Synthesis of Side Chain Liquid Crystal Polymers by Living Ring-Opening Metathesis Polymerization. 5. Influence of a Mesogenic Group and an Interconnecting Group on the Thermotropic Behavior of the Resulting Polymers

Zen Komiya[†] and Richard R. Schrock[*]

Department of Chemistry, 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received July 31, 1992; Revised Manuscript Received November 23, 1992

ABSTRACT: Norbornene derivatives containing ((4′-cyano-4-biphenyl)yl)oxy mesogens linked to the norbornene through methylene groups (n = 3–7, 9–12) and an ester were polymerized by Mo(CHR)(NAr)(O-t-Bu)$_2$ (Ar = 2,6-C_6H_3-i-Pr$_2$, R = t-Bu) in a living manner. Polymers in which n = 3 were amorphous, whereas all other polymers (n = 4–7, 9–12) displayed enantiotropic nematic mesophases that were independent of the molecular weight. Polymers having 9–12 methylene spacers did not undergo side chain crystallization and did not show an odd–even effect, in contrast to analogous polymers containing ((4′-methoxy-4-biphenyl)yl)oxy mesogens, which exhibited side chain crystallization when $n > 8$ and an odd–even effect when $n < 7$. The lower tendency to form a more ordered phase and the absence of an odd–even effect are attributed to dipole–dipole repulsions between ((4′-cyano-4-biphenyl)yl)oxy mesogens. Polymers containing ((4′-methoxy-4-biphenyl)yl)oxy mesogens attached through ether linkages gave highly crystalline SCLPCs, even with relatively few methylene units in the spacer (n = 4–6).

Introduction

Living polymerization methods allow one to synthesize polymers with well-defined and controlled chemical structures.[1–4] It is desirable to prepare side chain liquid crystalline polymers (SCLPCs) or block copolymers using living polymerization techniques, but tolerance of functionality is an obvious requirement of the catalyst. Group transfer polymerization and living cationic polymerization methods have been exploited to prepare (SCLCPs),[5–15] and we have demonstrated recently that the well-characterized molybdenum alkylidene complex Mo(CHR)(NAr)(O-t-Bu)$_2$ (Ar = 2,6-C_6H_3-i-Pr$_2$, R = t-Bu or CMe$_2$Ph)[16] can also be used for the synthesis of well-defined SCLCPs by ring-opening methathesis polymerization (ROMP).[17–20] Investigations of these well-defined SCLCPs have established the precise relationship between molecular weight and phase behavior and have elucidated the main chain length at which the phase transitions no longer vary as additional monomer units are added. Some of these studies also reveal the effect of spacer length and molecular weight distribution on the thermotropic behavior of SCLCPs. Systematic, detailed studies of this type should help establish trends in structure/property relationships of SCLCPs and provide a base of knowledge for preparing novel macromolecules with specific phases and transition temperatures.

Recent systematic studies of SCLCPs have raised questions concerning an odd–even spacer effect in SCLCPs. The odd–even effect of SCLCPs that exhibit a smectic phase has been explained in terms of arrangement of mesogenic groups. This explanation appears to be independent of the type of main chain and mesogenic group.[21–25] However, there is no satisfactory explanation of the odd–even effect exhibited in nematic SCLCPs.[17,18] Furthermore, basic information concerning the relationship between the mesogens and the phase type and how the phase behavior is related to the length of the connecting group is still too sparse to establish a concrete basis for molecular engineering of SCLCPs.

In this paper we report former systematic investigations of SCLCPs prepared by ring-opening metathesis polymerization (ROMP) using the Mo(CH-t-Bu)(NAr)(O-t-Bu)$_2$ (Ar = 1,6-C_6H_3-i-Pr$_2$). We already have prepared polymers that contain the ((4′-methoxy-4-biphenyl)yl)oxy group attached to the polymer main chain by an ester group.[17,18] In this paper, we report polymers containing a ((4′-cyano-4-biphenyl)yl)oxy group attached to the backbone by an ester linkage or a ((4′-methoxy-4-biphenyl)yl)oxy group attached to the polymer main chain by an ether group. The former provides information concerning the influence of the mesogenic group on the thermal behavior of SCLCPs, while the latter reveals the consequences of altering the connecting group. The former polymers were prepared from n-[((4′-cyano-4-biphenyl)yl)oxy]alkyl bicyclo[2.2.1]hept-2-ene-5-carboxylates (**1-n**) with n = 3–12, while the latter polymers were derived from n-[((4′-methoxy-4-biphenyl)yl)oxy]alkyl (bicyclo[2.2.1]hept-2-en-5-yl)methyl ether (**2-n**) in which n = 4–6.

Results

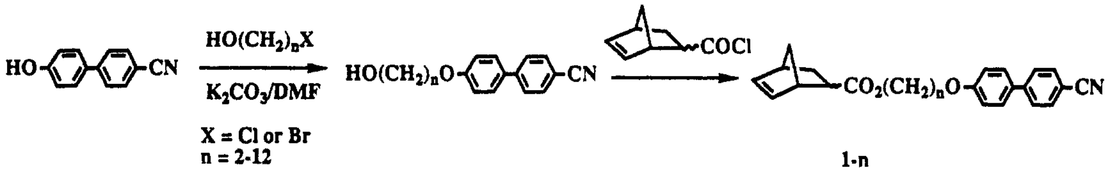
Synthesis of Monomers. The monomers **1-n** were synthesized as shown in Scheme I. The first nucleophilic displacement of halide of an n-haloalkan-1-ol with 4-cyano-4′-hydroxybiphenyl employed potassium carbonate in dimethylformamide. Use of sodium hydroxide resulted in hydration of the cyano group to yield 4-(4′-hydroxyphenyl)benzoic acid. In the case of 4-chlorobutanol, it was necessary to protect the hydroxy group because of facile intramolecular cyclization to give tetrahydrofuran (THF), as reported earlier.[17] The resulting mesogenic alcohols were then treated with an isomeric mixture of bicyclo[2.2.1]hept-2-ene-5-carbonyl chloride (exo:endo = 1:4). All attempts to crystallize **1-2** and **1-8** failed; only low-melting crystals (mp < 0 °C) were obtained. Consequently, **1-2** and **1-8** could not be obtained pure enough for polymerization. All other monomers could be obtained in crystalline form and were found to melt into the isotropic state with no evidence of any mesomorphic states.

---

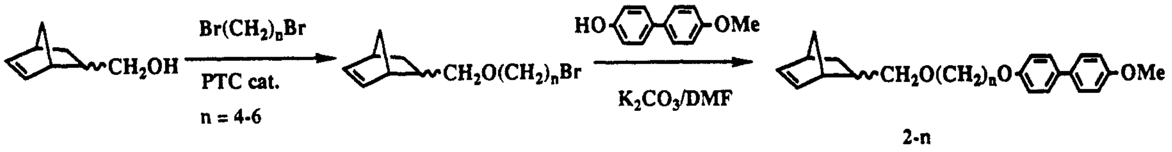
[*] To whom correspondence should be addressed.

[†] Present address: Japan Synthetic Rubber Co., Ltd., 100 Kawajiri-cho, Yokkaichi, 510 Japan.

