Synthesis of Side-Chain Liquid Crystal Polymers by Living Ring-Opening Metathesis Polymerization. 2. Influence of Molecular Weight, Polydispersity, and Flexible Spacer Length (*n* = 9–12) on the Thermotropic Behavior of the Resulting Polymers

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ABSTRACT: The living ring-opening metathesis polymerization of 5-[[[*n*-[(4′-methoxy-4-biphenylyl)oxy]alkyl]oxy]carbonyl]bicyclo[2.2.1]hept-2-ene (1-*n*, *n* = 9–12) with Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (Ar = 2,6-C_6H_3-*i*-Pr_2) is described. Polymers with degrees of polymerization from 5 to 100 and narrow molecular weight distributions (M_w/M_n = 1.07–1.28) were obtained in high yield. All polymers exhibit side-chain crystallization along with a nematic or smectic mesophase. Isotropization temperatures increase with increasing molecular weight and then become independent of molecular weight at approximately 30–50 repeat units. Side-chain crystallization is suppressed as molecular weight increases.

Introduction

Side-chain liquid crystalline polymers (SCLCP)s have been prepared mainly by radical polymerization of (meth)-acrylates and by the hydrosilation of poly(methylsiloxane) backbones with mesogenic olefins. Although extensive data have been accumulated on the structure/property relations of SCLCPs using these two synthetic routes, much of it is contradictory.[1] These findings demonstrated the need for more comprehensive and systematic studies of SCLCPs prepared using living polymerization methods.[2-6] Ideally, motions of mesogenic side chains should be completely decoupled from those of the polymeric main chain. Although the motions of the main chain and side chains are only partially decoupled by a spacer, decoupling becomes more efficient with increasing spacer length.[1] However, most SCLCPs containing long spacers undergo side-chain crystallization. Side-chain crystallization is depressed by polymerization of monomers which undergo conformational isomerism[7-9] and by copolymerization of constitutionally isomeric monomers;[10,11] decoupling is enhanced by phase separation of the main chain from the mesogenic side chains.[12-15]

A relatively recent method of preparing living polymers consists of ring-opening metathesis polymerization (ROMP) of strained cyclic olefins[16,17] by initiators whose activity has been "tuned" in order to limit secondary metathesis of the double bonds in the polymer chain. The most readily available and suitable cyclic olefins are norbornene and substituted norbornadiene derivatives. ROMP initiators with perhaps the greatest potential are molybdenum complexes of the type Mo(CHR)(NAr)(O-*t*-Bu)$_2$[18,19] (Ar = 2,6-C_6H_3-*i*-Pr_2, R = *t*-Bu or CMe_2Ph) since they appear to tolerate a large variety of functional groups on norbornene and norbornadiene monomers.[20,21] (So far the analogous tungsten derivatives[22] do not appear to be as tolerant). The molybdenum catalysts offer an opportunity to prepare new side-chain liquid crystalline polymers with controlled chain lengths.

In the first paper in this series[23] we described the living ROMP of 5-[[[*n*-[(4′-methoxy-4-biphenylyl)oxy]alkyl]oxy]carbonyl]bicyclo[2.2.1]hept-2-enes (1-*n*) with *n* = 2–8 and discussed the dependence of the thermotropic behavior of poly(1-*n*) on polymer molecular weight, polydispersity, and the length of the flexible spacer. In contrast to poly(1-*n*) with *n* = 2–8, polymers with *n* = 9–12 exhibit side-chain crystallization in addition to the nematic mesophase. In this paper we describe the synthesis and thermotropic behavior of poly(1-*n*) with crystallizable side chains as a function of molecular weight and spacer length.

Results and Discussion

Synthesis of Monomers. Monomers 1-*n* (exo:endo = 1:3) were synthesized as shown in Scheme I by reaction of the appropriate *n*-bromo 1-alcohol with 4-methoxy-4′-hydroxybiphenyl,[24] followed by esterification of the mesogenic alcohols with an isomeric mixture of 5-norbornene-2-carboxylic acid chloride. All monomers are crystalline and form no mesophase. They exhibit a single melting endotherm on heating and a single crystallization exotherm on cooling, as observed by differential scanning calorimetry (DSC). These findings contrast to analogous findings for monomers 1-*n* with shorter *n*-alkoxy substituents, which display crystalline polymorphism. The first and second heating scans are identical, as are all cooling scans.

Polymerization of 1-*n*. Monomer 1-*n* was quantitatively polymerized in 1 h in tetrahydrofuran (THF) at room temperature in a reaction initiated by Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$. The living polymer was quenched with benzaldehyde to give a benzylidene-terminated polymer upon reaction of the living alkylidene with benzaldehyde in a Wittig fashion (Scheme II). The molecular weight of poly(1-*n*) was controlled by varying the molar ratio of the monomer to Mo initiator ([M]/[I]). The polymerization is quantitative, and the polymers were free of unreacted monomer after a single precipitation.

The results of the polymerizations are summarized in Table I, and the gel permeation chromatograms (GPCs) of poly(1-9) and poly(1-11) are shown in Figure 1. The polydispersities (PDI = M_w/M_n) are lower than 1.20 in most cases but are as high as 1.28 for some of the higher molecular weight polymers as a result of small double molecular weight fraction. As shown in Figure 2, a linear relationship is obtained by plotting the number-average molecular weight (M_n) of poly(1-*n*) as a function of [M]/[I] for ratios up to 100. The linear relationships and low

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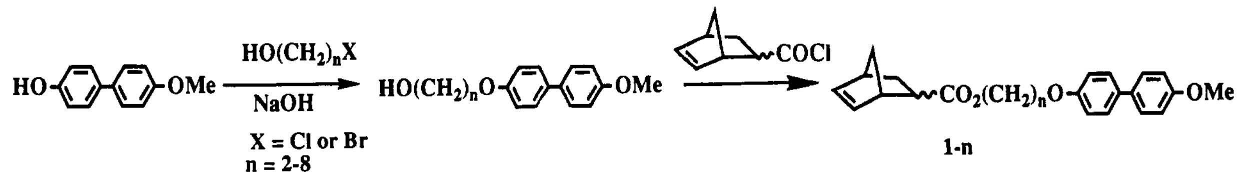
Scheme I



