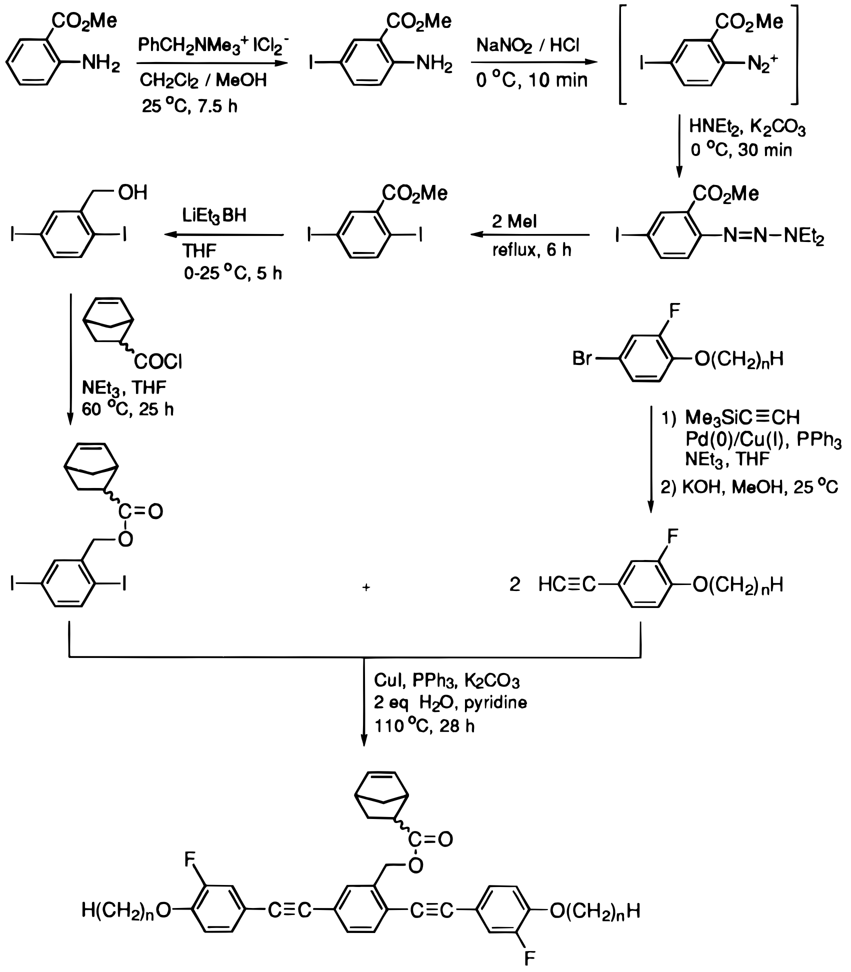


**Table 2. Thermal Transitions and Thermodynamic Parameters of 5-{[[2′,5′-Bis[2-(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzyl]oxy]carbonyl}-bicyclo[2.2.1]hept-2-enes (Monomers)[a]**

| *n* | Phase Transitions, °C (ΔH, kJ/mol) | |
|---|---|---|
| | Heating | Cooling |
| 1 | k 73 (25.5) i | i 19 (0.33) k |
| 2 | k 86 (14.0) k 90 (7.56) i | i 40 (0.37) k |
| 3 | k 67 (18.5) i | i 29 (0.38) k |
| 4 | k 85 (38.1) [n 55 (0.93)] i | i 51 (1.02) n |
| 5 | k 71 (33.7) [n 46 (0.94)] i | i 43 (1.01) n |
| 6 | k 53 (36.2) n 56 (1.43) i | i 53 (1.51) n |
| 7 | k 52 (34.0) [n 52 (1.39)] i | i 50 (1.45) n |
| 8 | k 68 (37.8) [n 61 (1.65)] i | i 57 (1.74) n |
| 9 | k 64 (48.3) [n 55 (1.80)] i | i 51 (1.78) n |
| 10 | k 50 (42.2) n 60 (2.21) i | i 56 (2.20) n |
| 11 | k 58 (47.1) [n 56 (2.05)] i | i 52 (1.94) n 8 (0.16) k |
| 12 | k 63 (51.5) [n 60 (2.26)] i | i 57 (2.53) n 23 (0.26) k |

[a] k = crystalline, n = nematic, i = isotropic, [monotropic].

less reliable than those of the nematic–isotropic transitions, with the crystalline transitions representing samples close to, though not necessarily at, thermodynamic equilibrium.

Table 2 demonstrates that those monomers with $n = 4-12$ exhibit either a monotropic or enantiotropic nematic mesophase over a very narrow temperature range.

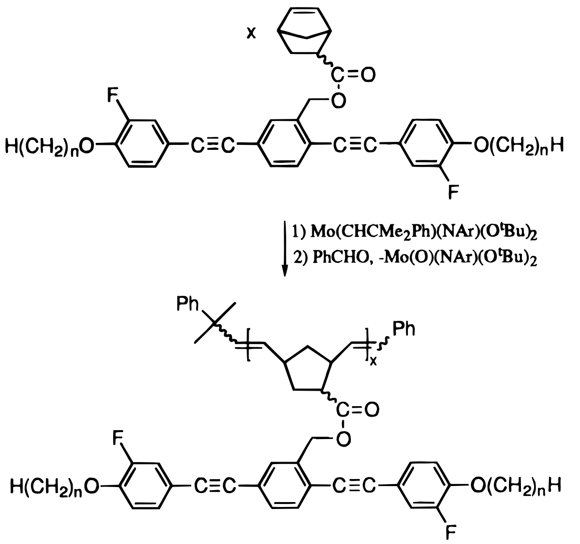
**Table 3. Polymerization of 5-{[[2′,5′-Bis[2-(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzyl]oxy]carbonyl}-bicyclo[2.2.1]hept-2-enes and Characterization of the Resulting Polymers[a]**

| *n* | $[M]_0/[I]_0$ | yield (%) | theoretical $10^{-4}M_n$ | GPC $10^{-4}M_n$ | GPC $DP_n$ | GPC pdi |
|---|---|---|---|---|---|---|
| 1 | 44 | 92 | 2.31 | 3.33[b] | 63[b] | 1.23[b] |
| 2 | 51 | 85 | 2.82 | 2.31 | 42 | 1.14 |
| 3 | 46 | 97 | 2.67 | 3.30[b] | 57[b] | 1.12[b] |
| 4 | 50 | 95 | 3.04 | 4.07 | 67 | 1.11 |
| 5 | 50 | 97 | 3.18 | 2.55 | 40 | 1.20 |
| 6 | 50 | 97 | 3.32 | 3.36 | 51 | 1.14 |
| 7 | 87 | 95 | 6.03 | 5.26 | 76 | 1.08 |
| 8 | 46 | 96 | 3.32 | 4.29 | 60 | 1.15 |
| 9 | 52 | 97 | 3.89 | 5.42 | 72 | 1.10 |
| 10 | 46 | 98 | 3.57 | 3.02 | 39 | 1.09 |
| 11 | 47 | 95 | 3.78 | 3.86 | 48 | 1.17 |
| 12 | 47 | 91 | 3.92 | 4.55 | 55 | 1.29 |

[a] Polymerized in THF at room temperature for 2 h; number average molecular weight ($M_n$), number average degree of polymerization ($DP_n$), and polydispersity (pdi = $M_w/M_n$) determined by gel permeation chromatography (GPC) relative to polystyrene using the mean of RI and UV detectors. [b] Following fractionation to remove a minor amount of low molecular weight oligomers.

Similarly, the reference monomers exhibit a monotropic or enantiotropic nematic mesophase when $n = 2-12$.[19] In contrast, the nematic mesophase of all of the corresponding R = H model compounds, even those with $n = 1-3$, are enantiotropic and occur over a relatively broad temperature window. This demonstrates that lateral substitution of the 1,4-bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzenes with bulky norbornene groups

**Scheme 2. Ring-Opening Metathesis Polymerization of 5-{[[2′,5′-Bis[2-(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzyl]oxy]carbonyl}bicyclo[2.2.1]hept-2-ene Monomers**



suppresses their ability to crystallize and organize into mesophases.

The nematic mesophases of the monomers are also more viscous than those of the model compounds, which results in the formation of much smaller nematic droplets upon cooling from the isotropic melt, as well as a higher number of inversion lines in the final texture observed by polarized optical microscopy. Unless very slow heating and cooling rates are used, the small size of the nematic droplets results in a fading in and out of the texture, much as with a polymeric liquid crystal.

**Synthesis and Thermotropic Behavior of Polymers.** Table 3 summarizes the results of the ring-opening metathesis polymerizations (ROMP) of the 5-{[[2′,5′-bis[2-(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzyl]oxy]carbonyl}bicyclo[2.2.1]hept-2-enes using Mo(CHCMe$_2$Ph)($N$-2,6-$^i$Pr$_2$Ph)(O$^t$Bu)$_2$ as the initiator (Scheme 2). With one exception, all of the polymerizations were performed using $[M]_0/[I]_0 \approx 50$ in order for the SCLCPs' thermotropic behavior to be independent of molecular weight ($DP_n \geq 25$). The resulting molecular weights determined by gel permeation chromatography (GPC) relative to polystyrene are generally within 20% of the values calculated by the monomer to initiator ratio. The polydispersities are also narrow (pdi = 1.08−1.29), indicating that chain transfer by secondary metathesis at the acetylene groups is not detectable at these molecular weights.

The thermotropic behavior of the title polymers is summarized in Table 4. In contrast to the R = H model compounds which exhibit a $s_E$−$s_C$−n phase sequence when $n$ = 6−12, the polymers generally exhibit only nematic mesophases. Confirmation of the nematic mesophase by polarized optical microscopy (Figure 1a) is unmistakable if the polymers are annealed in the biphasic region for several hours in order to observe nematic droplets developing upon cooling from the isotropic melt. If the polymers are not annealed in the biphasic region, a highly threaded schlieren texture appears without any evidence of nematic droplets. Well-defined threaded marbled nematic textures develop if the polymers are annealed for several hours at temperatures just below the biphasic region (Figure 1b).