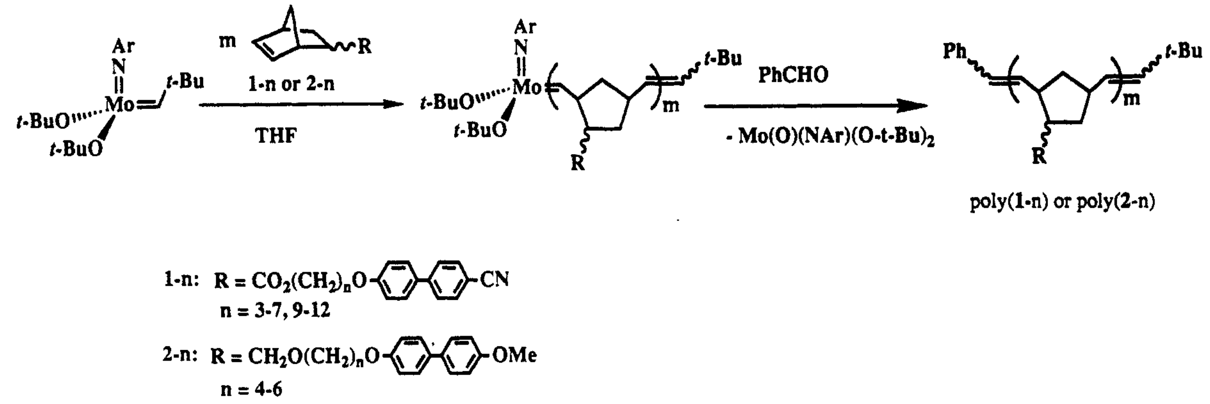
Scheme I



Scheme II



Scheme III



The synthesis of monomers 2-*n* is shown in Scheme II. The first step consists of the phase transfer catalyzed substitution of a 1,*n*-dibromoalkane by an exo:endo mixture (1:4) of 5-(hydroxymethyl)bicyclo[2.2.1]hept-2-ene,[26] followed by nucleophilic displacement of the resultant monobromide by 4-methoxy-4′-hydroxybiphenyl. Although monomers 2-*n* exhibit several crystalline modifications, none shows any mesogenic phases. The most stable crystalline modifications are obtained by recrystallization from solution.

Polymerization of 1-*n* and 2-*n*. Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ was the initiator employed to polymerize 1-*n* and 2-*n* (Scheme III) because it is more tolerant of functional groups than the analogous tungsten catalyst and because even endo-substituted norbornene derivatives are polymerized.[27,28] The Mo catalyst was added to *m* equiv of 1-*n* or 2-*n* in tetrahydrofuran (THF). After 1 h at room temperature, benzaldehyde was added to give a benzylidene-terminated polymer. The molecular weight of poly(1-*n*) and poly(2-*n*) was controlled by varying the molar ratio of the monomer to the catalyst ([M]/[I]). The polymer yields were quantitative in all cases. The polymers were purified by at least one precipitation and were free of unreacted monomer. The results of polymer characterizations are presented in Table I and Figure 1. A linear relationship for M_n (as determined by gel permeation chromatography (GPC) versus polystyrene standards) as a function of [M]/[I] for ratios up to 100 is observed for poly(1-5) and poly(2-4) (Figure 1). Similar plots were obtained for all other polymers. The living nature of the polymerizations is suggested by the linearity of these plots and the fact that the molecular weight distributions (PDI = M_w/M_n) are narrow and independent of molecular weight. The fact that the lines do not extrapolate to the origin suggests that the true molecular weights differ slightly from those determined by comparison with polystyrene standards. The molecular weight of the poly(2-6) made from 5 equiv of 2-6 was determined by vapor pressure osmometry (VPO); the molecular weight obtained by VPO was slightly lower than that of GPC (by VPO: M_n = 2825; by GPC: M_n = 3834).

The molecular weights of the polymers obtained when 100 equiv of monomer was used tend to deviate more from theory than molecular weights of shorter polymers, because of the sensitivity of the catalyst to both extraneous substances and experimental error in measuring small amounts of catalyst. The highest molecular weight polymers sometimes show a small amount of double molecular weight peak (see, for example, Figure 2). However, the PDIs of higher molecular weight polymers are still less than 1.27.

Proton NMR spectra of poly(1-*n*) and poly(2-*n*) showed broad resonances at 5.2–5.6 ppm for the olefinic protons and broad resonances at 1.6–2.0 and 2.2–3.0 ppm for protons of the five-membered ring, consistent with a ring-opened structure. The broad resonances show complex fine structure because the monomer is a mixture of exo and endo isomers and the polymer contains cis and trans double bonds and head-to-head, head-to-tail, and tail-to-tail arrangements of the repeat unit. The aromatic resonances of the mesogenic biphenyl group are relatively sharp.

Thermal Characterization of Poly(1-*n*). Poly(1-*n*) was characterized by a combination of differential scanning calorimetry (DSC) and thermal polarized optical microscopy. The first and subsequent DSC scans were essentially identical, and all heating and cooling scans were completely reproducible. Figure 3 shows the second heating and first cooling scans of poly(1-3) with a degree of polymerization (as determined by GPC) between 9 and 176. Poly(1-3) shows only a glass transition, no mesophases, consistent with the amorphous nature of the polymer. The DSC traces of poly(1-11) with degrees of polymerization 9–205 are typical of those obtained for the polymers with other spacer lengths (*n* = 4–7, 9–12). The DSC thermograms of poly(1-11) (Figure 4) show a glass transition and one first-order transition. The complete thermal transitions

Table I
Polymerization of 1-*n* and 2-*n* and Characterization of the Resulting Polymers