Scheme II

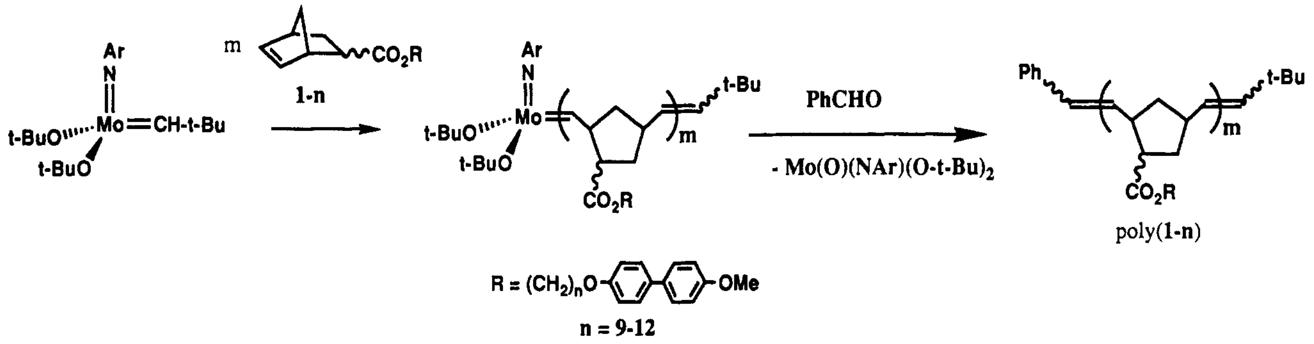


Table I
Polymerization of 1-n and Characterization of the Resulting Polymers

[1-*n*]/[Mo]			GPC			phase transitions (°C) and corresponding enthalpy changes (kJ/mru)[a]	
1-*n*	mol/mol	theor M_n	M_n	PDI	DP	heating	cooling
1-9	100	46262	47949	1.07	104	g 29 n 91 (2.24) i	i 85 (2.21) n 22 g
1-9	50	23121	18997	1.08	41	g 25 n 87 (1.85) i	i 80 (2.16) n 15 g
1-9	20	9252	8649	1.13	19	g 23 k 54 (0.66) n 83 (1.76) i	i 77 (1.54) n 42 (0.66) k 19 g
1-9	10	4926	5114	1.14	10	g 21 k 57 (–) n 78 (4.28)[b] i	i 71 (1.54) n 42 (0.66) k 17 g
1-9	5	2123	3220	1.17	7	g 18 k 61 (–) n 71 (6.99)[b] i	i 65 (1.28) n 40 (2.77) k 32 g
1-10	100	47665	62683	1.26	132	g 23 n 87 (1.85) i	i 81 (2.04) n 26 g
1-10	50	23833	24378	1.13	51	g 24 n 87 (1.98) i	i 79 (1.91) n 29 g
1-10	20	9533	8137	1.12	17	g 23 k 55 (2.02) n 84 (1.76) i	i 76 (1.74) n 44 (1.70) k 26 g
1-10	10	4767	4710	1.14	10	g 19 k 51 (2.37) k 60 (0.96) n 78 (1.34) i	i 71 (1.77) n 41 (2.12) k 23 g
1-10	5	2383	3230	1.16	7	g 36 k 60 (4.71) n 78 (1.35) i	i 67 (1.75) n 39 (3.52) k 28 g
1-11	100	49068	35086	1.23	72	g 40 k 49 (1.01) s 84 (3.56) i	i 78 (3.30) s 45 (1.06) k 32 g
1-11	50	24534	16272	1.12	33	g 39 k 52 (0.95) s 83 (3.07) i	i 77 (2.91) s 47 (1.25) k 34 g
1-11	20	9814	7226	1.12	15	g 36 k 52 (1.90) s 79 (2.64) i	i 73 (2.35)[c] s 45 (2.36) k 31 g
1-11	10	4907	4683	1.15	10	g 25 k 50 (1.43) k 55 (–1.95) k 63 (5.08) s 75 (–)[b] i	i 69 (2.67)[c] s 44 (2.71) k 30 g
1-11	5	2453	3183	1.18	6	g 29 k 62 (10.0) s 69 (–)[b] i	i 63 (2.57)[c] s 44 (4.00) k 34 g
1-12	100	50471	49568	1.28	98	g 23 k 61 (2.99) s 89 (2.70) i	i 83 (2.58) s 52 (2.16) k 34 g
1-12	50	25236	20830	1.22	41	g 22 k 64 (4.83) s 88 (2.56) i	i 82 (2.38) s 55 (2.16) k 38 g
1-12	20	10094	9022	1.13	18	g 38 k 66 (2.78) s 85 (3.37) i	i 78 (3.34) s 58 (3.27) k 43 g
1-12	10	5047	5306	1.15	11	g 43 k 63 (2.64) s 80 (3.01) i	i 74 (3.18)[c] s 55 (3.23) k 39 g
1-12	5	2524	3421	1.17	7	g 43 k 70 (–) s 75 (11.70)[b] i	i 68 (3.15)[c] s 52 (9.28) k 37 g

[a] All data except T_gs are from second heating and first cooling scans; T_gs were determined on heating scans by quenching the samples in liquid nitrogen. [b] Overlapped with a previous transition. [c] Accompanied by a small transition peak (see text).

polydispersities are consistent with a living polymerization under the conditions employed.

Proton NMR resonances of poly(1-*n*) at 5.2–5.6 ppm (olefinic protons) and at 1.6–2.2 and 2.2–3.0 ppm (cyclopentane ring protons) are quite broad as a result of the lack of stereoregularity of the main chain. In contrast, the aromatic resonances are relatively sharp. All spectral data are consistent with the ring-opened structure.