The freshly precipitated polymers generally exhibit an ordering exotherm on the first DSC heating scan over a temperature range encompassing the glass transition. This indicates that the polymers are not organized in solution. On subsequent heating and cooling scans, all of the polymers exhibit only a glass transition and a nematic−isotropic transition. However, once the precipitated polymers or thermally treated polymers anneal at room temperature for several days or several months, those with $n$ = 3−12 exhibit an additional endotherm. As shown in Figure 2, this endotherm coincides with the glass transition. (The change in enthalpy of the nematic−isotropic transition of the $n$ = 1 derivative is also low if it is not annealed at room temperature for several days.)

**Table 4. Thermal Transitions and Thermodynamic Parameters of Poly{5-{[[2′,5′-bis[2-(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzyl]oxy]carbonyl}-bicyclo[2.2.1]hept-2-ene}s[a]**

| *n* | Phase Transitions, °C (ΔH, kJ/mru) | | | | |
|---|---|---|---|---|---|
| | Heating | | | Cooling | |
| 1 | g 90 | | n 122 (1.54) i | i 117 (0.49) n | 87 g |
| 2 | g 87 | | n 139 (2.48) i | i 136 (1.84) n | 84 g |
| 3 | g 76 | k 74 (0.87) | n 115 (1.58) i | i 111 (1.52) n | 73 g |
| 4 | g 64 | k 68 (1.58) | n 115 (1.74) i | i 112 (1.77) n | 62 g |
| 5 | g 56 | k 64 (2.09) | n 105 (1.49) i | i 102 (1.35) n | 52 g |
| 6 | g 53 | k 62 (2.95) | n 106 (2.03) i | i 104 (1.96) n | 48 g |
| 7 | g 47 | k 55 (3.36) | n 100 (1.81) i | i 96 (1.70) n | 42 g |
| 8 | g 45 | k 55 (3.48) | n 103 (2.22) i | i 100 (1.96) n | 46 g |
| 9 | g 43 | k 52 (2.44) | n 101 (2.50) i | i 98 (2.70) n | 41 g |
| 10 | g 44 | k 51 (2.90) | n 99 (2.77) i | i 97 (3.00) n | 38 g |
| 11 | g 41 | k 51 (4.42) | n 99 (2.75) i | i 96 (2.90) n | 37 g |
| 12 | g 36 | k 47 (3.69) | n 93 (2.52) i | i 90 (2.50) n | 31 g |

[a] mru = mol repeat units; g = glass, k = crystalline, n = nematic, i = isotropic.

Preliminary X-ray scattering of the room-temperature-annealed (8 days) SCLCP with $n$ = 12 confirms that the phase associated with the additional endotherm is highly ordered. That is, the X-ray pattern of the glassy state demonstrates that the ordered phase is orthogonal with an orthorhombic arrangement of the mesogens within the layers. This indicates that the phase has $s_E$ alignment, which is consistent with the thermotropic behavior of the R = H model compounds with $n$ = 6−12. However, the only change detectable by polarized optical microscopy is a roughening of the nematic texture (Figure 1c). Although a natural texture should develop upon cooling from either the isotropic melt or a nematic meophase, neither the platelet nor mosaic textures characteristic of a $s_E$ mesophase are observed.[30] However, this ordered alignment is actually developing in the glassy state, which may impede formation of a distinctive texture and thereby result in a "paramorphotic" texture. Since a $s_E$ phase is a highly ordered smectic phase, and highly ordered smectic phases are rare in SCLCPs, we will conservatively refer to this highly organized phase as a crystalline phase throughout the rest of this paper.

Crystallization is impeded by its proximity to the glass transition. As shown by the DSC thermograms of the $n$ = 12 polymer in Figure 3, the temperature and enthalpy of melting increases as the room-temperature-annealing time increases, with the sample annealed for 13 days achieving 70% of the $\Delta H_m$ of that annealed at room temperature for 9 months. In addition, the time required for the SCLCPs to crystallize increases as the

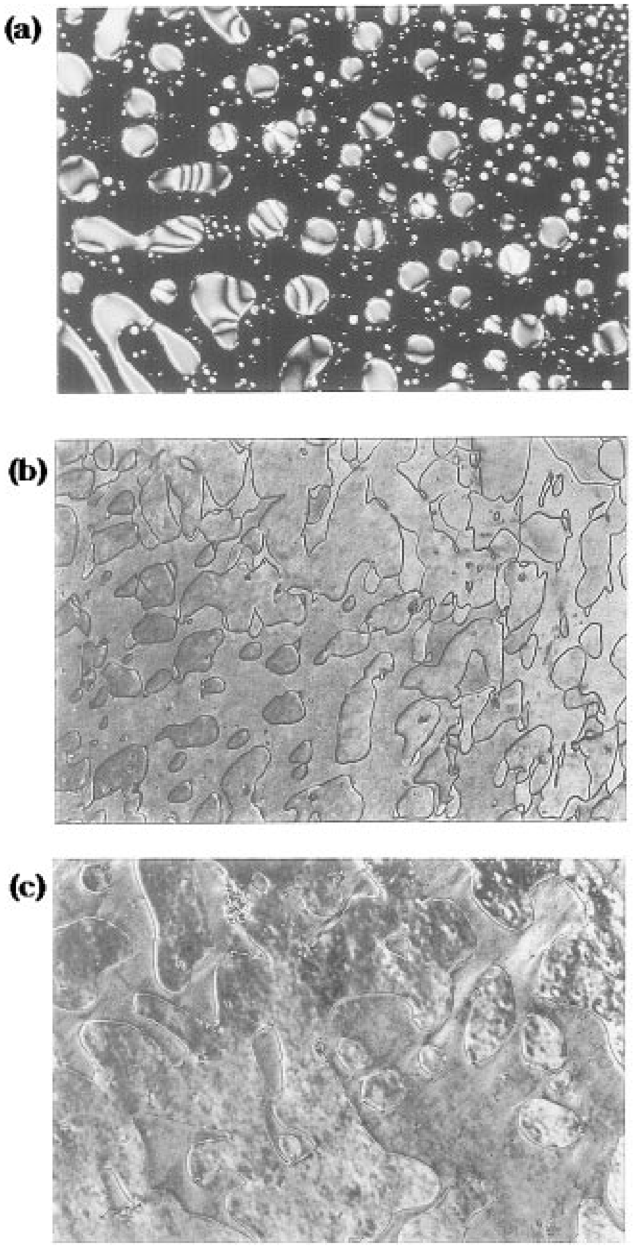


**Figure 1.** Polarized optical micrographs (200×) observed on cooling poly{5-{[[2′,5′-bis[2-(3′-fluoro-4-*n*-alkoxyphenyl)ethynyl]-benzyl]oxy]carbonyl}bicyclo[2.2.1]hept-2-ene} ($n = 12$) from the isotropic melt: (a) 93.7 °C, nematic droplets formed by annealing at 93.7 °C for 11 h; (b) 89.9 °C, threaded marbled nematic texture formed by annealing at 89.9 °C for 3.5 h; (c) room temperature, semicrystalline or paramorphotic $s_E$ after annealing at room temperature for 51 days. Figure reproduced at 50% for publication.

length of the *n*-alkoxy substituents decreases, and therefore as their ability to plasticize the polymer decreases. For example, although crystalline melting is not observed after annealing the polymer with $n = 3$ at room temperature for 5 months, it does crystallize after 15 months. Figure 2 also demonstrates that the polymers with $n \geq 5$ crystallize much more rapidly than those with $n = 3-4$. This substituent length ($n = 5$) corresponds to the discontinuity shown in Figure 4 in the decrease in the glass transition temperature of the SCLCPs with increasing *n*-alkoxy substituent length. None of the polymers crystallize by annealing at the glass transition temperature for 0.5−15 h.

Since short spacers generally preclude smectic layering,[3] it is not surprising that none of the title polymers exhibit a $s_C$ mesophase. Nevertheless, their ability to crystallize (or form a $s_E$ phase) at such a short spacer length demonstrates that SCLCPs with laterally attached 1,4-bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzene mesogens organize into layers much more readily than those with laterally attached 1,4-bis[(4′-*n*-alkoxybenzoyl)oxy]benzene[31] mesogens. Now that we have systematically determined the effect of changing only the laterally attached mesogen from one that normally forms only a nematic mesophase to one that exhibits a $s_C$−n phase sequence, we can increase the spacer length in order to favor smectic mesophase formation.[32]

**Synthesis and Thermotropic Behavior of 1,4-Bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]toluenes (R = $CH_3$ Model Compounds).** In order to determine whether or not an alkyl substituent is necessary for low molar mass 1,4-bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzenes to mimic the thermotropic behavior of the title polymers, we have synthesized the corresponding 1,4-bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]toluenes, which contain a lateral methyl substituent. The R = $CH_3$ model compounds with $n = 3$, 4, 7−10 were synthesized by coupling 2,5-dibromotoluene with 2-methyl-3-butyn-2-ol and the appropriate 1-bromo-3-fluoro-4-*n*-alkoxybenzene using the same one-pot method used to synthesize the R = H model compounds. The low yields (13−25%) indicate that the *o*-methyl substituent retards aryl−acetylene coupling, such that side reactions such as bromine reduction compete effectively. As shown in Scheme 3, the remaining members of the series were synthesized in 32−67% yield by a route similar to that used to synthesize the monomers, starting with *o*-toluidine instead of methyl anthranilate. The resulting 2,5-diiodotoluene was then coupled with 2 equiv of the preformed 1-(3′-fluoro-4′-*n*-alkoxyphenyl)-acetylenes.

Table 5 summarizes the equilibrium thermal transitions obtained on both heating and on cooling the R = $CH_3$ model compounds; only a few of these compounds require short annealing times at elevated temperatures to reach thermodynamic equilibrium. As confirmed by the representative polarized optical micrograph shown in Figure 5a, all of these compounds exhibit a nematic mesophase. However, only the $n = 9-12$ derivatives exhibit an enantiotropic ($n = 10-12$) or monotropic ($n = 9$) $s_C$ mesophase. The polarized optical micrographs shown in Figure 5b,c are characteristic of the n−$s_C$ transition, and the focal conic fan and schlieren regions of a $s_C$ texture, respectively.[6] None of the R = $CH_3$ model compounds exhibit a $s_E$ mesophase.