				GPC		phase transition (°C) and corresponding enthalpy change (kJ/mru)[a]	
monomer	[1 or 2]/[Mo] (mol/mol)	theor M_n (×10^{-3})	M_n (×10^{-3})	PDI	DP	heating	cooling
1-3	100	37.3	65.7	1.23	176	g78i	i72g
1-3	50	18.7	23.9	1.13	64	g76i	i70g
1-3	20	7.5	7.7	1.12	21	g75i	i70g
1-3	10	3.7	4.5	1.13	12	g67i	i53g
1-3	5	1.9	3.5	1.16	9	g63i	i56g
1-4	100	38.7	52.0	1.17	134	g66n103(1.58)i	i97(1.67)n60g
1-4	50	19.4	25.3	1.08	65	g63n99(1.53)i	i94(1.55)n59g
1-4	20	7.8	9.3	1.12	24	g62n94 (1.31)i	i88(1.47)n57g
1-4	10	3.9	4.8	1.12	12	g50n77(1.06)i	i70(1.09)n45g
1-4	5	1.9	3.4	1.11	9	g42n65(1.01)i	i59(0.66)n40g
1-5	100	40.2	42.8	1.18	107	g54n92(1.58)i	i86(1.29)n49g
1-5	50	20.1	23.9	1.13	60	g55n90(1.64)i	i84(1.39)n49g
1-5	20	8.0	7.9	1.16	20	g51n85(1.41)i	i78(1.23)n45g
1-5	10	4.0	4.5	1.14	11	g46n77(1.23)i	i71(1.12)n40g
1-5	5	2.0	3.2	1.13	8	g42n67(0.87)i	i60(0.75)n35g
1-6	100	41.6	64.6	1.27	155	g48n92(1.84)i	i86(1.77)n41g
1-6	50	20.8	24.9	1.12	60	g47n91(1.80)i	i86(1.87)n40g
1-g	20	8.3	9.0	1.12	22	g44n87(1.60)i	i81(1.53)n38g
1-6	10	4.2	5.1	1.15	12	g31n71(1.44)i	i66(1.31)n25g
1-6	5	2.1	3.4	1.13	8	g29n66(1.16)i	i60(0.99)n23g
1-7	100	43.0	124.8	1.27	290	g45n95(2.15)i	i87(2.20)n38g
1-7	80	34.4	49.2	1.15	114	g45n95(2.43)i	i88(2.37)n38g
1-7	50	21.5	30.4	1.14	71	g45n94(2.17)i	i87(2.34)n38g
1-7	20	8.6	10.1	1.23	24	g43n91(2.10)i	i82(2.18)n35g
1-7	10	4.3	5.6	1.15	13	g36n81(1.84)i	i75(1.72)n30g
1-7	5	2.1	3.9	1.15	9	g28n70(1.83)i	i64(1.58)n22g
1-9	100	45.8	91.5	1.20	200	g41n96(2.80)i	i91(2.70)n36g
1-9	50	22.9	38.2	1.19	83	g34n89(2.48)i	i83(2.54)n28g
1-9	20	9.2	11.3	1.11	25	g36n90(2.43)i	i86(2.46)n31g
1-9	10	4.6	5.9	1.15	13	g32n82(2.17)i	i74(2.16)n25g
1-9	5	2.3	4.1	1.19	9	g29n74(1.75)i	i68(1.86)n23g
1-10	100	47.2	44.8	1.27	95	g36n94(3.23)i	i90(3.10)n32g
1-10	50	23.6	20.7	1.15	44	g35n93(3.02)i	i88(2.91)n31g
1-10	20	9.4	10.7	1.14	25	g32n88(2.90)i	i82(2.94)n27g
1-10	10	4.7	5.5	1.13	12	g28n81(2.57)i	i75(2.50)n22g
1-10	5	2.4	3.8	1.13	8	g25n74(2.36)i	i67(2.34)n18g
1-11	100	48.6	99.5	1.20	205	g43n97(3.12)i	i90(3.21)n36g
1-11	50	24.3	35.9	1.16	74	g42n94(3.09)i	i89(3.00)n36g
1-11	20	9.7	11.4	1.08	24	g39n91(2.98)i	i85(2.77)n33g
1-11	10	4.9	6.1	1.12	13	g33n83(2.64)i	i77(2.81)n27g
1-11	5	2.4	4.5	1.13	9	g29n77(2.73)i	i71(2.78)n23g
1-12	100	45.0	52.9	1.24	106	g27n85(3.46)i	i80(3.05)n20g
1-12	50	25.0	21.4	1.20	43	g29n88(3.64)i	i80(3.39)n21g
1-12	20	10.0	7.6	1.26	15	g25n81(3.31)i	i76(2.99)n18g
1-12	10	4.5	5.3	1.15	11	g22n77(3.14)i	i71(2.83)n16g
1-12	5	2.5	3.6	1.14	7	g21n74(3.66)i	i67(3.39)n14g
2-4	100	37.8	44.7	1.15	118	g54[b]k108(8.45)i	i88(7.80)k – g
2-4	50	18.9	16.6	1.19	44	g53[b]k108(9.61)i	i86(7.68)k – g
2-4	20	7.6	7.4	1.25	19	g51[b]k101(10.10)i	i75(8.32)k – g
2-4	10	3.8	4.8	1.31	13	g48[b]k98(10.50)i	i73(8.87)k – g
2-4	5	1.9	3.3	1.27	9	g – k94(11.70)i	i71(9.44)k – g
2-5	100	39.2	79.5	1.14	202	g – k92(7.60)i	i73(7.20)k – g
2-5	50	19.6	20.2	1.19	51	g – k94(8.60)i	i72(7.70)k – g
2-5	20	7.8	8.5	1.16	22	g – k93(9.50)i	i71(8.20)k–g
2-5	10	3.9	5.3	1.15	13	g – k91(10.19)i	i72(8.70)k – g
2-5	5	2.0	3.7	1.19	9	g – k88(10.63)i	i68(9.20)k – g
2-6	200	81.2	139.1	1.13	342	g – k89(8.50)i	i76(7.80)k – g
2-6	100	40.6	49.4	1.12	122	g – k94(9.15)i	i78(8.42)k – g
2-6	50	20.3	22.9	1.11	56	g – k95(10.08)i	i78(9.11)k – g
2-6	20	8.1	8.4	1.11	21	g – k95(10.94)i	i76(9.84)k – g
2-6	10	4.1	5.4	1.12	13	g – k93(11.63)i	i74(10.49)k – g
2-6	5	2.0	3.8	1.15	9	g – k89(12.32)i	i72(11.02)k – g

[a] Data from second heating and first cooling scans. [b] Obtained by liquid nitrogen quenching experiment.

from the second heating and first cooling scans of all poly(1-*n*)s are summarized in Table I.

Poly(1-*n*) (*n* = 4–7, 9–12) polymers, which contain longer flexible spacers, display an enantiotropic nematic me-

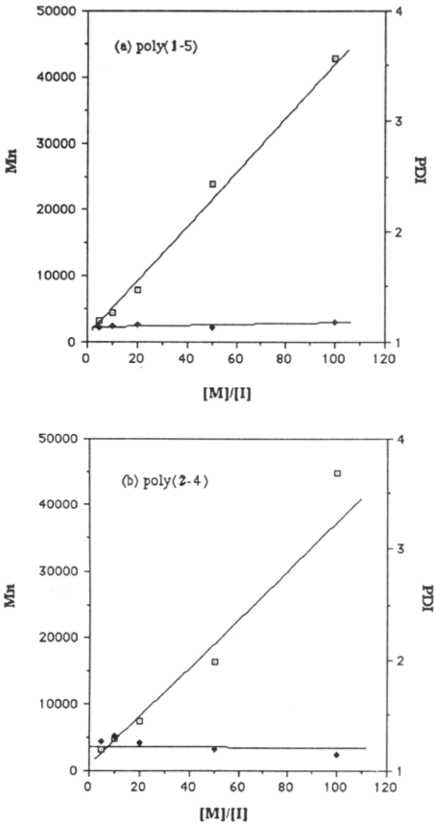


Figure 1. Plots of the number-average molecular weight (M_n) and the polydispersity (PDI = M_w/M_n) of (a) poly(1-5) and (b) poly(2-4) versus the molar ratio of monomer to initiator ([M]/[I]).