Thermal Characterization of Polymers. Thermal characterization of poly(1-*n*) was carried out by a combination of DSC and thermal polarized optical microscopy. All DSC cooling scans and the second and subsequent heating scans were identical when the same rates were used. The complete thermal transitions from the second heating and first cooling scans are summarized in Table I.

DSC traces of the second heating and first cooling scans of poly(1-9) and poly(1-10) are shown in Figures 3 and 4, respectively. Oligomers with less than approximately 50 repeat units exhibit crystalline melting in addition to a nematic–isotropic transition. In these cases, the melting and crystallization transitions overlap the glass transition, which makes T_g difficult to determine accurately. T_g values reported for those polymers which do not crystallize therefore are more reliable than values for the crystallizable oligomers. More reliable T_g values were obtained for the crystallizable polymers by analyzing samples quenched from the isotropic melt using liquid nitrogen. However, even the quenched samples of the lowest molecular weight oligomers and poly(1-11) tend to crystallize during the next heating scan and T_g values of these samples are therefore still less reliable than those for noncrystalline samples.

Oligomers of 1-9 and 1-10 evidently crystallize in two different modifications. This is obvious with poly(1-10), which exhibits two melting endotherms in some cases. As shown in Figure 4, the 10-mer of poly(1-10) crystallizes in only the more stable modification if it is annealed at 49 °C for 1 h, and the extent of crystallization increases with annealing (ΔH = 5.94 kJ/mru). Although poly(1-9) exhibits only a single melting endotherm, Figure 3 shows that annealing the 10-mer at 50 °C for 1 h also results in a more stable crystalline modification (T_m = 64 °C, ΔH = 3.54 kJ/mru). Since side-chain crystallization is kinet-

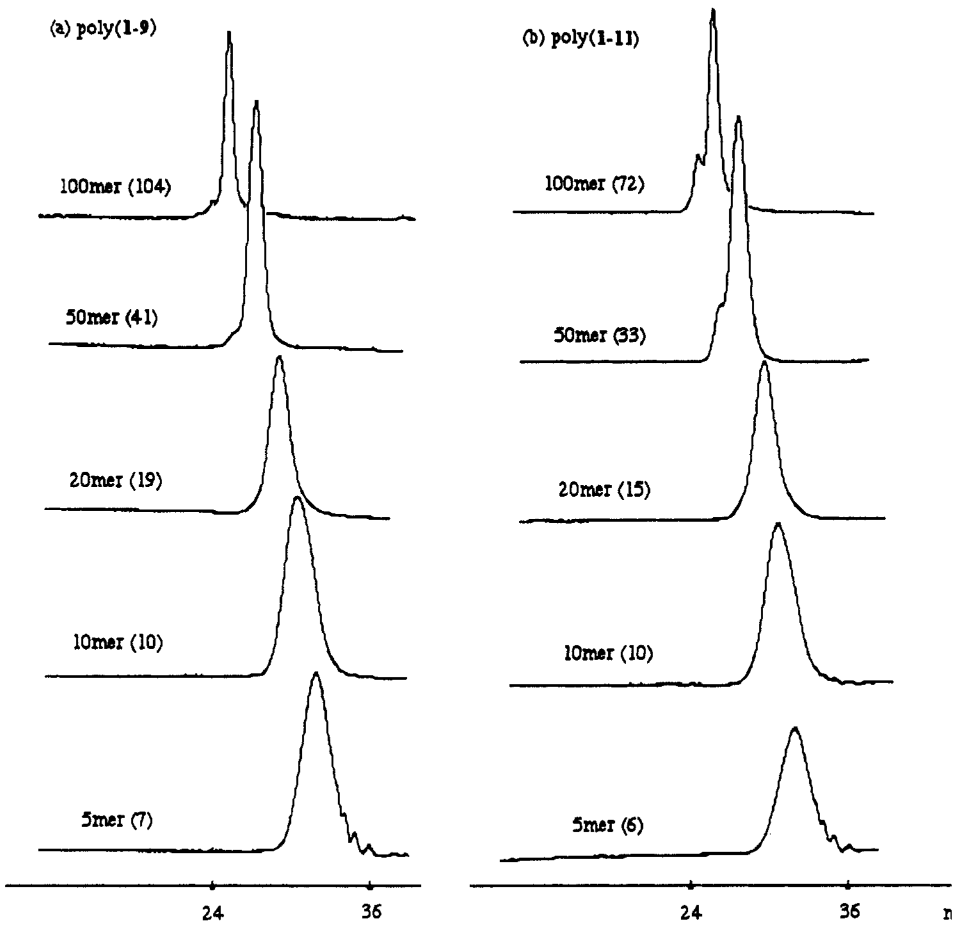


Figure 1. GPC traces of (a) poly(1-9) and (b) poly(1-11). The theoretical and observed (in parentheses) degrees of polymerization (DP) are shown on each trace.