Figure 4 compares the phase diagrams of the title polymers and their potential model compounds. The R = H model compounds exhibit a $s_E$−$s_C$−n phase sequence when $n = 6-12$. In contrast, the polymers do not exhibit a $s_C$ mesophase at any substituent length, although all of the polymers ($n = 1-12$) exhibit a nematic mesophase, and perhaps a $s_E$ phase when $n = 3-12$. The 1,4-bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]-benzenes are therefore not appropriate model compounds for these polynorbornenes, evidently because they do not take the benzylic spacer into account. In contrast, the corresponding R = $CH_3$ model compounds exhibit only a nematic mesophase at most substituent lengths, in addition to a monotropic or an enantiotropic $s_C$ mesophase over an extremely narrow temperature range when $n = 9-12$. The 1,4-bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]toluenes are therefore more appropriate model compounds for the poly{5-{[[2′,5′-bis[2-(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzyl]oxy]-

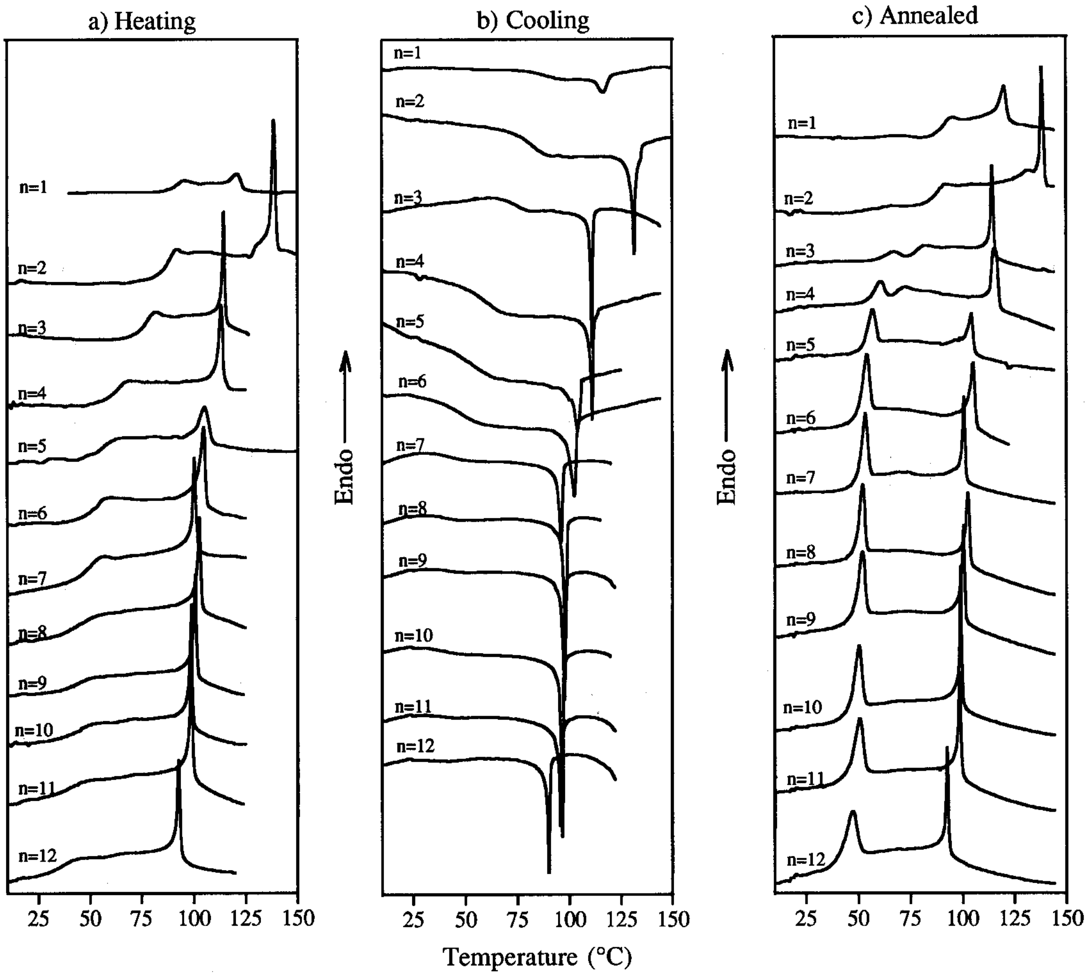


**Figure 2.** Normalized differential scanning calorimetry traces (10 °C/min) of poly{5-{[[2′,5′-bis[2-(3′-fluoro-4′-*n*-alkoxyphenyl)-ethynyl]benzyl]oxy]carbonyl}bicyclo[2.2.1]hept-2-ene}s observed on (a) second and subsequent heating scans, (b) cooling scans, and (c) heating scans of samples annealed at room temperature for 7−13 days.

carbonyl}bicyclo[2.2.1]hept-2-ene}s than the 1,4-bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzenes.

## Conclusions

Model compounds which take into account only the mesogen and spacer of a given SCLCP mimic the latter's thermotropic behavior well. Whereas 1,4-bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzenes exhibit a k−$s_E$−$s_C$−n−i phase sequence when $n = 6-12$, the poly{5-{[[2′,5′-bis[2-(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzyl]oxy]-carbonyl}bicyclo[2.2.1]hept-2-ene}s exhibit only a nematic mesophase on second and subsequent heating scans. The corresponding 1,4-bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]toluenes laterally substituted with a methyl group to mimic the benzylic spacer of the polymers also exhibit only a nematic mesophase at most substituent lengths ($n = 1-8$). In addition to a nematic mesophase, the R = $CH_3$ model compounds exhibit an enantiotropic $s_C$ mesophase over a very narrow temperature range when $n = 10-12$; the $s_C$ mesophase is monotropic when $n = 9$. However, the polymers also organize very slowly into a crystalline or $s_E$ phase when $n = 3-12$, which indicates that the side chains organize into layers much more readily than those containing 1,4-bis[(4′-*n*-alkoxybenzoyl)oxy]benzene mesogens.

## Experimental Section

**Materials.** 4-Bromo-2-fluorophenol (98%), 1-bromododecane (98%), 1-bromohexane (98%), cuprous iodide (>99.9%), dimethyl sulfate (99%), 2-iodobenzyl alcohol, and tetrabutylammonium hydrogen sulfate (TBAH) (97%) were used as received from Aldrich. Bis(triphenylphosphine)palladium(II) chloride (98%), 1-bromodecane (98%), 1-bromoheptane (99%), 1-bromononane (99%), 1-bromooctane (98%), 1-bromopentane (99%), 1-bromoundecane (98%), 1,4-diiodobenzene (98%), *o*-toluidine (98%), and triphenylphosphine (98%) were used as received from Lancaster. 1-Bromobutane (99%), 1-bromopropane (99%), diethyl sulfate (99%), 2-methyl-3-butyn-2-ol (98%), methyl iodide (99%), and (trimethylsilyl)acetylene (98%) were used as received from Janssen. Lithium triethylborohydride (1.0 M THF solution) was used as received from Alfa. Methyl anthranilate (Janssen, 99%) was distilled before use. Diethylamine (Fisher, reagent grade) and triethylamine (Lancaster) were distilled from KOH under $N_2$. Benzaldehyde (Aldrich, 99%) was distilled under $N_2$. Benzyltrimethylammonium dichloroiodate was synthesized according to a literature[33] procedure from benzyltrimethylammonium chloride (Lancaster, 97%) and iodine monochloride (Aldrich, 1.0 M $CH_2Cl_2$ solution). Mo(CHCMe$_2$Ph)(*N*-2,6-$^i$Pr$_2$Ph)(O$^t$Bu)$_2$ was synthesized by a literature procedure,[34] except that hexane was used instead of pentane throughout the synthesis. Bicyclo[2.2.1]-hept-2-ene-5-carbonyl chloride (73:27 endo:exo) was synthesized as described previously.[18,35] Dry $CH_2Cl_2$ was purified and dried by washing with 10% $HNO_3$ in $H_2SO_4$, stored over $CaCl_2$, and then distilled from $CaH_2$ under $N_2$. Reagent grade tetrahydrofuran (THF) and toluene were dried by distillation from purple sodium benzophenone ketyl under $N_2$. THF used as a polymerization solvent was vacuum transferred from purple sodium benzophenone ketyl on a high vacuum line, and then vigorously degassed by several freeze−pump−thaw cycles immediately before use. All other reagents and solvents were commercially available and were used as received.

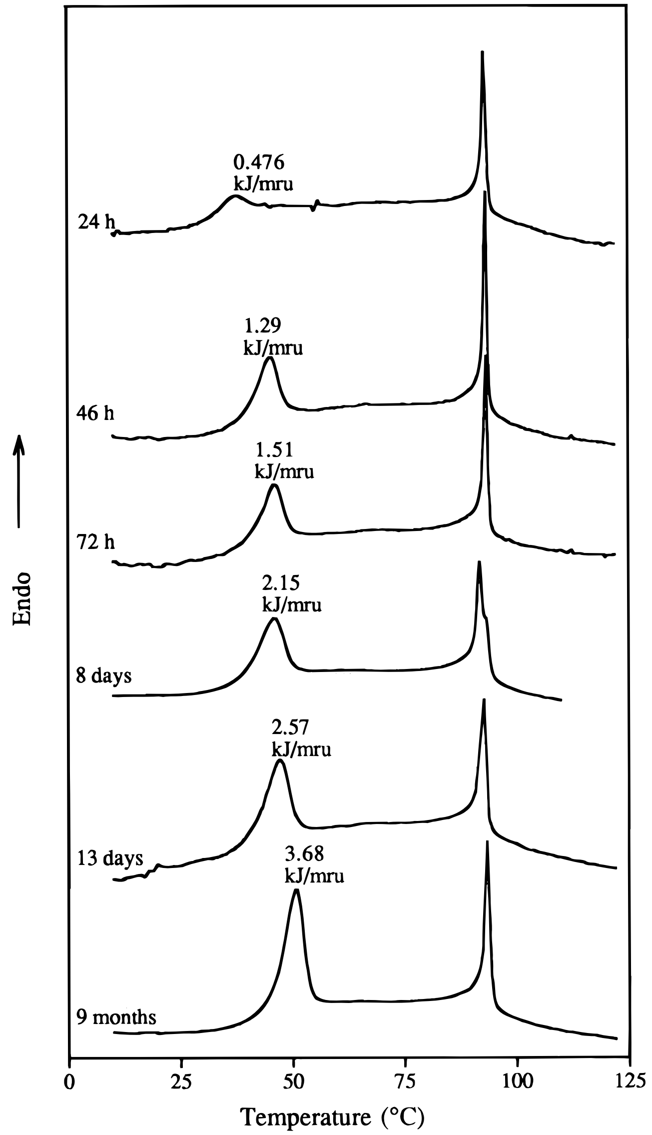


**Figure 3.** Normalized differential scanning calorimetry traces (10 °C/min) of poly{5-{[[2′,5′-bis[2-(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzyl]oxy]carbonyl}bicyclo[2.2.1]hept-2-ene} ($n = 12$) as a function of room temperature annealing time, i.e., time since cooled at 10 °C/min to 0 °C from the isotropic melt.