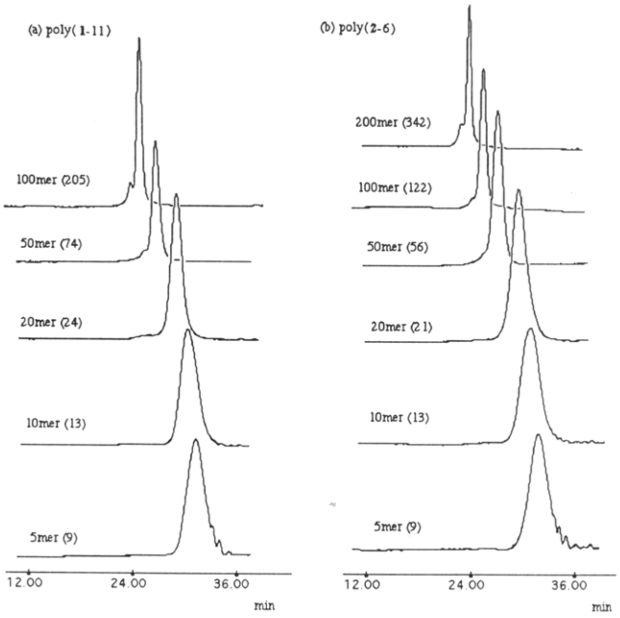


Figure 2. GPC traces of (a) poly(1-11) and (b) poly(2-6). The theoretical and observed (in parentheses) degrees of polymerization (DP) are shown on each trace.

sophase over the entire range of molecular weights and flexible spacer lengths. These polymers exhibit the small enthalpy changes characteristic of nematic mesophases. The schlieren textures observed by polarized optical microscopy are also typical of nematic mesophases. Figure 5 presents a typical schlieren texture of poly(1-7) obtained by thermal polarized optical microscopy. Although poly(1-*n*) (*n* = 9–12) has a long alkyl chain, polarized optical microscopy shows not only schlieren textures but droplets, which is another characteristic texture of a nematic phase, excluding the smectic C phase, which also shows a similar schlieren texture (Figure 6).

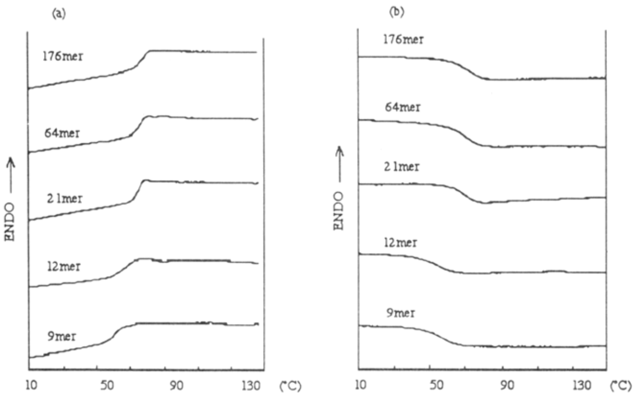


Figure 3. Normalized DSC thermograms of poly(1-3) (a) on the second heating and (b) first cooling scans.

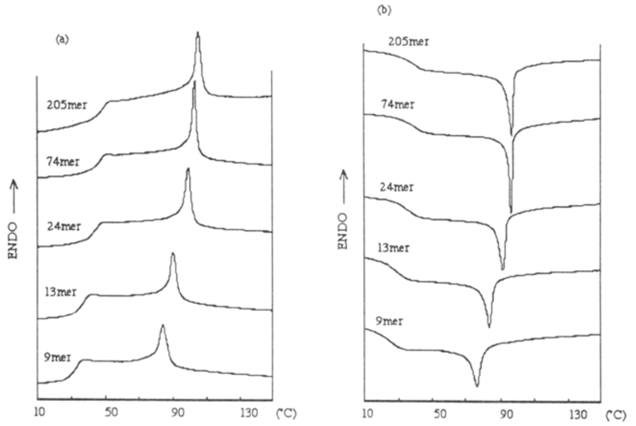


Figure 4. Normalized DSC thermograms of poly(1-11) (a) on the second heating and (b) first cooling scans.

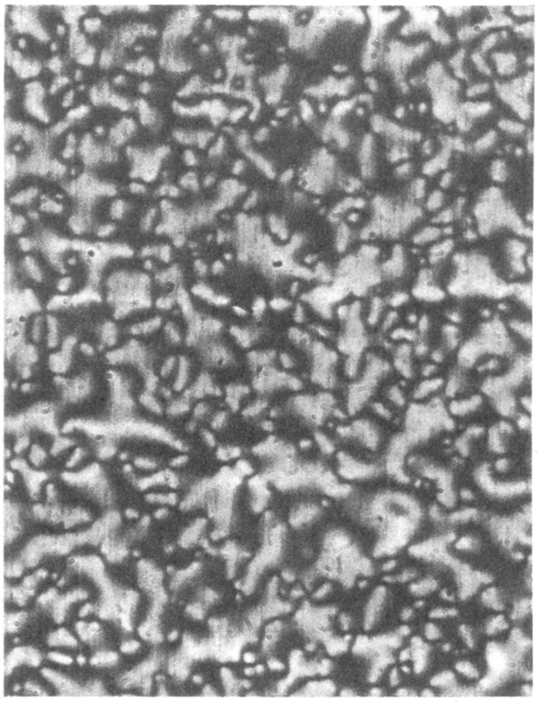


Figure 5. Polarized optical micrograph (magnification 160×) of the nematic schlieren texture observed on cooling poly(1-7) 13-mer from the isotropic state; 80 °C.

Figure 7 presents representative plots of transition temperatures obtained on heating scans versus degree of polymerizations of poly(1-*n*) (*n* = 3, 5, 7, 10–12). Poly(1-*n*) (*n* = 4, 6) samples give similar plots. The transition

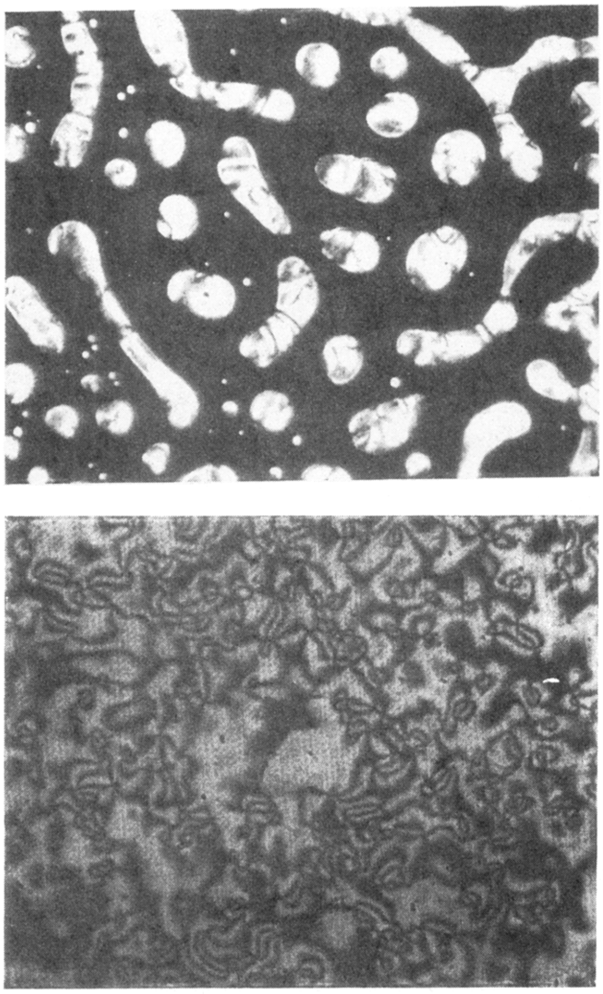


Figure 6. Polarized optical micrographs (magnification 80×) of the (a, top) nematic droplet texture observed on cooling poly(1-11) 9-mer from the isotropic state (73 °C) and (b, bottom) nematic schlieren texture observed on cooling poly(1-12) 106-mer from the isotropic state (83 °C).

temperature increases with increasing molecular weight and levels off at approximately 30–50 repeat units, regardless of the spacer length. It should also be noted that the length of the spacer does not affect the molecular weight at which the phase transitions become independent. These results are fully compatible with those reported for other systematically studied well-defined SCLCPs.[5,9–15,17,18,29–31]

The change in enthalpy is relatively independent of molecular weight, yet the values are scattered because of the small enthalpy changes involved. However, the lowest molecular weight oligomers appear to have smaller enthalpy changes, while polymers with longer spacers exhibit larger enthalpy changes.