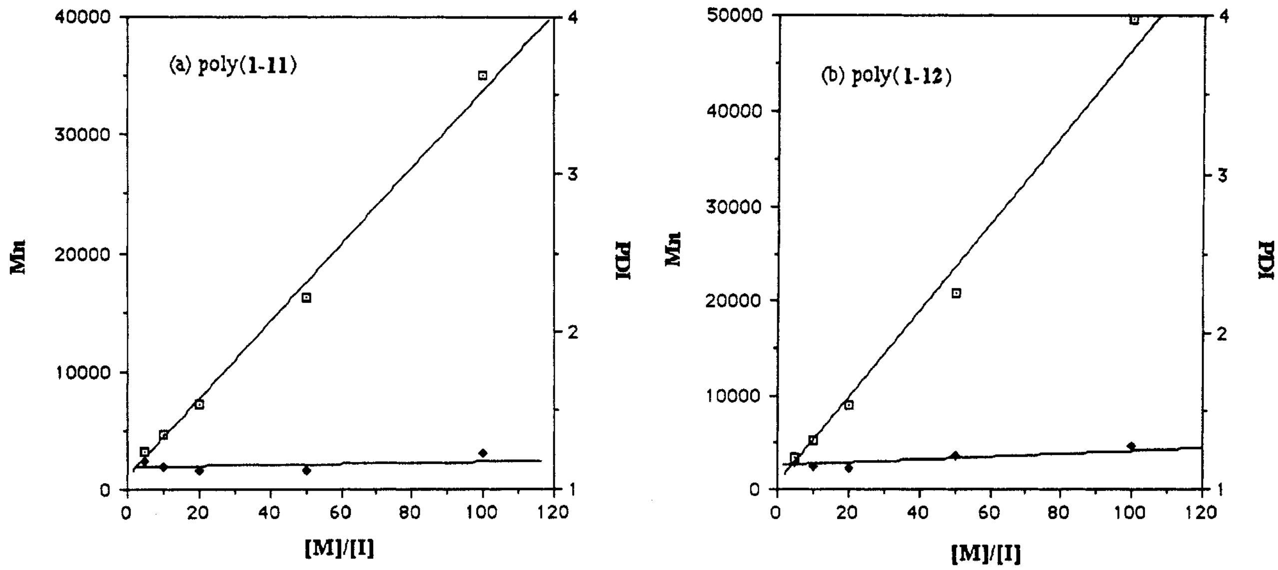


Figure 2. Dependence of the number-average molecular weight (M_n) and the polydispersity (PDI = M_w/M_n) of (a) poly(1-11) and (b) poly(1-12) on the molar ratio of monomer to initiator ([M]/[I]).

ically controlled and the rate of crystallization decreases as molecular weight increases, crystallization is suppressed as the molecular weight increases and disappears in any polymer that contains more than approximately 50 repeat units. Annealing the 51-mer of poly(1-10) at 55 °C for 1 h does induce a slight amount of crystallization (T_m = 62 °C, ΔH = 0.84 kJ/mru; Figure 4).

The thermal behavior of poly(1-11) is almost the same as that of poly(1-10). Oligomers also crystallize in two different modifications (Figure 5), although annealing induces crystallization of only the more stable modification. For example, a 10-mer of poly(1-11) which had crystallized on cooling at 44 °C showed two melting endotherms, while only a single melting endotherm ascribable to the more stable crystalline form (T_m = 62 °C, ΔH = 6.53 kJ/mru) was observed after the sample was annealed at 46 °C for 1 h. All polymers also exhibit an enantiotropic mesophase.

In the polymer that contains the largest methylene side chain (poly(1-12)), the side chains have the greatest tendency to crystallize. Although the mesophase appears to be enantiotropic for all chain lengths (Figure 6), it is

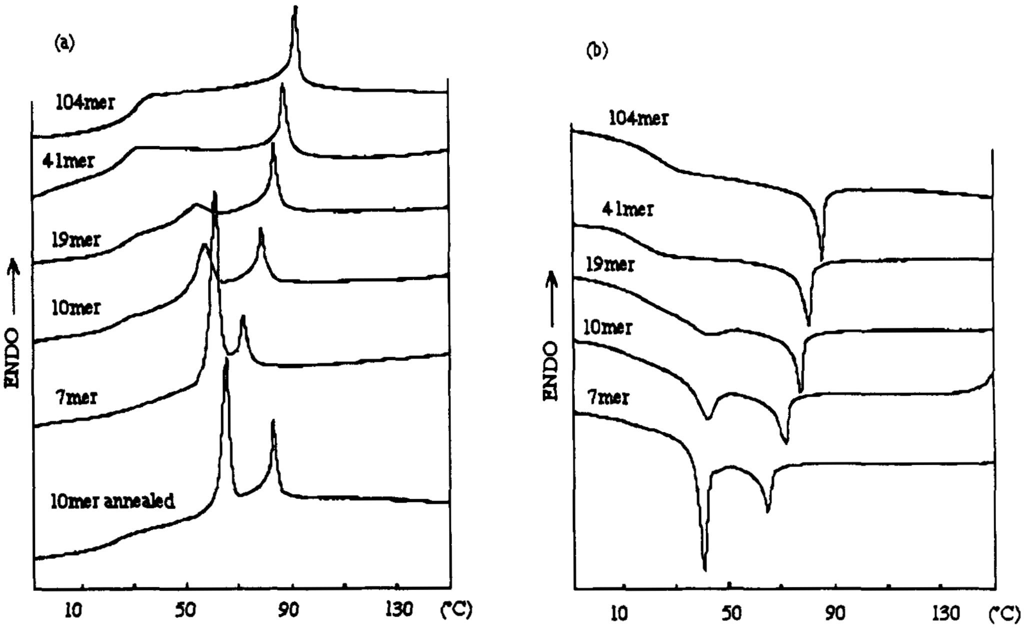


Figure 3. Normalized DSC thermograms of poly(1-9) observed (a) on the second heating and (b) first cooling scans.