**Techniques.** All polymerizations were performed under a $N_2$ atmosphere in a Vacuum Atmospheres drybox. All other reactions were performed outside the drybox under a $N_2$ atmosphere. $^1$H-NMR spectra ($\delta$, ppm) were recorded on either a Bruker AC-200 (200 MHz) or a Bruker AM-300 (300 MHz) spectrometer. Unless noted otherwise, all spectra were recorded in $CDCl_3$ with TMS as an internal standard. Relative molecular weights were determined by gel permeation chromatography (GPC) at 35 °C using THF as solvent (1.0 mL/min), a set of 50, 100, 500, $10^4$, and linear ($50-10^4$) Å Styragel 5 $\mu$ columns, a Waters 486 tunable UV/vis detector set at 290 nm, and a Waters 410 differential refractometer.

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 that were read as the maximum or minimum of the endothermic or exothermic peaks, respectively. 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. Both enthalpy changes and transition temperatures were calibrated using indium and zinc standards. A Leitz Laborlux 12 Pol S polarized optical microscope (magnification 200×) equipped with a Mettler FP82 hot stage and a Mettler FP90 central processor was used to analyze the thermal transitions and anisotropic textures.[30] 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.

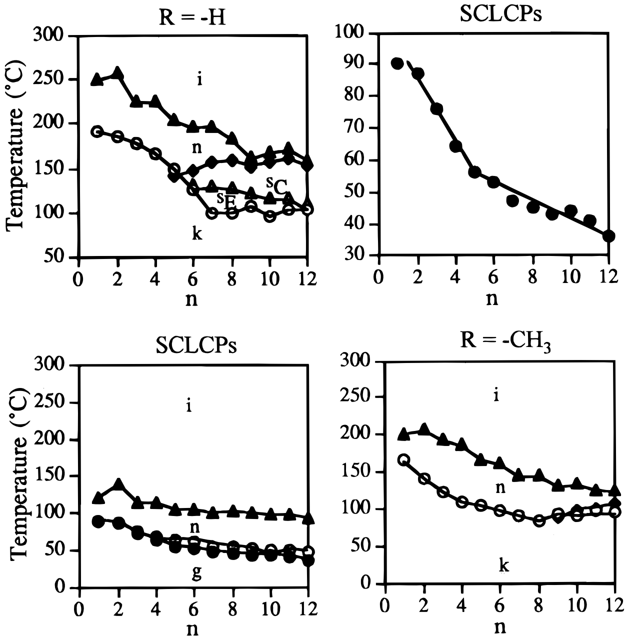
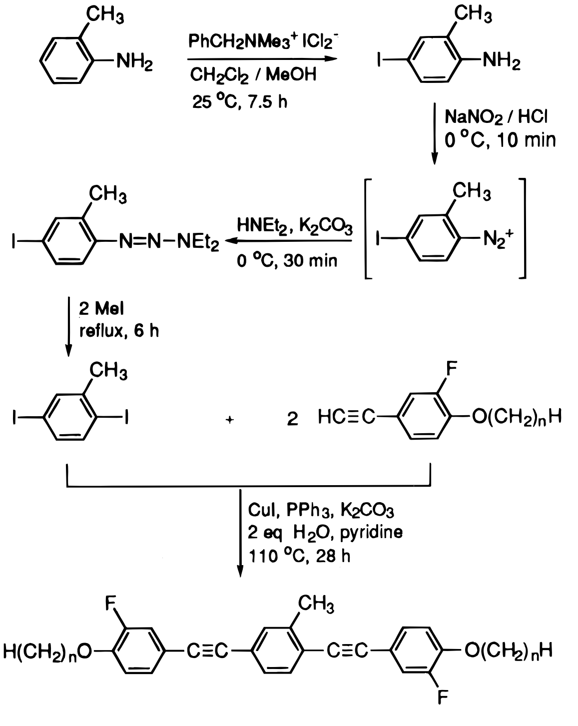


**Figure 4.** Transition temperatures of 1,4-bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzenes (R = H model compounds), poly{5-{[[2′,5′-bis[2-(3″-fluoro-4″-*n*-alkoxyphenyl)ethynyl]benzyl]oxy]carbonyl}bicyclo[2.2.1]hept-2-ene}s (SCLCPs), and 1,4-bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]toluenes (R = $CH_3$ model compounds) from the glassy (●), crystalline (○), $s_E$ (△), $s_C$ (◆), and nematic (▲) states as a function of the length of the *n*-alkoxy substituents.

### Scheme 3. Synthesis of the 2,5-Bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]toluenes (R = $CH_3$ Model Compounds)



Polymer samples were ground and packed into 1.5 mm quartz capillary tubes (Charles Supper) and flame sealed under atmospheric conditions for X-ray scattering. The filled capillaries were heated at 110 °C for 30 min and then cooled to 30 °C at a nominal rate of 5 °C/min. Room temperature

**Table 5. Thermal Transitions and Thermodynamic Parameters of 2,5-Bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]toluenes ($R = CH_3$ Model Compounds)[a]**

| *n* | Phase Transitions, °C (ΔH, kJ/mol) | |
|---|---|---|
| | Heating | Cooling |
| 1 | k 167 (36.6) n 201 (1.10) i | i 197 (0.28) n 149 (35.7) k |
| 2 | k 143 (33.2) n 207 (1.90) i | i 205 (1.47) n 99 (24.4) k |
| 3 | k 123 (29.0) n 194 (0.97) i | i 192 (0.74) n 104 (29.0) k |
| 4 | k 111 (29.6) n 187 (1.06) i | i 184 (1.03) n 85 (20.7) k |
| 5 | k 29 (4.66) k 106 (26.1) n 168 (0.95) i | i 165 (1.15) n 85 (21.4) k 68 (2.32) k |
| 6 | k 45 (11.1) k 99 (29.9) n 163 (1.37) i | i 160 (1.39) n 80 (30.3) k 39 (10.0) k |
| 7 | k 91 (44.8) n 147 (1.08) i | i 143 (1.19) n 71 (45.0) k |
| 8 | k 85 (42.9) n 146 (1.15) i | i 143 (1.17) n 68 (43.1) k |
| 9 | k 42 (5.32) k 95 (63.9) [$s_C$ 89[b] ] n 134 (1.39) i | i 134 (1.56) n 86 (0.54) $s_C$ 83 (64.1) k 26 (4.46) k |
| 10 | k 92 (59.4) $s_C$ 99 (0.50) n 135 (1.55) i | i 132 (1.52) n 97 (0.48) $s_C$ 79 (59.0) k |
| 11 | k 61 (8.58) k 99 (69.9) $s_C$ 100 (0.51) n 126 (1.67) i | i 123 (1.81) n 96 (0.68) $s_C$ 85 (70.4) k 45 (6.83) k |
| 12 | k 97 (70.3) $s_C$ 109 (0.71) n 126 (1.94) i | i 124 (1.90) n 106 (0.69) $s_C$ 87 (70.5) k |

[a] k = crystalline, $s_C$ = smectic C, n = nematic, i = isotropic, [monotropic]. [b] From microscope; sample crystallizes before transition on heating can be obtained by DSC.

(20 °C) scattering experiments were recorded using a Ni-filtered beam of Cu Kα radiation from a Rigaku Geigerflex CN4012K1 spectrometer operating at 1 kW (40 kV, 25 mA) and a homemade Furnas camera.

**Synthesis of Monomers and Precursors. Methyl 2-Amino-5-iodobenzoate.** Methyl 2-amino-5-iodobenzoate was synthesized in 67–79% yield as in the following example. A solution of methyl anthranilate (15 g, 99 mmol) in $CH_2Cl_2$ (500 mL) and methanol (200 mL) was added all at once to a mixture of benzyltrimethylammonium dichloroiodate (35 g, 0.10 mol) and $CaCO_3$ (20 g, 0.20 mol). The reaction mixture was stirred at room temperature for 7.5 h. Excess $CaCO_3$ was filtered off, and the resulting organic solution was washed twice with 5% aqueous $NaHSO_3$ (600 mL total) and then dried over magnesium sulfate. After filtration, the solvent was removed by rotary evaporation, and the orange residue was purified by column chromatography using silica gel as the stationary phase and hexanes as the eluant. The eluant was concentrated to yield 22 g (79%) of methyl 2-amino-5-iodobenzoate as white crystals; mp 64–66 °C. $^1$H-NMR: 3.86 (s, $-OCH_3$), 5.76 (bs, $-NH_2$), 6.44 (d, 1 aromatic H ortho to $-NH_2$), 7.46 (dd, 1 aromatic H para to $-CO_2CH_3$), 8.13 (d, 1 aromatic H ortho to −I).