Thermal Characterization of Poly(2-*n*). The thermal behavior of poly(2-*n*) was analyzed by DSC. The first and subsequent heating scans are identical, and all heating and cooling scans are reproducible. Unexpectedly, all poly(2-*n*) samples (*n* = 4–6) exhibit highly crystalline character (e.g., Figure 8). All samples of poly(2-*n*) show a single melting peak with a large enthalpy change and supercooling (~20 °C) on the cooling scan. The glass transition is barely observable. The isotropic melts of poly(2-*n*) were quenched in liquid nitrogen, and the quenched samples were analyzed by DSC. However, the crystallization rates of poly(2-6) and poly(2-5) are too fast to observe any distinct glass transition. Only poly(2-4) samples (except the lowest molecular weight oligomer) exhibit glass transitions in liquid nitrogen quenching experiments. All thermal data are presented in Table I.

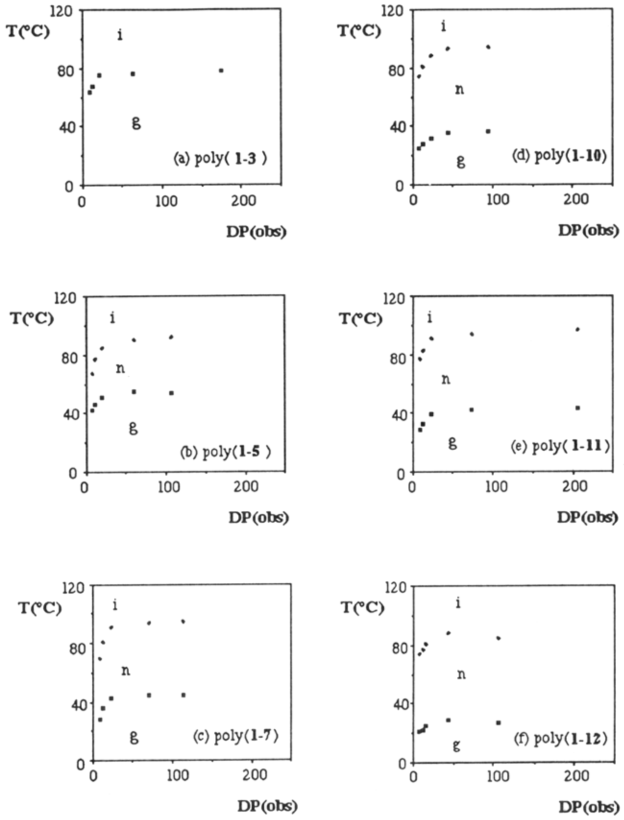


Figure 7. Dependence of the phase transition temperatures on the GPC-determined degree of polymerization of (a) poly(1-3), (b) poly(1-5), (c) poly(1-7), (d) poly(1-10), (e) poly(1-11), and (f) poly(1-12). All of the data are from the second heating scans.

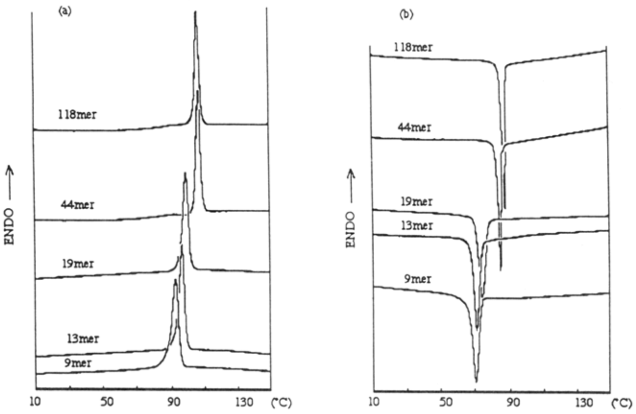


Figure 8. Normalized DSC thermograms of poly(2-4) (a) on the second heating and (b) first cooling scans.

Discussion

We have already investigated SCLCPs derived from *n*-[((4′-methoxy-4-biphenyl)yl)oxy]alkyl bicyclo[2.2.1]hept-2-ene-5-carboxylates by living ROMP.[17,18] The only difference between this polymer and poly(1-*n*) is the terminal substituent of mesogenic biphenyl. The SCLCP with a methoxy group exhibits only an enantiotropic nematic phase for spacers containing 2–8 methylenes.[17] It seems that poly(1-*n*) less readily forms a mesophase, despite the highly polarized nature of the ((4′-cyano-4-biphenyl)yl)oxy group. For example, poly(1-3) is an amorphous glass throughout the range of molecular weights, whereas the analogous polymer containing a methoxy group instead of a cyano group exhibits an enantiotropic nematic phase. The same methoxy-sub-

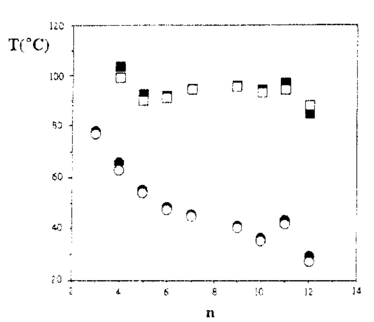


Figure 9. Dependence of the phase transition temperatures on the flexible spacer lengths (*n* methylene units) of the samples prepared by 100 equiv (T_i (■), T_g (●)) and 50 equiv (T_i (□), T_g (○)) of 1-*n*.

stituted polymer having only two methylene spacers also exhibits an enantiotropic nematic phase. Unfortunately, as we mentioned previously, 1-2 could not be purified enough for polymerization.

Poly(1-*n*) is also reluctant to form a more ordered phase when it has a longer, flexible spacer. Poly(1-12) exhibits only an enantiotropic nematic phase, even when it has only seven repeating units. In contrast, the side chains in ((4′-methoxy-4-biphenyl)yl)oxy analogs start to crystallize when as few as nine methylene spacers are present. As far as we know, this is the first example which shows an enantiotropic nematic phase (with a long flexible spacer) with no side chain crystallization.

It is known that the presence of a polarizable group such as a methoxy or cyano group guarantees good low molecular weight liquid crystalline compounds.[32] It is also known that cyano-substituted biphenyls pair in an antiparallel fashion to give stable mesophases.[33] However, when the ((4′-cyano-4-biphenyl)yl)oxy group is attached to a polymer backbone as a mesogenic side group, it cannot pair in an antiparallel fashion unless two polymer main chains aggregate. Our results indicate the antiparallel pairing between two polymer main chains is less likely. If this is the case, the mesophase would be more likely to form a smectic phase with a layered structure. It seems that the structure of poly(1-*n*) not only prevents the cyanobiphenyl side groups from pairing in an antiparallel fashion but also forces them to form a nematic phase, in spite of dipole–dipole repulsion when the spacer has more than three methylene units. Moreover, the ((4′-cyano-4-biphenyl)yl)oxy group cannot form favorable dipole pairs, and the side chains therefore cannot form a highly ordered crystalline state. This result is in complete accord with the observations of Sagane and Lenz,[6,8] who systematically investigated poly(vinyl ether)s containing a ((4′-methoxy-4-biphenyl)yl)oxy or ((4′-cyano-4-biphenyl)yl)oxy side group. Since their polymers have very short, flexible spacers (two methylene units, but the main chain is different from those prepared here[17]), cyano-substituted polymers with relatively high molecular weights were amorphous glasses, whereas the methoxy-substituted poly(vinyl ether)s showed nematic and smectic phases, depending on the molecular weight distribution.