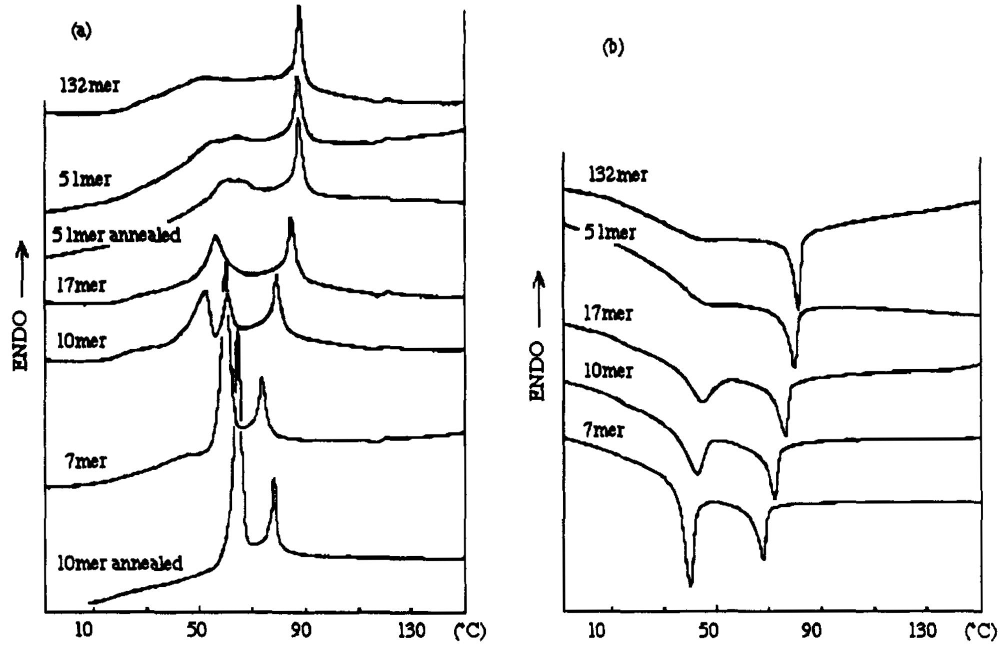


Figure 4. Normalized DSC thermograms of poly(1-10) observed (a) on the second heating and (b) first cooling scans.

actually monotropic in the two shortest oligomers. The isotropization of the 7-mer is seen as a shoulder on the melting endotherm in the second heating scan shown in Figure 6. However, this sample exhibits a single melting peak at 87 °C (ΔH = 10.5 kJ/mru) on the first heating scan, which is higher than the isotropization temperature. Annealing the 11-mer of poly(1-12) also leads to crystallization of a modification which melts at a temperature exceeding that at which isotropization takes place.

Thermal polarized optical microscopy demonstrates that poly(1-9) and poly(1-10) exhibit textures characteristic of nematic mesophases. A representative threaded marbled nematic texture of poly(1-9) (19-mer) is shown in Figure 7a. Poly(1-11) and poly(1-12) exhibit fine schlieren textures attributable to the nematic or smectic C phase as shown in Figure 7b. There is a small exothermic peak overlapping the exotherm for mesophase formation in the DSC traces of oligo(1-11) and oligo(1-12). In order to acquire information about this small transition, these samples were cooled or heated very slowly and annealed at the temperature just below the isotropization temperature. In spite of these efforts, these textures do not change. However, DSC traces of oligo(1-11) and oligo(1-12) seem to show the isotropic–nematic–smectic transition sequence. Due to the higher sensitivity of the smectic–nematic transition temperature relative to the nematic–isotropic transition temperature at high molecular weights, both polymers seem to display only the smectic phase.[4] According to this consideration this mesophase is tentatively marked as s (unidentified smectic phase).

The phase transition temperatures of each polymer obtained upon heating are plotted in Figure 8 as a function of the degree of polymerization, as determined by GPC. Regardless of the length of the spacer and whether the side-chain crystallizes or not, isotropization temperatures become independent of molecular weight at approximately 30–50 repeat units, as found also for the poly(1-n) with shorter spacers (n = 2–8).[23] These results are comparable to those reported for mesogenic polysiloxanes (DP ~ 12),[25] poly(vinyl ethers) (DP ~ 10–20),[2-6,25] polyacrylates (DP ~ 12–40),[26,27] and polymethacrylates (DP ~ 12).[28] The

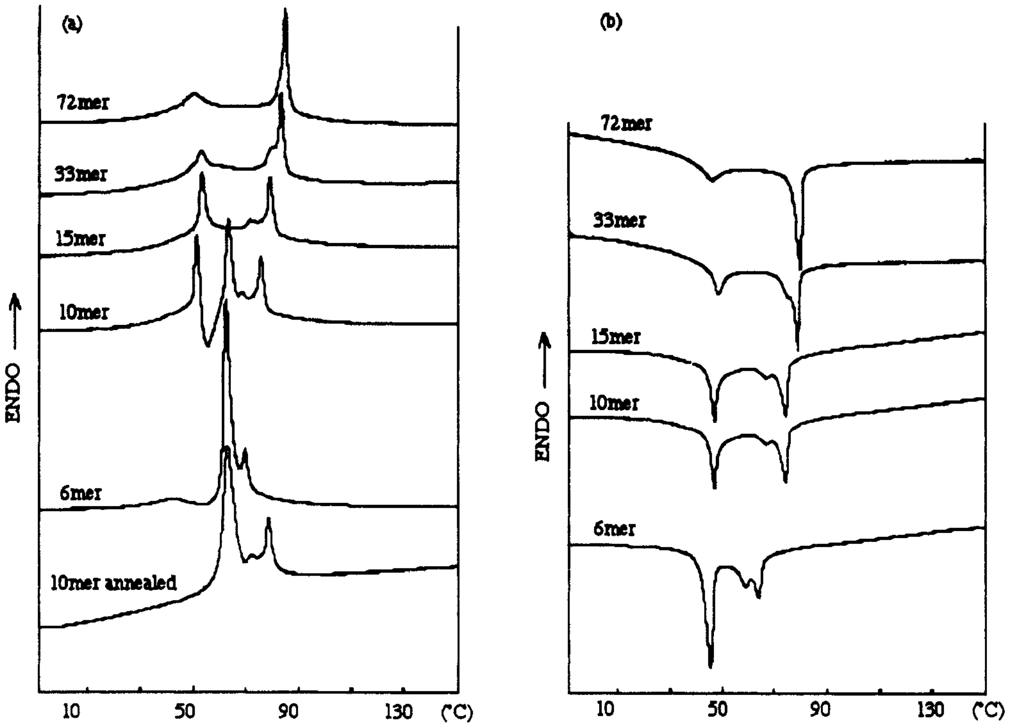


Figure 5. Normalized DSC thermograms of poly(1-11) observed (a) on the second heating and (b) first cooling scans.