**2-Amino-5-iodotoluene.** Starting from *o*-toluidine, 2-amino-5-iodotoluene was prepared in 71–76% yield by the same procedure described above to synthesize methyl 2-amino-5-iodobenzoate; mp 86–88 °C. $^1$H-NMR: 2.11 (s, $-CH_3$), 3.60 (bs, $-NH_2$), 6.44 (d, 1 aromatic H ortho to $-NH_2$), 7.28 (dd, 1 aromatic H para to $-CH_3$), 7.33 (d, 1 aromatic H ortho to −I).

**1-[2′-(Methoxycarbonyl)-4′-iodophenyl]-3,3-diethyltriazene.** 1-[2′-(Methoxycarbonyl)-4′-iodophenyl]-3,3-diethyltriazene was synthesized in 54–83% yield as in the following example. A solution of $NaNO_2$ (4.0 g, 59 mmol) in water (10 mL) was added dropwise to an ice-cooled solution of methyl 2-amino-5-iodobenzoate (7.4 g, 26 mmol) and concentrated HCl (7 mL, 0.7 mmol) in water (70 mL) and acetonitrile (70 mL). After the reaction mixture was stirred at 0 °C for 1 h, it was added dropwise to an ice-cooled solution of $K_2CO_3$ (6.8 g, 49 mmol) in diethyl amine (3.6 g, 50 mmol) and stirred for 1 h at 0 °C. The reaction mixture was then extracted three times with $Et_2O$ (300 mL total) and dried over $MgSO_4$. After filtration and removal of the solvent by rotary evaporation, the resulting reddish oil (7.9 g, 83%) was used immediately without further purification. $^1$H-NMR: 1.27 (bs, $-N(CH_2CH_3)_2$), 3.72 (q, $-N(CH_2-)_2$), 3.85 (s, $-CO_2CH_3$), 7.16 (d, 1 aromatic H ortho to $-N_3Et_2$), 7.67 (dd, 1 aromatic H para to $-CO_2CH_3$), 7.91 (d, 1 aromatic H ortho to $-CO_2CH_3$).

**1-(2′-Methyl-4′-iodophenyl)-3,3-diethyltriazene.** Starting from 2-amino-5-iodotoluene, 1-(2′-methyl-4′-iodophenyl)-3,3-diethyltriazene was prepared in 66–91% yield by the same procedure described above to synthesize 1-[2′-(methoxycarbonyl)-4′-iodophenyl]-3,3-diethyltriazene. $^1$H-NMR: 1.26 (t, $-N(CH_2CH_3)_2$), 2.36 (s, $ArCH_3$), 3.75 (q, $-N(CH_2-)_2$), 7.08 (d, 1 aromatic H ortho to $-N_3Et_2$), 7.43 (dd, 1 aromatic H para to $-CH_3$), 7.50 (d, 1 aromatic H ortho to $-CH_3$).

**Methyl 2,5-Diiodobenzoate.** Methyl 2,5-diiodobenzoate was synthesized in 84–90% yield as in the following example. 1-[2′-(Methoxycarbonyl)-4′-iodophenyl]-3,3-diethyltriazene (5.0 g, 14 mmol) and freshly distilled methyl iodide (80 mL) were placed in a 500 mL Schlenk flask with a screw cap, and the reaction mixture was degassed by several freeze–pump–thaw cycles. The reaction flask was filled with $N_2$, sealed, and heated at 100 °C until the starting material was completely consumed (6 h).[25] The reaction mixture was then poured into 300 mL of petroleum ether and filtered, and the filtrate was dried over MgSO4. After filtration and removal of the solvent by rotary evaporation, a slightly yellow solid was obtained that was recrystallized from hexanes (80 mL) to yield 4.8 g (90%) of methyl 2,5-diiodobenzoate; mp 72–74 °C. $^1$H-NMR: 3.91 (s, $-CO_2CH_3$), 7.44 (dd, 1 aromatic H para to $-CO_2CH_3$), 7.68 (d, 1 aromatic H meta to $-CO_2CH_3$), 8.10 (d, 1 aromatic H ortho to $-CO_2CH_3$).

**2,5-Diiodotoluene.** Starting from 1-(2′-methyl-4′-iodophenyl)-3,3-diethyltriazene, 2,5-diiodotoluene was prepared in 76–88% yield by the same procedure described above to synthesize methyl 2,5-diiodobenzoate; mp 26–28 °C. $^1$H-NMR: 2.37 (s, $ArCH_3$), 7.17 (dd, 1 aromatic H para to $-CH_3$), 7.49 (d, 1 aromatic H meta to $-CH_3$), 7.57 (d, 1 aromatic H ortho to $-CH_3$).

**2,5-Diiodobenzyl Alcohol.** 2,5-Diiodobenzyl alcohol was synthesized in 78–90% yield. In a typical example, lithium triethylborohydride in THF (1.0 M, 10 mL, 10 mmol) was added via a syringe to a solution of methyl 2,5-diiodobenzoate (1.5 g, 3.8 mmol) in dry THF (40 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 5 h before quenching with water (30 mL). It was

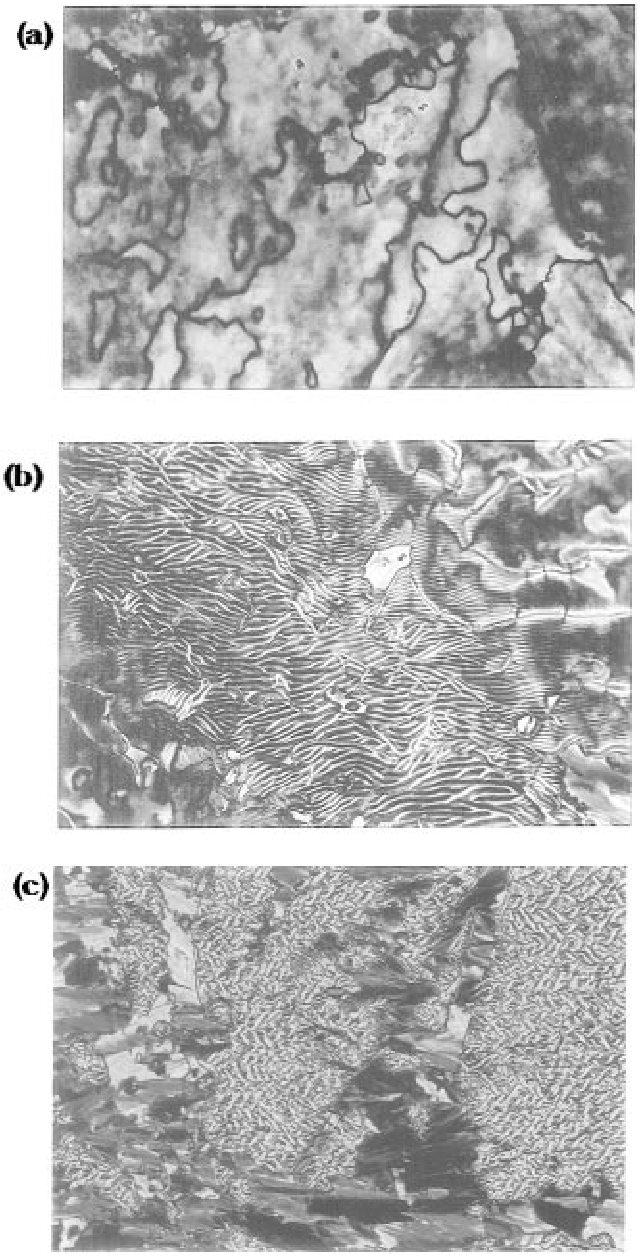


**Figure 5.** Polarized optical micrographs (200×) observed on cooling 2,5-bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]toluene (R = $CH_3$ model compound, $n = 12$) from the isotropic melt: (a) 127.1 °C, threaded marbled nematic texture; (b) 110.5 °C, n−$s_C$ transition; (c) 108.9 °C, $s_C$ schlieren and focal conic fan textures. Figure reproduced at 50% for publication.

then poured into 50 mL of water, saturated with sodium chloride, and extracted three times with $Et_2O$ (300 mL total), and the organic extracts were dried over $MgSO_4$. Filtration and removal of the solvent by rotary evaporation yielded 1.2 g of a colorless solid (90%): mp 95−97 °C. $^1$H-NMR: 1.96 (t, $-OH$), 4.61 (d, $-CH_2OH$), 7.32 (dd, 1 aromatic H para to $-CH_2$-OH), 7.50 (d, 1 aromatic H meta to $-CH_2OH$), 7.79 (d, 1 aromatic H ortho to $-CH_2OH$).

**5-{[(2′,5′-Diiodobenzyl)oxy]carbonyl}bicyclo[2.2.1]hept-2-ene.** 5-{[(2′,5′-Diiodobenzyl)oxy]carbonyl}bicyclo[2.2.1]hept-2-ene was synthesized in 75−92% yield as in the following example. A solution of bicyclo[2.2.1]hept-2-ene-5-carboxyl chloride (3.5 g, 22 mmol) in dry THF (20 mL) was added dropwise to a solution of 2,5-diiodobenzyl alcohol (4.0 g, 11 mmol) and triethylamine (2.2 g, 22 mmol) in dry THF (40 mL) in a drybox. The reaction flask was then taken out of the drybox and heated at 60 °C for 7 h; $NEt_3H^+Cl^-$ immediately precipitated. The reaction mixture was poured into water (150 mL) and extracted five times with $Et_2O$ (400 mL total), and the organic extracts were dried over $MgSO_4$. A slightly yellow oil was obtained by filtration and removal of the solvent by rotary evaporation. The resulting oil was passed through a short column of silica gel using hexanes/$CH_2Cl_2$ (7:3) as the eluant to yield 4.5 g (84%) of 5-{[(2′,5′-diiodobenzyl)oxy]-carbonyl}bicyclo[2.2.1]hept-2-ene as a colorless viscous liquid. $^1$H-NMR resonances at 1.26 (d), 1.45 (m), 1.93 (m), 2.32 (m), 2.91 (s), 3.09 (m), and 3.22 (d) are due to the nonolefin norbornene protons of both isomers; 4.99 (s, $-CH_2Ar$, exo, 1 H), 5.05 (s, $-CH_2Ar$ endo, 1 H), 5.94 (m, 1 olefin H, endo), 6.15 (m, 2 olefin H, exo), 6.22 (m, 1 olefin H, endo), 7.34 (dd, 1 aromatic H para to $-CH_2-$), 7.53 (dd, 1 aromatic H meta to $-CH_2-$), 7.67 (dd, 1 aromatic H ortho to $-CH_2-$).