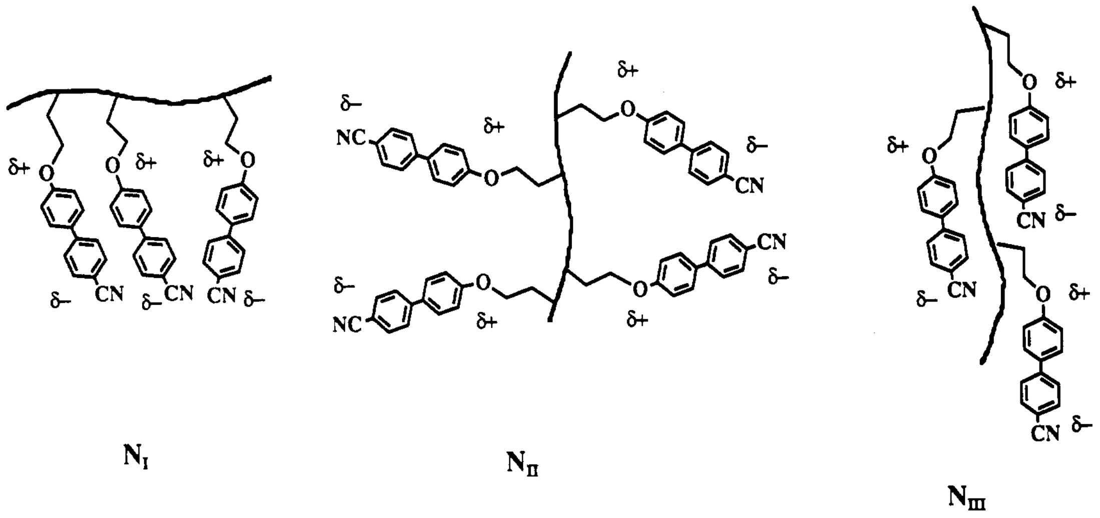
The spacer length also affects the phase transition temperatures. The transition temperatures determined on the second heating scans are plotted in Figure 9 as a function of the number of methylene units in the flexible spacer. The data used here are obtained from the polymers whose transition temperatures are independent of the molecular weight, thereby eliminating the effect of the polymer main chain length on the transition temperatures. The glass transition temperature decreases rapidly with increasing spacer length up to $n = 7$ as a consequence of decreased packing density of the chains. The isotropization temperature generally decreases slightly as the spacer length increases, *without* odd–even alternation, and levels off at a spacer length of 6. The rapidly decreasing glass transition temperature and relatively independent isotropization temperature produce a broader temperature window of the mesophase in poly(1-*n*) having a longer methylene chain. This tendency is well-documented by various series of SCLCPs, except that the increasing isotropization temperature of some SCLCPs that exhibit a smectic phase also accelerates the broadening of the mesophase temperature range.[13,23,24]

For SCLCPs showing a smectic phase, there are several studies on the effects of spacer length in polystyrenes,[21,22] polysiloxanes.[23,24] and polyacrylates.[25] All these polymers exhibit an odd–even effect. If one considers the total number of atoms between the backbone and the mesogen as part of the "spacer", including the interconnecting units, every SCLCP showing a smectic phase reported so far has higher smectic–isotropic transition temperatures with "even-spacer" lengths, regardless of the type of main chain and mesogen. This effect is explained in terms of the arrangement of mesogenic side chains.[21,34] When a spacer has an even number of atoms, the mesogenic unit is orthogonal with respect to the backbone. This arrangement makes it easier to form the layered structure required for smectic phases, assuming the backbone lies in a plane orthogonal to the mesogens. However, there are few studies on the effect of spacer length on the transition temperatures of nematic phases forming SCLCPs. The nematic–isotropic transition temperatures of poly(vinyl ether)s containing ((4′-cyano-4-biphenyl)yl)oxy mesogens with short spacers are higher for odd-numbered spacers then for even-numbered spacers.[13] We found that the SCLCP derived by living ROMP of norbornene monomers with ((4′-methoxy-4-biphenyl)yl)oxy mesogen exhibits an enantiotropic nematic phase with an odd–even effect when less than seven methylene spacers are present.[17] However, in this case, the substituted carbon atom of the five-membered ring in the polymer main chain can be considered as part of the spacer or part of the main chain.

The fact that poly(1-*n*) that exhibits a nematic phase does not show an odd–even effect further confuses this issue. However, the absence of the odd–even effect for poly(1-*n*) may be attributed to the different arrangement of side chains relative to the polymer main chain. It is predicted that there are three possible nematic phases in SCLCPs defined by the relative orientation of the mesogenic side chain and the polymer backbone, as shown in Scheme IV.[35] Considering the polarized nature of the ((4′-cyano-4-biphenyl)yl)oxy moiety, the nematic phase N_I seems least favorable because of the dipole–dipole repulsion between adjacent mesogens. On the other hand, the polymer with ((4′-methoxy-4-biphenyl)yl)oxy mesogenic side chains does not appear to be restricted from forming any of these three types of nematic phase. Therefore, we speculate that the nature of the nematic phase may depend on the mesogen, even when the polymer backbones have the same structure.

Highly crystalline poly(2-*n*) is an unexpected result. The crystalline phase is likely to be formed by side chains because ^{1}H NMR spectra of poly(2-*n*) indicates the stereorandom nature of the polymer main chain. It is also known that ring-opened norbornene-derived polymers can exhibit a crystalline state only when the polymer has a highly stereoregular structure.[28] It is interesting to compare poly(2-*n*) in which an ester connecting group is present instead of an ether connecting group.[17,18] The ester polymer exhibits side chain crystallization when the flexible spacer contains more than 8 methylene units. When the polymer contains 2–8 methylene spacers, the

Scheme IV



polymer shows only an enantiotropic nematic phase. This dramatic change of the mesomorphic character is attributable to the different flexibility of an ester group and an ether linkage. (The charge-separated resonance form of the ester makes it difficult to rotate around the carbon–oxygen single bond.) On the other hand, there is no such restriction of rotation around the carbon–oxygen bond of the ether linkage. The difference between ester and ether linkages was recently investigated when the linkages were part of the mesogenic group.[34] In this case, the mesogenic group preserves its mesogenic character because of the dynamic equilibrium between stable conformations. Obviously, this is not the case for the linkage between the polymer main chain and the side chain. As demonstrated for poly(2-n), replacing an ester group by a methylene ether group seems to allow more conformations and freedom of the side chain relative to the polymer main chain.

Conclusion

n-[((4′-Cyano-4-biphenyl)yl)oxy]alkyl bicyclo[2.2.1]-hept-2-ene-5-carboxylates with n = 3–7 and 9–12 were polymerized by ring-opening metathesis polymerization in a living manner to give a series of well-defined SCLCPs. All polymers (except n = 3) exhibit an enantiotropic nematic phase without side chain crystallization, even when they contain relatively long spacers (n = 9–12). The transition temperatures become independent of molecular weight when the main chains have 30–50 repeat units. The isotropization temperature decreases slightly with increasing spacer length, and there is no odd–even alternation.

n-[((4′-Methoxy-4-biphenyl)yl)oxy]alkyl (bicyclo[2.2.1]-hept-2-en-5-yl)methyl ethers with n = 4–6 were also polymerized successfully. These polymers are highly crystalline because of side chain crystallization, in contrast to the ester-linked polymers, which exhibit an enantiotropic nematic phase.