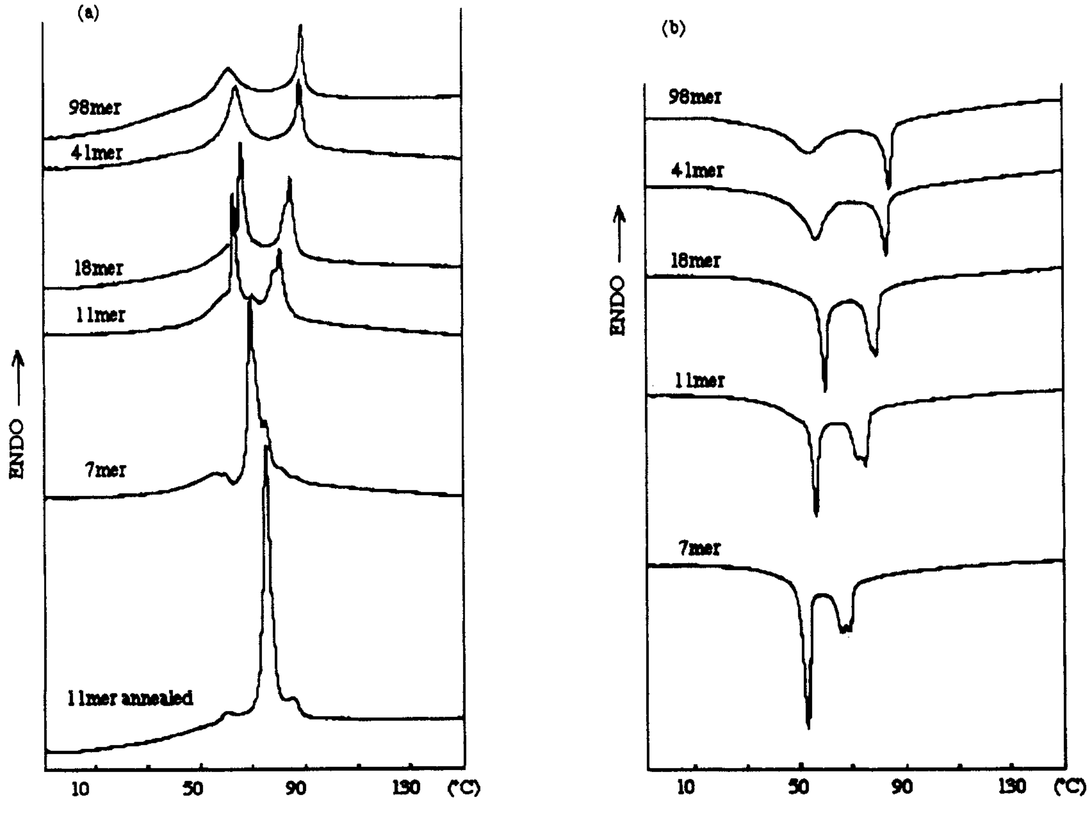


Figure 6. Normalized DSC thermograms of poly(1-12) observed (a) on the second heating and (b) first cooling scans.

melting temperatures depend on chain length as discussed earlier. That is, although T_m increases with increasing molecular weight, the primary effect of increasing molecular weight is to decrease the extent and the rate of side-chain crystallization, especially in the most stable modification. Therefore, crystallization and melting are not observed at high molecular weights for poly(1-9) and poly(1-10). At all chain lengths the side chains in poly(1-11) and poly(1-12) crystallize to some extent, although the extent of side-chain crystallization and the change in enthalpy of melting decrease with increasing chain length. Although the enthalpy change of the nematic–isotropic transition is small and somewhat scattered as a function of chain length, it is relatively independent of molecular weight.

Conclusions

5-[[[*n*-[(4′-Methoxy-4-biphenylyl)oxy]alkyl]oxy]carbonyl]bicyclo[2.2.1]hept-2-enes with *n* = 9–12 were polymerized by ring-opening metathesis polymerization in a living manner. This series of SCLCPs with systematically varying molecular weights exhibit monotropic or enantiotropic nematic or smectic mesophases in addition to side-chain crystallization. Side-chain crystallization is highly kinetically controlled and therefore is suppressed by increasing molecular weight; i.e., the change in enthalpy of melting and therefore the extent of crystallinity decrease as chain length increases. Side chains do not crystallize in high molecular weight poly(1-9) and poly(1-10), which also exhibit enantiotropic nematic mesophases. All side chains of poly(1-11) and poly(1-12) crystallize to some extent, although crystallization is suppressed sufficiently at higher molecular weights that the monotropic mesophase of oligo(1-12) becomes enantiotropic. The isotropization temperatures increase with increasing molecular weight up to 30–50 repeat units and then become independent of molecular weight.