**1-Bromo-3-fluoro-4-*n*-alkoxybenzenes (*n* = 1−12).** The 1-bromo-3-fluoro-4-*n*-alkoxybenzenes were prepared in 64−98% yield by Williamson etherification of 4-bromo-3-fluorophenol with either an *n*-bromoalkane or dimethyl or diethyl sulfate as described previously.[36]

**1-Bromo-3-fluoro-4-methoxybenzene.** $^1$H-NMR: 3.87 (s, $-OCH_3$), 6.83 (dd, 1 aromatic H ortho to $-OCH_3$), 7.19 (m, 2 aromatic H ortho to −Br).

**1-Bromo-3-fluoro-4-ethoxybenzene.** $^1$H-NMR: 1.43 (t, $-CH_3$), 4.07 (q, $-OCH_2-$), 6.81 (dd, 1 aromatic H ortho to −OEt), 7.20 (m, 2 aromatic H ortho to −Br).

**1-Bromo-3-fluoro-4-*n*-propoxybenzene.** $^1$H-NMR: 1.03 (t, $-CH_3$), 1.77 (m, $-CH_2CH_2O-$), 3.93 (t, $-OCH_2-$), 6.80 (dd, 1 aromatic H ortho to −OPr), 7.18 (m, 2 aromatic H ortho to −Br).

**1-Bromo-3-fluoro-4-*n*-butoxybenzene.** $^1$H-NMR: 0.95 (t, $-CH_3$), 1.51 (m, $-CH_2CH_2CH_2O-$), 1.82 (m, $-CH_2CH_2O-$), 3.98 (t, $-OCH_2-$), 6.82 (dd, 1 aromatic H ortho to −OBu), 7.19 (t, 2 aromatic H ortho to −Br).

The $^1$H-NMR spectra of the 1-bromo-3-fluoro-4-*n*-alkoxybenzenes ($n = 5−12$) are identical: 0.89 (t, $-CH_3$), 1.37 (m, $-(CH_2)-_{n-3}$), 1.80 (m, $-CH_2CH_2O-$), 3.98 (t, $-OCH_2-$), 6.80 (dd, 1 aromatic H ortho to −OR), 7.19 (t, 2 aromatic H ortho to −Br).

**1-(3′-Fluoro-4′-*n*-alkoxyphenyl)-2-(trimethylsilyl)acetylenes (*n* = 1−12).** The 1-(3′-fluoro-4′-*n*-alkoxyphenyl)-2-(trimethylsilyl)acetylenes were synthesized in 44−98% yield as in the following example. A solution of 4-bromo-2-fluoroanisole (8.5 g, 41 mmol), (trimethylsilyl)acetylene (4.9 g, 50 mmol), and triethylamine (8.4 g, 84 mmol) in dry THF (30 mL) was added to a mixture of CuI (1.3 g, 6.8 mmol), $PdCl_2(PPh_3)_2$ (1.3 g, 6.8 mmol) and triphenylphosphine (2.3 g, 8.9 mmol), and the reaction mixture was heated at reflux for 24 h. It was then cooled to room temperature and added to dilute aqueous $NH_4Cl$, and the resulting mixture was extracted five times with $CH_2Cl_2$ (250 mL total). The $CH_2Cl_2$ extracts were dried over $MgSO_4$ and filtered, and the solvent was removed by rotary evaporation. The resulting reddish liquid residue was purified by column chromatography using silica gel as the stationary phase and $CH_2Cl_2$/hexanes (1:4) as the eluant to yield 1-(3′-fluoro-4′-methoxyphenyl)-2-(trimethylsilyl)acetylene as a colorless liquid (7.2 g, 78%). $^1$H-NMR: 0.22 (s, $-Si(CH_3)_3$), 3.88 (s, $-OCH_3$), 6.85 (dd, 1 aromatic H ortho to $-OCH_3$), 7.18 (m, 2 aromatic H meta to $-OCH_3$).

**1-(3′-Fluoro-4′-ethoxyphenyl)-2-(trimethylsilyl)acetylene.** $^1$H-NMR: 0.22 (s, $-Si(CH_3)_3$), 1.44 (t, $-CH_3$), 4.08 (q, $-OCH_2-$), 6.84 (dd, 1 aromatic H ortho to −OEt), 7.17 (m, 2 aromatic H meta to −OEt).

**1-(3′-Fluoro-4′-*n*-propoxyphenyl)-2-(trimethylsilyl)acetylene.** $^1$H-NMR: 0.22 (s, $-Si(CH_3)_3$), 1.05 (t, $-CH_3$), 1.84 (m, $-CH_2CH_2O-$), 3.98 (t, $-OCH_2-$), 6.83 (dd, 1 aromatic H ortho to −OPr), 7.14 (m, 2 aromatic H meta to −OPr).

**1-(3′-Fluoro-4′-*n*-butoxyphenyl)-2-(trimethylsilyl)acetylene.** $^1$H-NMR: 0.21 (s, $-Si(CH_3)_3$), 0.95 (t, $-CH_3$), 1.48 (m, $-CH_2CH_2CH_2O-$), 1.79 (m, $-CH_2CH_2O-$), 4.02 (t, $-OCH_2-$), 6.82 (dd, 1 aromatic H ortho to −OBu), 7.15 (m, 2 aromatic H meta to −OBu).

The $^1$H-NMR spectra of the 1-(3′-fluoro-4′-*n*-alkoxyphenyl)-2-(trimethylsilyl)acetylenes ($n = 5−12$) are identical: 0.23 (s, $-Si(CH_3)_3$), 0.89 (t, $-CH_3$), 1.37 (m, $-(CH_2)-_{n-3}$), 1.80 (m, $-CH_2CH_2O-$), 4.02 (t, $-OCH_2-$), 6.83 (dd, 1 aromatic H ortho to −OR), 7.15 (m, 2 aromatic H meta to −OR).

**1-(3′-Fluoro-4′-*n*-alkoxyphenyl)acetylenes (*n* = 1−12).** The 1-(3′-fluoro-4′-*n*-alkoxyphenyl)-2-(trimethylsilyl)acetylenes were deprotected in 43−98% yield. In a typical procedure, aqueous 1 N KOH (16 mL, 16 mmol) was added dropwise to a solution of 1-(3′-fluoro-4′-methoxyphenyl)-2-(trimethylsilyl)acetylene (3.5 g, 16 mmol) in methanol (30 mL), and the reaction mixture was stirred at room temperature for 5.5 h. It was then extracted three times with Et$_2$O (210 mL total) and the organic extracts were dried over MgSO$_4$. After filtration and removal of the solvent by rotary evaporation, a yellow liquid was obtained that solidified on standing (2.0 g, 85% yield); mp 32−34 °C. $^1$H-NMR: 3.00 (s, ≡C*H*), 3.89 (s, −OC*H*$_3$), 6.88 (dd, 1 aromatic H ortho to −OCH$_3$), 7.22 (m, 2 aromatic H meta to −OCH$_3$).

**1-(3′-Fluoro-4′-ethoxyphenyl)acetylene.** $^1$H-NMR: 1.45 (t, −C*H*$_3$), 3.00 (s, ≡C*H*), 4.11 (q, −OC*H*$_2$-), 6.87 (dd, 1 aromatic H ortho to −OEt), 7.19 (m, 2 aromatic H meta to −OEt).

**1-(3′-Fluoro-4′-*n*-propoxyphenyl)acetylene.** $^1$H-NMR: 1.05 (t, −C*H*$_3$), 1.86 (m, −C*H*$_2$CH$_2$O−), 3.01 (s, ≡C*H*), 3.97 (t, −OC*H*$_2$−), 6.85 (dd, 1 aromatic H ortho to −OPr), 7.18 (m, 2 aromatic H meta to −OPr).

**1-(3′-Fluoro-4′-*n*-butoxyphenyl)acetylene.** $^1$H-NMR: 0.97 (t, −C*H*$_3$), 1.49 (m, −C*H*$_2$CH$_2$CH$_2$O−), 1.82 (m, −C*H*$_2$CH$_2$O−), 2.99 (s, ≡C*H*), 4.03 (t, −OC*H*$_2$−), 6.87 (dd, 1 aromatic H ortho to −OBu), 7.18 (m, 2 aromatic H meta to −OBu).

The $^1$H-NMR spectra of the 1-(3′-fluoro-4′-*n*-alkoxyphenyl)acetylenes (*n* = 5−12) are identical: 0.89 (t, −C*H*$_3$), 1.37 (m, −(C*H*$_2$)−$_{n-3}$), 1.80 (m, −C*H*$_2$CH$_2$O−), 3.00 (s, ≡C*H*), 4.02 (t, −OC*H*$_2$−), 6.85 (dd, 1 aromatic H ortho to −OR), 7.18 (m, 2 aromatic H meta to −OR).

**1,4-Bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzenes (*n* = 1−6).** The 1,4-bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzenes were prepared in 31−62% yield by the one-pot, phase-transfer, Pd(0)/Cu(I)-catalyzed, three-step coupling of 1,4-diiodobenzene with 2-methyl-3-butyn-2-ol and the appropriate 1-bromo-3-fluoro-4-*n*-alkoxybenzene described previously.[6]

**1,4-Bis[(3′-fluoro-4′-methoxyphenyl)ethynyl]benzene.** $^1$H-NMR: 3.90 (s,−OC*H*$_3$, 6 H), 6.91 (dd, 2 aromatic H ortho to −OCH$_3$), 7.23 (d, 4 aromatic H ortho to −C≡CAr), 7.44 (s, 4 aromatic H of central ring). Anal. Calcd for $C_{24}H_{16}F_2O_2$: C, 76.99; H, 4.30. Found: C, 76.74; H, 4.62.