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. Diethyl ether and THF used for monomer synthesis were distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane 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-Cyano-4′-hydroxybiphenyl (95%) was used as received from TCI America Inc. 5-Norbornene-2-methanol (98%), 4,4′-dihydroxybiphenyl (97%), 3-chloro-1-propanol (98%), 6-chloro-1-hexanol (97%), 7-bromo-1-heptanol (95%), and 8-bromo-1-octanol (95%), 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. 4-Chloro-1-butanol (Aldrich, 85%) was washed with aqueous NaHCO$_3$, dried with MgSO$_4$, and distilled. 5-Bromo-1-pentanol,[15] 2-norbornene-5-carbonyl chloride (exo/endo = 1/4),[36] 4′-methoxy-4-hydroxybiphenyl,[37] and Mo(CHR)(NAr)(O-t-Bu)$_2$ (Ar = 2,6-C$_6$H$_3$-i-Pr$_2$)[16] were prepared as described in the literature. All other reagents and solvents were commercially available and used as received.

300-MHz ^{1}H NMR spectra were recorded on a Varian XL-300 spectrometer. All spectra were recorded in CDCl$_3$. All chemical shifts are given in ppm and are referenced to tetramethylsilane using the protons in the NMR solvent. Obvious multiplicites and routine coupling constants are usually not listed. GC analyses were carried out on a Shimadzu GC-9A gas chromatograph equipped with an fid detector and methyl phenyl 5 capillary column (Quadrex Corp. 1.5 m × 0.5 mm) using nitrogen as the carrier gas. 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 Å, 2 × 10^3 Å, 2 × 10^4 Å, 1 × 10^5 Å, and a precolumn, respectively), a Knauer differential refractometer, and a Spectroflow 757 absorbance detector set at 330 nm on 0.1–0.3% (w/v) 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 or exothermic peaks, respectively. All heating and cooling rates were 20 °C/min. Glass transition temperatures (T_g's) were read as the middle of the change in the heat capacity. All second and subsequent heating scans are identical. Both enthalpy changes and transition temperatures were determined using indium as a calibration standard. A Nikon optical polarized microscope (magnification 160× or 80×) equipped with a Mettler FP82 hot stage and a Mettler FP800 center processor was used to observe the thermal transitions and to analyze the anisotropic textures.[38,39]

Synthesis of n-[((4′-Cyano-4-biphenyl)yl)oxy]alkan-1-ol (n = 2–12). All compounds except that where n = 4 were synthesized by the following method. 8-Bromo-1-octanol (6.0 g, 0.029 mol) was added to a solution of 4′-cyano-4-hydroxybiphenyl (5 g, 0.026 mol) and K$_2$CO$_3$ (4.0 g, 0.029 mol) in DMF (ca. 50 mL). After stirring the reaction at 100 °C for 48 h, it was poured into dilute HCl solution, and the precipitated product was extracted with chloroform. The combined chloroform extracts were washed with water and dried over MgSO$_4$. MgSO$_4$ was removed by filtration and the resultant solution was concentrated in vacuo to give crude crystals, which were recrystallized from ethanol (4.3 g plus 1.9 g, 74%).

4-[((4′-Cyano-4-biphenyl)yl)oxy]butan-1-ol was prepared using the modified method described previously.[17] All compounds were identified by comparison of their ^{1}H NMR spectra with those reported.[9–15]

Synthesis of *n*-[((4′-Cyano-4-biphenyl)yl)oxy]alkyl Bicyclo[2.2.1]hept-2-ene-5-carboxylates (1-*n*, *n* = 3–7, 9–12). The monomers 1-*n* were prepared as in the following example. A solution of 2-norbornene-5-carbonyl chloride (1.95 g, 0.012 mol) in THF (5 mL) was added dropwise to a solution of 11-[((4′-cyano-4-biphenyl)yl)oxy]-1-undecanol (4.02 g, 0.011 mol) and triethylamine (1.26 g, 0.012 mol) in THF (40 mL) at room temperature. The solution was stirred at reflux for 24 h. 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 water and then dried over anhydrous $MgSO_4$. Concentration of the filtered chloroform solution yielded crude 1-11. The product was purified by column chromatography on alumina using toluene as the eluent followed by recrystallization from ether to give 3.7 g (69%) of colorless crystals.

Monomers that were pure enough for polymerization were obtained after at least two recrystallizations under dinitrogen from ether, ether–pentane, or ether–dichloromethane. All monomers were recrystallized until no improvement was seen in the polydispersity of polymers prepared using 100 equiv of monomer. ^{1}H NMR: resonances at 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) are due to the non-olefinic norbornene protons of both isomers; δ 5.95 (dd) and 6.21 (dd) are due to the endo olefinic protons, and δ 6.15 (m) is due to the 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), 6.95 (d, 2 H, aromatic ortho to OCH_2), 7.48 (d, 2 H, aromatic meta to OCH_2), 7.63 (dd, 4 H aromatic ortho and meta to OCN). All monomers gave satisfactory elemental analyses. The melting points were determined by DSC: 1–3, 74 °C; 1-4, 70 °C; 1–5, 89 °C; 1-6, 70 °C; 1-7, 78 °C; 1-9, 70 °C; 1-10, 62 °C; 1-11, 71 °C; 1-12, 78 °C.

Synthesis of (Bicyclo[2.2.1]hept-2-en-5-yl)methyl *n*-Bromoalkyl Ether. All of the compounds (*n* = 4–6) were synthesized in 54–70% yield as in the following example. 5-Norbornene-2-methanol (12.4 g, 0.10 mol), 1,4-dibromobutane (32.4 g, 0.15 mol), and tetrabutylammonium hydrogen sulfate (2 g) were dissolved in cyclohexane (74 mL). The organic solution was mixed with 48 g of 50% aqueous sodium hydroxide solution, and the resultant two-phase mixture was stirred vigorously at room temperature for 21 h. The reaction mixture was poured into 150 mL of water, and the organic layer was separated. The aqueous solution was extracted with ether (75 mL × 2), and the combined organic solution was dried over $MgSO_4$. Concentration of the filtered solution gave a crude oil, which was fractionally distilled under reduced pressure to yield (bicyclo[2.2.1]hept-2-en-5-yl)methyl 4-bromobutyl ether as a colorless liquid (18.6 g, 72% yield; 96% pure by GC). ^{1}H NMR resonances at δ 0.45 (m), 1.1 (b), 1.3 (m), 1.9 (m), 1.8 (m), 2.3 (m), 2.75 (br s), and 2.85 (br s) are due to the non-olefinic norbornene protons of both isomers: δ 5.88 (dd) and 6.10 (dd) are due to the olefinic protons of the endo isomer, and δ 6.05 (m) is due to the olefinic protons of the exo isomer; δ 2.95 (t) and 3.10 (t) are due to the endo diastereotopic methylene protons next to the ether oxygen; δ 1.6–1.9 (m, $2[n-2]$H, $[CH_2]_{n-2}$), 3.95 (t, CH_2O), 3.3–3.5 (m, 4 H, $OCH_2(CH_2)_n$ and CH_2Br).