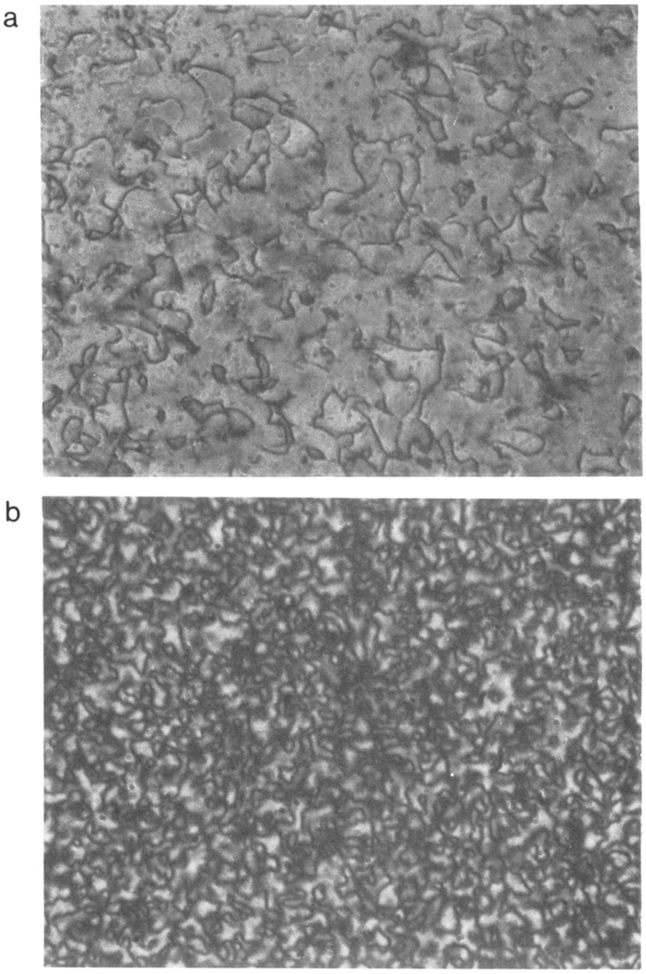


Figure 7. Polarized optical micrographs of the nematic textures observed on cooling (a) poly(1-9) 19-mer from the isotropic state, 80 °C (magnification 80×), and (b) poly(1-11) 33-mer from the isotropic state, 81 °C (magnification 160×).

Experimental Section

Materials and Methods. All polymerizations were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox. Tetrahydrofuran (THF) used for polymerizations was vacuum transferred from sodium benzophenone ketyl just before use. Ether and THF used for monomer syntheses were distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane used for purification of monomers was distilled from calcium hydride under nitrogen. Pentane was washed with 5% nitric acid in sulfuric acid, stored over calcium chloride, and then distilled from sodium benzophenone ketyl under nitrogen. 4,4′-Dihydroxybiphenyl (97%), 9-bromo-1-nonanol (97%), 10-bromo-1-decanol (90%), 11-bromo-1-undecanol (98%), and 12-bromo-1-dodecanol (99%) were used as received from Aldrich. 2-Norbornene-5-carboxylic acid chloride (exo:endo = 1:3)[29] and 4′-methoxy-4-hydroxybiphenyl[30] were prepared as described in the literature. All other reagents and solvents were available commercially and used as received.

300-MHz ^{1}H-NMR spectra were recorded on a Varian XL-300 spectrometer. All spectra were recorded in $CDCl_3$ with TMS as internal standard. The relative molecular weights were determined by gel permeation chromatography (GPC) at room temperature using a set of Shodex KF802.5, 803, 804, 805, and 800P columns (700, 2×10^3, 2×10^4, and 1×10^5 Å and a precolumn, respectively), a Knauer differential refractometer, and a Spectroflow 757 absorbance detector set at 300 nm on 0.1–0.3% w/v

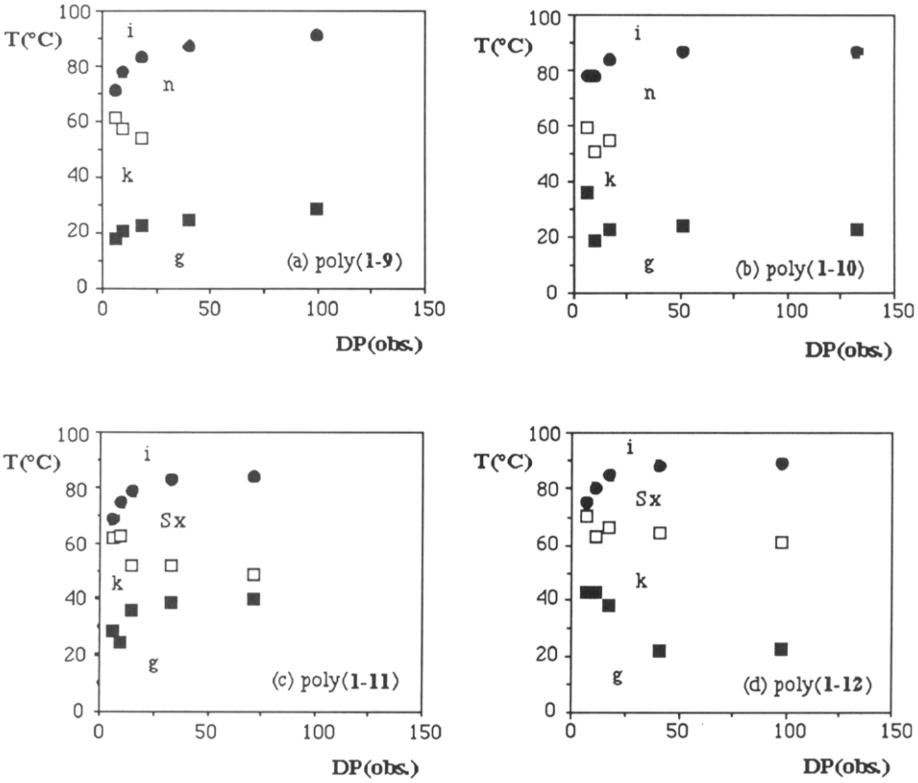


Figure 8. Dependence of the phase transition temperatures on the GPC-determined degrees of polymerization of (a) poly(1-9), (b) poly(1-10), (c) poly(1-11), and (d) poly(1-12). All of the data are from the second heating scans: (■) g–k, (□) k–n(s), (●) n(s)–i.

samples in THF. The GPC columns were calibrated using polystyrene standards (Polymer Laboratories Ltd.) ranging from 1206 to 1.03 × 10^6 MW. A Perkin-Elmer DSC-7 differential scanning calorimeter was used to determine the thermal transitions, which were read as the maxima and minima of the endothermic and exothermic peaks, respectively. All heating and cooling rates were 20 °C/min unless noted otherwise. Glass transition temperatures (T_gs) were read as the middle of the change in the heat capacity. All second and subsequent heating scans are identical. A Nikon optical polarized microscope equipped with a Mettler FP82 hot stage and a Mettler FP800 central processor was used to observe the thermal transitions and to analyze the anisotropic textures.