**1,4-Bis[(3′-fluoro-4′-ethoxyphenyl)ethynyl]benzene.** $^1$H-NMR: 1.45 (t, −C*H*$_3$, 6 H), 4.12 (q, −OC*H*$_2$−, 4 H), 6.90 (dd, 2 aromatic H ortho to −OEt), 7.23 (d, 4 aromatic H ortho to −C≡CAr), 7.45 (s, 4 aromatic H of central ring). Anal. Calcd for $C_{26}H_{20}F_2O_2$: C, 77.59; H, 5.00. Found: C, 77.28; H, 5.08.

**1,4-Bis[(3′-fluoro-4′-*n*-propoxyphenyl)ethynyl]benzene.** $^1$H-NMR: 1.05 (t, −C*H*$_3$, 6 H), 1.87 (m, −C*H*$_2$CH$_2$O−, 4 H), 4.01 (t, −OC*H*$_2$−, 4 H), 6.89 (dd, 2 aromatic H ortho to −OPr), 7.23 (d, 4 aromatic H ortho to −C≡CAr), 7.46 (s, 4 aromatic H of central ring). Anal. Calcd for $C_{28}H_{24}F_2O_2$: C, 78.12; H, 5.61. Found: C, 78.26; H, 5.85.

**1,4-Bis[(3′-fluoro-4′-*n*-butoxyphenyl)ethynyl]benzene.** $^1$H-NMR: 1.00 (t, −C*H*$_3$, 6 H), 1.50 (m, −C*H*$_2$CH$_2$CH$_2$O−, 4 H), 1.80 (m, −C*H*$_2$CH$_2$O−, 4 H), 4.05 (t, −OC*H*$_2$−, 4 H), 6.92 (dd, 2 aromatic H ortho to −OBu), 7.25 (d, 4 aromatic H ortho to −C≡CAr), 7.48 (s, 4 aromatic H of central ring). Anal. Calcd for $C_{30}H_{28}F_2O_2$: C, 78.58; H, 6.15. Found: C, 78.46; H, 6.10.

The $^1$H-NMR spectra of the 1,4-bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzenes with *n* = 5, 6 are identical: 0.94 (t, −C*H*$_3$, 6 H), 1.36 (m, −[C*H*$_2$]−$_{n-3}$, 4(*n* − 3)H), 1.77 (m, −OCH$_2$C*H*$_2$−, 4 H), 4.03 (t, −OC*H*$_2$−, 4 H), 6.90 (dd, 2 aromatic H ortho to −OR), 7.25 (s, 4 aromatic H ortho to −C≡CAr), 7.46 (s, 4 aromatic H of central ring). Anal. Calcd for $C_{32}H_{32}F_2O_2$: C, 76.98; H, 6.62. Found: C, 79.07; H, 6.57. Anal. Calcd for $C_{34}H_{36}F_2O_2$: C, 79.34; 7.05. Found: 79.55; H, 7.10.

**2,5-Bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]toluenes (*n* = 1−12).** Starting from 2,5-dibromotoluene, the 1,4-bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]toluenes with *n* = 3, 4, 7−10 were synthesized in 13−25% yield by the same one-pot method used to synthesize the 1,4-bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzenes.[6] The remaining compounds (*n* = 1, 2, 5, 6, 11, 12) were synthesized in 32−67% yield as in the following example. A solution of 2,5-diiodotoluene (5.7 g, 17 mmol), 1-[3′-fluoro-4′-methoxyphenyl]acetylene (5.5 g, 36 mmol), and water (0.75 g, 41 mmol) in pyridine (98 mL) was added all at once to a mixture of CuI (0.35 g, 1.8 mmol), triphenylphosphine (0.88 g, 3.3 mmol), and K$_2$CO$_3$ (6.9 g, 52 mmol). The reaction mixture was heated at 110 °C for 41 h until complete conversion. The reaction mixture was cooled to room temperature and then added to aqueous NH$_4$Cl. The resulting white precipitate was collected, dried, and purified by column chromatography using silica gel as the stationary phase and toluene as the eluant. Recrystallization from CH$_2$Cl$_2$ (125 mL) yielded 4.4 g (67%) of 2,5-bis[(3′-fluoro-4′-methoxyphenyl)ethynyl]toluene as a crystalline white solid. $^1$H-NMR: 2.48 (s, ArC*H*$_3$), 3.91 (s, −OC*H*$_3$, 6 H), 6.92 (dd, 2 aromatic H ortho to −OCH$_3$), 7.24 (d, 4 aromatic H ortho to −C≡CAr), 7.30 (dd, 1 aromatic H para to −CH$_3$), 7.38 (s, 1 aromatic H ortho to −CH$_3$), 7.43 (d, 1 aromatic H meta to −CH$_3$). Anal. Calcd for $C_{25}H_{18}F_2O_2$: C, 77.30; H, 4.67. Found: C, 77.32; H, 4.90.

**2,5-Bis[(3′-fluoro-4′-ethoxyphenyl)ethynyl]toluene.** $^1$H-NMR: 1.47 (t, −C*H*$_3$, 6 H), 2.48 (s, ArC*H*$_3$), 4.13 (q, −OC*H*$_2$−, 4 H), 6.91 (dd, 2 aromatic H ortho to −OEt), 7.24 (d, 4 aromatic H ortho to −C≡CAr), 7.29 (dd, 1 aromatic H para to −CH$_3$), 7.38 (s, 1 aromatic H ortho to −CH$_3$), 7.42 (d, 1 aromatic H meta to −CH$_3$). Anal. Calcd for $C_{27}H_{22}F_2O_2$: C, 77.87; H, 5.32. Found: C, 77.14; H, 5.48.

**2,5-Bis[(3′-fluoro-4′-*n*-propoxyphenyl)ethynyl]toluene.** $^1$H-NMR: 1.06 (t, −C*H*$_3$, 6 H), 1.86 (m, −C*H*$_2$CH$_2$O−, 4 H), 2.48 (s, ArC*H*$_3$), 4.01 (t, −OC*H*$_2$−, 4 H), 6.91 (dd, 2 aromatic H ortho to −OPr), 7.24 (d, 4 aromatic H ortho to −C≡CAr), 7.30 (dd, 1 aromatic H para to −CH$_3$), 7.37 (s, 1 aromatic H ortho to −CH$_3$), 7.42 (d, 1 aromatic H meta to −CH$_3$). Anal. Calcd for $C_{29}H_{26}F_2O_2$: C, 78.36; H, 5.90. Found: C, 78.34; H, 6.08.

**2,5-Bis[(3′-fluoro-4′-*n*-butoxyphenyl)ethynyl]toluene.** $^1$H-NMR: 0.98 (t, −C*H*$_3$, 6 H), 1.51 (m, −C*H*$_2$CH$_2$CH$_2$O−, 4 H), 1.82 (m, −C*H*$_2$CH$_2$O−, 4 H), 2.48 (s, ArC*H*$_3$), 4.05 (t, −OC*H*$_2$−, 4 H), 6.91 (dd, 2 aromatic H ortho to −OBu), 7.24 (d, 4 aromatic H ortho to −C≡CAr), 7.30 (dd, 1 aromatic H para to −CH$_3$), 7.37 (s, 1 aromatic H ortho to −CH$_3$), 7.43 (d, 1 aromatic H meta to −CH$_3$). Anal. Calcd for $C_{31}H_{30}F_2O_2$: C, 78.79; H, 6.40. Found: C, 78.66; H, 6.50.

The $^1$H-NMR spectra of the 2,5-bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]toluenes with *n* = 5−12 are identical: 0.91 (t, −C*H*$_3$, 6 H), 1.37 (m, −[C*H*$_2$]−$_{n-3}$, 4(*n* - 3)H), 1.83 (m, −OCH$_2$C*H*$_2$−, 4 H), 2.48 (s, ArC*H*$_3$), 4.04 (t, −OC*H*$_2$−, 4 H), 6.91 (dd, 2 aromatic H ortho to −OR), 7.23 (s, 4 aromatic H ortho to −C≡CAr), 7.30 (dd, 1 aromatic H para to −CH$_3$), 7.37 (s, 1 aromatic H ortho to −CH$_3$), 7.43 (d, 1 aromatic H meta to −CH$_3$). Anal. Calcd for $C_{33}H_{34}F_2O_2$: C, 79.17; H, 6.84. Found: C, 79.50; H, 6.98. Anal. Calcd for $C_{35}H_{38}F_2O_2$: C, 79.52; H, 7.24. Found: C, 79.52; H, 7.42. Anal. Calcd for $C_{37}H_{42}F_2O_2$: C, 79.82; H, 7.60. Found: C, 79.38; H, 7.74. Anal. Calcd for $C_{39}H_{46}F_2O_2$: C, 80.10; H, 7.93. Found: C, 80.08; H, 8.06. Anal. Calcd for $C_{41}H_{50}F_2O_2$: C, 80.36, H, 8.22. Found: C, 80.22; H, 8.39. Anal. Calcd for $C_{43}H_{54}F_2O_2$: C, 80.59; H, 8.49. Found: C, 80.48; H, 8.54. Anal. Calcd for $C_{45}H_{58}F_2O_2$: C, 80.80; H, 8.74. Found: C, 80.72; H, 8.84. Anal. Calcd for $C_{47}H_{60}F_2O_2$: C, 80.99; H, 8.96. Found: C, 81.08; H, 8.86.