Synthesis of *n*-[((4′-Methoxy-4-biphenyl)yl)oxy]alkyl (Bicyclo[2.2.1]hept-2-en-5-yl)methyl Ether (2-*n*). All the monomers **2-n** (*n* = 4–6) were synthesized in 50–66% yield as in the following example. (Bicyclo[2.2.1]hept-2-en-5-yl)methyl 5-bromopentyl ether (5.6 g, 0.019 mol) and 4′-methoxy-4-hydroxybiphenyl (4.0 g, 0.020 mol) were heated at 100 °C in 40 mL of dimethylformamide in the presence of potassium carbonate (2.76 g, 0.020 mol) for 29 h. The mixture was poured into 200 mL of a 10% sodium hydroxide aqueous solution and the solution was stirred for 10 min. The separated crystals were filtered off and dried in air. The crude crystals were recrystallized from ethanol and then from a mixture of ether and methylene chloride (5:1) to give pure 2-5 (4.96 g, 66%). ^{1}H NMR resonances at δ 0.45 (m), 1.1–1.4 (m), 2.3 (m), 2.75 (br s), and 2.85 (br s) are due to the non-olefinic norbornene protons of both isomers; δ 5.90 (dd) and 6.10 (dd) are due to the olefinic protons of the endo isomer, and δ 6.05 (m) is due to the olefinic protons of the exo isomer; δ 3.0 (t) and 3.1 (t) are due to the endo diastereotopic methylene protons next to the ether oxygen; δ 3.3–3.5 (m) are due to the protons α to the ether linkage, including the exo diastereotopic protons next to the oxygen; δ 1.5–1.91 (m, $2[2-n]$H, $[CH_2]_{n-2}$), 3.8 (s, 3 H, OCH_3), 3.95 (t, 2 H, CH_2OAr). All monomers gave satisfactory elemental analyses. Melting points (by DSC) are as follows: 2-4, 86 °C; 2-5, 86 °C, 2-6, 79 °C.

Polymerization Procedure. A solution of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (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 solution was stirred for 1 h. The polymerization was quenched by adding 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 and 40 μL of benzaldehyde was used for quenching. ^{1}H NMR of poly(1-*n*): 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, arom H), 7.51 (br d, arom H). ^{1}H NMR of poly(**2**-*n*): 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), 6.95 (br d, arom H), 7.5 (br d, arom H), 7.6 (br, arom H.

Acknowledgment. R.R.S. thanks the Office of Naval Research and Z.K. thanks the Japan Synthetic Rubber Co. for support.

References and Notes

(1) Rempp, P.; Merrill, E. W. *Polymer Synthesis*; Huethig and Wepf: New York, 1986.
(2) Rempp, P.; Fanta, E.; Herz, J. *ACS Symp. Ser.* **1981**, *No. 166*, 59.
(3) Sogah, D. Y. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, *29* (2), 3.
(4) Odian, G. *Principles of Polymerization*; Wiley: New York, 1981.
(5) Percec, V.; Tomazos, D.; Pugh, C. *Macromolecules* **1989**, *22*, 3259.
(6) Sagane, T.; Lenz, R. W. *Polym. J.* **1988**, *20*, 923.
(7) Sagane, T.; Lenz, R. W. *Polymer* **1989**, *30*, 2269.
(8) Sagane, T.; Lenz, R. W. Macromolecules **1989**, *22*, 3763.
(9) Percec, V.; Lee, M.; Jonsson, H. *J. Polym. Sci., Polym. Chem. Ed.* **1991**, *29*, 327.
(10) Percec, V.; Lee, M. *Macromolecules* **1991**, *24*, 1017.
(11) Percec, V.; Lee, M. *Polym. Bull.* **1991**, *25*, 123.
(12) Percec, V.; Lee, M. *J. Macromol. Sci., Chem.* **1991**, *A28*, 651.
(13) Percec, V.; Lee, M. *Macromolecules* **1991**, *24*, 2780.
(14) Percec, V.; Lee, M. *Polymer* **1991**, *32*, 2862.
(15) Percec, V.; Lee, M.; Ackerman, C. *Polymer* **1992**, *33*, 703.
(16) Schrock, R. R.; Murdzek, J. S., Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.
(17) Komiya, Z.; Pugh, C.; Schrock, R. R. *Macromolecules* **1992**, *25*, 3609.
(18) Komiya, Z.; Pugh, C.; Schrock, R. R. *Macromolecules* **1992**, *25*, 6586.
(19) Pugh, C.; Schrock, R. R. *Macromolecules* **1992**, *25*, 6593.
(20) Komiya, Z.; Schrock, R. R., see preceding paper in this issue.
(21) Imrie, C. T.; Karasz, F. E.; Attard, G. S. *Macromolecules* **1992**, *25*, 1278.
(22) Attard, G. S.; Dave, J. S.; Wallington, A.; Imrie, C. T.; Karasz, F. E. *Makromol. Chem.* **1991**, *192*, 1495.
(23) Mauzac, M.; Hardouin, F.; Richard, H.; Achard, M. F.; Sigaud, G.; Gasparoux, H. *Eur. Polym. J.* **1986**, *22*, 137.
(24) Gemmel, P. A.; Gray, G. W.; Lacey, D. *Mol. Cryst. Liq. Cryst.* **1985**, *122*, 205.
(25) Gemmel, P. A.; Gray, G. W.; Lacey, D.; Alimoglu, A. K.; Ledwith, A. *Polymer* **1985**, *26*, 615.
(26) Cho, H., private communication.
(27) Bazan, G. C.; Schrock, R. R.; Cho, H.; Gibson, V. C. *Macromolecules* **1991**, *24*, 4495.
(28) Bazan, G.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Regan, M. B.; Thomas, J. K.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 8378.
(29) Portugall, M.; Ringsdorf, H.; Zental, R. *Makromol. Chem.* **1982**, *183*, 2311.
(30) Uchida, S.; Morita, K.; Miyoshi, K.; Hashimoto, K.; Kawasaki, K. *Mol. Cryst. Liq. Cryst.* **1988**, *155*, 93.

(31) Stevens, H.; Rehage, G.; Finkelmann, H. *Macromolecules* **1984**, *17*, 851.

(32) Gray, G. W. *Molecular Structure and the Properties of Liquid Crystals*; Academic Press: London, 1962.

(33) Gray, G. W. In *Polymer Liquid Crystals*; Ciferri, A., Krigbaum, W., Meyer, R. B., Eds.; Academic Press: New York, 1982; Vol., Chapter 1.

(34) Percec, V.; Pugh, C. In *Side Chain Liquid Crystal Polymers*; McArdle, C. B., Ed.; Chapman and Hall: New York, 1989; p 30.

(35) Warner, M. In *Side Chain Liquid Crystal Polymers*; McArdle, C. B., Ed.; Chapman and Hall: New York, 1989; p 7.

(36) Jacobine, A. F.; Glaser, D. M.; Nakos, S. T. *Polym. Mater. Sci. Eng.* **1989**, *60*, 211.

(37) Rodriguez-Parada, J. M.; Percec, V. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *24*, 1363.

(38) Dennis, D.; Richter, L. *Textures of Liquid Crystals*; Verlag Chemie: Weinheim, 1978.

(39) Gray, G. W.; Goodby, J. W. *Smectic Liquid Crystals Textures and Structures*; Leonard Hill: Glasgow, 1984.