Synthesis of *n*-[4′-Methoxy-4-biphenylyl)oxy]alkan-1-ol (*n* = 9–12). All compounds were synthesized by the same procedure used for the analogs with smaller values of n^{23} as illustrated by the following example. 5-Bromo-1-pentanol (4.9 g, 0.022 mol) was added to a solution of 4′-methoxy-4-hydroxybiphenyl (4.0 g, 0.020 mol) and NaOH (0.89 g, 0.022 mol) in a mixture of ethanol (40 mL) and water (5 mL). After stirring at reflux for 24 h, the reaction mixture was poured into water and the precipitated product was filtered and washed with 150 mL of 10% aqueous NaOH in water. Recrystallization from ethanol yielded 6.11 g (89%) of colorless crystals.

***n*-[(4′-Methoxy-4-biphenylyl)oxy]-1-alkanol.** The proton NMR spectra of the *n*-[(4′-methoxy-4-biphenylyl)oxy]-1-alkanols, *n* = 9–12, are identical: δ 1.25 (t, 1 H, O*H*), 1.3–1.7 (m, 2[*n* − 3] H, $[CH_2]_{n-3}$), 1.83 (q, 2 H, CH_2CH_2OAr), 3.65 (q, 2 H, CH_2OH), 3.85 (s, 3 H, CH_3O), 4.00 (t, 2 H, CH_2OAr), 6.96 (dd, 4 aromatic H), 7.46 (dd, 4 aromatic H).

Synthesis of 5-[[[*n*-[(4′-Methoxy-4-biphenylyl)oxy]alkyl]oxy]carbonyl]bicyclo[2.2.1]hept-2-enes (1-*n*, *n* = 9–12). The 1-*n* monomers were prepared in 70–80% yield as in the following example. A solution of 2-norbornene-5-carboxylic acid chloride (1.71 g, 0.0104 mmol) in THF (5 mL) was added dropwise to a refluxing slurry of 12-[(4′-methoxy-4-biphenylyl)oxy]-1-dodecanol (4.0 g, 0.010 mmol) and triethylamine (1.1 g, 0.011 mmol) in THF (40 mL). The solution was stirred at reflux for 24 h. The solution was cooled to room temperature, and the solvent was removed on a rotary evaporator. The residue was dissolved in chloroform, and the solution was washed with aqueous K_2CO_3 and then water and dried over anhydrous $MgSO_4$. Concentration of the filtered chloroform solution yielded 4.4 g (84%) of 1-12.

Monomers 1-9 and 1-10 were purified by column chromatography using Al_2O_3 as the stationary phase and THF as eluent, followed by at least two recrystallizations in the drybox from ether, ether/pentane, or ether/methylene chloride. Following chromatography on Al_2O_3, 1-11 and 1-12 were purified by precipitation of a THF solution into methanol because they did not recrystallize well. All monomers were recrystallized or reprecipitated until no improvement was seen in the polydispersity of polymers prepared using 100 equiv of monomer; ^{1}H NMR δ 1.32 (d), 1.5 (m), 1.6 (d), 1.94 (m), 2.31 (dd), 2.98 (br s), 3.06 (td), 3.12 (br s) and 3.30 (br s), all non-olefinic norbornene protons of both isomers, 5.95 (dd) and 6.21 (dd), endo olefinic protons, 6.15 (m), exo olefinic protons, 1.2–2.0 (m, 2[*n* − 2] H, $[CH_2]_{n-2}$, 3.86 (s, 3 H, OCH_3), 4.07 (t, 2 H, CH_2OAr), 4.18 (m, 2 H, CH_2OOC). The melting points determined by DSC are as follows: 1-9, 78 °C; 1-10, 68 °C; 1-11, 83 °C; 1-12, 77 °C.

Polymerization Procedure. A solution of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2^{18}$ (0.2 mL, 0.0205 mol/L) in THF was added in one portion to a rapidly stirred solution of monomer (3 mL, 0.137 mol/L, 100 equiv) in THF, and the reaction mixture was stirred for 1 h. The polymerization was quenched by addition of 20 μL of benzaldehyde. After 30 min, the solution was added dropwise to methanol (~50 mL) and the precipitated polymer was isolated by centrifugation, washed with methanol, and dried in vacuo. In all cases, polymer yields were more than 90% and GPC analyses showed no traces of monomer. Further purification of samples by reprecipitation had no effect on their thermotropic behavior. When 20 equiv or less of monomer was used, the catalyst concentration was adjusted to 0.205 mol/L: ^{1}H NMR δ 1.0 (m, terminal *t*-Bu), 1.2–2.2 (br), 2.2–3.2 (br), 3.85 (s, OCH_3), 4.07 (br, CH_2OAr), 4.26 (br, CH_2OOC), 5.15–5.55 (br, olefinic H), 6.97 (br d, atomatic H), 7.51 (br d, aromatic H).

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Registry No. 1 (*n* = 9), 143903-10-0; 1 (*n* = 9) (free alcohol), 143903-08-6; 1 (*n* = 9) (homopolymer), 143903-38-2; 1 (*n* = 10), 143903-11-1; 1 (*n* = 10) (free alcohol), 127870-08-0; 1 (*n* = 10) (homopolymer), 143903-39-3; 1 (*n* = 11), 143903-12-2; 1 (*n* = 11) (free alcohol), 105531-80-4; 1 (*n* = 11) (homopolymer), 143903-40-6; 1 (*n* = 12), 143903-13-3; 1 (*n* = 12) (free alcohol), 143903-09-7; 1 (*n* = 12) (homopolymer), 143903-41-7; 4-hydroxy-4′-methoxy-1,1′-biphenyl, 16881-71-3; 2-norbornene-5-carbonyl chloride, 27063-48-5.