**5-{[[2′,5′-Bis[2-(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzyl]oxy]carbonyl}bicyclo[2.2.1]hept-2-enes (*n* = 1−12, 51−75% endo).** The norbornene monomers were synthesized in 40−93% yield as in the following example. A solution of 5-{[(2′,5′-diiodobenzyl)oxy]carbonyl}bicyclo[2.2.1]hept-2-ene (1.8 g, 3.8 mmol) and water (0.15 g, 8.8 mmol) in pyridine (22 mL) was added all at once to a mixture of CuI (0.08 g, 0.4 mmol), triphenylphosphine (0.2 g, 0.8 mmol), K$_2$CO$_3$ (1.5 g, 11 mmol), and 1-(3′-fluoro-4′-methoxyphenyl)acetylene (1.2 g, 8.3 mmol). The reaction mixture was heated at 110 °C for 64 h until the conversion was constant and almost complete as calculated by NMR. The reaction mixture was allowed to cool to room temperature and then added to cold aqueous NH$_4$Cl (80 mL). This was extracted three times with CHCl$_3$ (360 mL total) and the combined organic extracts were dried over Na$_2$SO$_4$. After filtering and distilling off the pyridine, the remaining dark liquid was passed through a column of silica gel using hexanes/CH$_2$Cl$_2$ (2:1) as eluant to yield a yellow oil (1.6 g, 83%). The monomer was purified for polymerization by flash chromatography on silica gel using hexanes as eluant, followed by two recrystallizations in the drybox from a mixture of hexanes (10 mL) and toluene (2 mL); 51% endo. $^1$H-NMR resonances at 1.29 (d), 1.41 (m), 1.96 (m), 2.33 (m), 2.90 (s), 3.06 (m), and 3.25 (s) are due to the nonolefin norbornene protons of both isomers; 3.94 (s, $-\mathrm{OC}H_3$, 6 H), 5.25 (s, $-\mathrm{C}H_2\mathrm{Ar}$, endo), 5.28 (d, $-\mathrm{C}H_2\mathrm{Ar}$, exo), 5.94 (m, 1 olefin H, endo), 6.12 (m, 2 olefin H, exo), 6.14 (m, 1 olefin H, endo), 6.91 (dd, 2 aromatic H ortho to $-\mathrm{OCH_3}$), 7.24 (m, 4 aromatic H ortho to $-\mathrm{C{\equiv}CAr}$), 7.46 (m, 3 aromatic H of central ring). Anal. Calcd for $\mathrm{C_{33}H_{26}F_2O_4}$: C, 75.56; H, 4.99. Found: C, 75.54; H, 5.22.

**5-{[[2′,5′-Bis[2-(3′-fluoro-4′-ethoxyphenyl)ethynyl]-benzyl]oxy]carbonyl}bicyclo[2.2.1]hept-2-ene; 61% endo.** $^1$H-NMR: 1.29 (d), 1.40 (m), 1.95 (m), 2.33 (m), 2.90 (s), 3.06 (m), and 3.25 (s) are due to the nonolefin norbornene protons of both isomers; 1.47 (t, $-\mathrm{C}H_3$, 6 H), 4.13 (q, $-\mathrm{OC}H_2-$, 4 H), 5.26 (s, $-\mathrm{C}H_2\mathrm{Ar}$, endo), 5.32 (d, $-\mathrm{C}H_2\mathrm{Ar}$, exo), 5.94 (m, 1 olefin H each of both isomers), 6.12 (m, 1 olefin H, exo), 6.14 (m, 1 olefin H, endo), 6.91 (dd, 2 aromatic H ortho to $-\mathrm{OEt}$), 7.24 (m, 4 aromatic H ortho to $-\mathrm{C{\equiv}CAr}$), 7.48 (m, 3 aromatic H of central ring). Anal. Calcd for $\mathrm{C_{35}H_{30}F_2O_4}$: C, 76.07; H, 5.47. Found: C, 76.13; H, 5.63.

**5-{[[2′,5′-Bis[2-(3′-fluoro-4′-*n*-propoxyphenyl)ethynyl]-benzyl]oxy]carbonyl}bicyclo[2.2.1]hept-2-ene; 64% endo.** $^1$H-NMR: 1.29 (d), 1.44 (m), 1.95 (m), 2.33 (m), 2.90 (s), 3.06 (m), and 3.25 (s) are due to the nonolefin norbornene protons of both isomers; 1.06 (t, $-\mathrm{C}H_3$, 6 H), 1.86 (m, $-\mathrm{C}H_2\mathrm{CH_2O}-$, 4 H), 4.05 (t, $-\mathrm{OC}H_2-$, 4 H), 5.26 (s, $-\mathrm{C}H_2\mathrm{Ar}$, endo), 5.32 (d, $-\mathrm{C}H_2\mathrm{Ar}$, exo), 5.94 (m, 1 olefin H each of both isomers), 6.12 (m, 1 olefin H, exo), 6.15 (m, 1 olefin H, endo), 6.91 (dd, 2 aromatic H ortho to $-\mathrm{OPr}$), 7.24 (m, 4 aromatic H ortho to $-\mathrm{C{\equiv}CAr}$), 7.48 (m, 3 aromatic H of central ring). Anal. Calcd for $\mathrm{C_{37}H_{34}F_2O_4}$: C, 76.53; H, 5.90. Found: C, 76.74; H, 5.96.

**5-{[[2′,5′-Bis[2-(3′-fluoro-4′-*n*-butoxyphenyl)ethynyl]-benzyl]oxy]carbonyl}bicyclo[2.2.1]hept-2-ene; 60% endo.** $^1$H-NMR: 1.30 (d), 1.43 (m), 1.95 (m), 2.31 (m), 2.90 (s), 3.06 (m), and 3.25 (s) are due to the nonolefin norbornene protons of both isomers; 0.91 (t, $-\mathrm{C}H_3$, 6 H), 1.52 (m, $-\mathrm{C}H_2\mathrm{CH_2CH_2O}-$, 4 H), 1.83 (m, $-\mathrm{C}H_2\mathrm{CH_2O}-$, 4 H), 4.04 (t, $-\mathrm{OC}H_2-$, 4 H), 5.27 (s, $-\mathrm{C}H_2\mathrm{Ar}$, endo), 5.32 (d, $-\mathrm{C}H_2\mathrm{Ar}$, exo), 5.93 (m, 1 olefin H each of both isomers), 6.12 (m, 1 olefin H, exo), 6.15 (m, 1 olefin H, endo), 6.92 (dd, 2 aromatic H ortho to $-\mathrm{OBu}$), 7.24 (m, 4 aromatic H ortho to $-\mathrm{C{\equiv}CAr}$), 7.49 (m, 3 aromatic H of central ring). Anal. Calcd for $\mathrm{C_{39}H_{38}F_2O_4}$: C, 76.95; H, 6.29. Found: C, 77.50; H, 6.47.

The $^1$H-NMR spectra of the 5-{[[2′,5′-bis[2-(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]benzyl]oxy]carbonyl}bicyclo[2.2.1]hept-2-enes with $n = 5-12$ are identical: 1.30 (d), 1.41 (m), 1.95 (m), 2.31 (m), 2.90 (s), 3.06 (m), and 3.25 (s) are due to the nonolefin norbornene protons of both isomers; 0.91 (t, $-\mathrm{C}H_3$, 6 H), 1.33 (m, $-[\mathrm{C}H_2]-_{n-3}$, $4(n-3)$H), 1.83 (m, $-\mathrm{C}H_2\mathrm{CH_2O}-$, 4 H), 4.05 (t, $-\mathrm{OC}H_2-$, 4 H), 5.27 (s, $-\mathrm{C}H_2\mathrm{Ar}$, endo), 5.32 (d, $-\mathrm{C}H_2\mathrm{Ar}$, exo), 5.94 (m, 1 olefin H each of both isomers), 6.12 (m, 1 olefin H, exo), 6.15 (m, 1 olefin H, endo), 6.91 (dd, 2 aromatic H ortho to $-\mathrm{OR}$), 7.24 (m, 4 aromatic H ortho to $-\mathrm{C{\equiv}CAr}$), 7.48 (m, 3 aromatic H of central ring). Anal. Calcd for $\mathrm{C_{41}H_{42}F_2O_4}$, 75% endo: C, 77.34; H, 6.65. Found: C, 77.56; H, 6.86. Anal. Calcd for $\mathrm{C_{43}H_{46}F_2O_4}$, 62% endo: C, 77.69; H, 6.97. Found: C, 77.82; H, 7.12. Anal. Calcd for $\mathrm{C_{45}H_{50}F_2O_4}$, 56% endo: C, 78.00; H, 7.27. Found: C, 77.42; H, 7.33. Anal. Calcd for $\mathrm{C_{47}H_{54}F_2O_4}$, 54% endo: C, 78.30; H, 7.55. Found: C, 78.58; H, 7.60. Anal. Calcd for $\mathrm{C_{49}H_{58}F_2O_4}$, 56% endo: C, 78.58; H, 7.80. Found: C, 78.26; H, 7.85. Anal. Calcd for $\mathrm{C_{51}H_{62}F_2O_4}$, 55% endo: C, 78.83; H, 8.04. Found: C, 78.38; H, 8.18. Anal. Calcd for $\mathrm{C_{53}H_{66}F_2O_4}$, 73% endo: C, 79.07; H, 8.26. Found: C, 79.08; H, 8.42. Anal. Calcd for $\mathrm{C_{55}H_{70}F_2O_4}$, 53% endo: C, 79.29; H, 8.47. Found: C, 79.09; H, 8.61.

**Polymerizations.** In a typical procedure, a solution of 5-{[[2′,5′-bis[2-(3′-fluoro-4′-methoxyphenyl)ethynyl]benzyl]oxy]-carbonyl}bicyclo[2.2.1]hept-2-ene (0.21 g, 0.40 mmol) in dry THF (4.1 g) was added dropwise over 1 min to a solution of $\mathrm{Mo(CHCMe_2Ph)}(N\text{-}2,6\text{-}{}^i\mathrm{Pr_2Ph})(\mathrm{O}^t\mathrm{Bu})_2$ (5 mg, 9 $\mu$mol) in dry THF (0.40 g). After stirring at room temperature for 2 h, the orange solution was quenched with benzaldehyde (20 $\mu$L, 0.20 mmol) and was then stirred for 30 min. The solution was taken outside of the drybox and precipitated in methanol (60 mL) followed by the addition of 3 drops of concentrated HCl. The precipitate was collected, reprecipitated from THF (10 mL) into methanol (60 mL), and dried to yield 0.19 g (92%) of polymer as a white powder; $M_\mathrm{n} = 3.3 \times 10^4$, $M_\mathrm{w}/M_\mathrm{n} = 1.23$.

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**Supporting Information Available:** Differential scanning calorimetry traces of the 2,5-bis[(3′-fluoro-4′-*n*-alkoxyphenyl)ethynyl]toluenes (1 page). Ordering information is given on any current masthead page.

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