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## Synthesis of Side Chain Liquid Crystal Polymers by Living Ring-Opening Metathesis Polymerization. 1. Influence of Molecular Weight, Polydispersity, and Flexible Spacer Length ( $n = 2-8$ ) 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-biphenyl)oxy]alkyl]carbonyl]bicyclo[2.2.1]hept-2-ene (1- $n$ ,  $n = 2-8$ ) by  $\text{Mo}(\text{CH-}t\text{-Bu})(\text{NAr})(\text{O-}t\text{-Bu})_2$  ( $\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{-}i\text{-Pr}_2$ ) is described. Polymers with degrees of polymerization from 5 to 100 and narrow molecular weight distributions ( $M_w/M_n = 1.05-1.24$ ) were obtained in high yield. All polymers exhibit an enantiotropic nematic mesophase. Glass transition and isotropization temperatures increase with increasing molecular weight and become independent at approximately 30–50 repeat units. The change in enthalpy of isotropization is relatively independent of molecular weight. Using polymer blends, it was shown that polydispersity has no effect on either the transition temperatures or the temperature range of isotropization. Isotropization alternates in an odd–even manner up to spacer lengths of  $n = 6$  and then levels off.

### Introduction

Living polymerization methods allow one to synthesize polymers with well-defined structures.<sup>1–5</sup> Although anionic polymerization has been exploited the most, the living nature of the system is often impeded by the presence of polar substituents on the monomer.<sup>6</sup> Recently, well-characterized molybdenum alkylidene complexes of the type  $\text{Mo}(\text{CHR})(\text{NAr})(\text{O-}t\text{-Bu})_2$  ( $\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{-}i\text{-Pr}_2$ ,  $\text{R} = t\text{-Bu}$  or  $\text{CMe}_2\text{Ph}$ )<sup>7</sup> have been shown to initiate the living ring-opening metathesis polymerization (ROMP) of functionalized norbornenes and norbornadienes.<sup>5,8–14</sup> Because this initiator tolerates a variety of functional groups, the molecular engineering of polymers with novel structures and functionalities, including side chain liquid crystalline polymers (SCLCPs), should be possible. Related tungsten complexes<sup>15</sup> have also been shown to behave as initiators for certain living polymerization reactions,<sup>16,17</sup> although tungsten complexes do not appear to tolerate functionalities as well as molybdenum complexes.<sup>5</sup>

SCLCPs have been prepared mainly by radical polymerization of mesogenic acrylates and methacrylates and by hydrosilating mesogenic olefins with Si–H groups in polysiloxane backbones. Because it is difficult to control both the molecular weight and the polydispersity of the

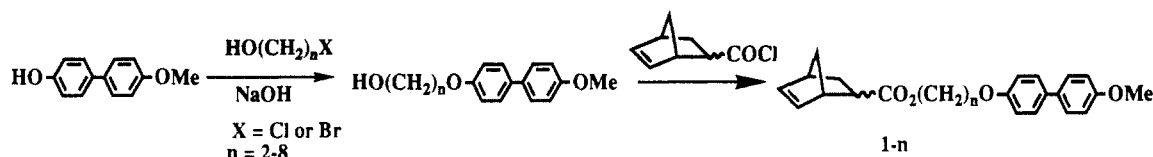
resulting polymers by either of these methods, they are of limited use for determining the influence of molecular weight and molecular weight distribution on the phase behavior of SCLCPs.<sup>18</sup> However, recently both group transfer polymerization and living cationic polymerization of vinyl ethers<sup>19</sup> have been applied successfully to the synthesis of SCLCPs with narrow molecular weight distributions.<sup>20–28</sup> These reports established the precise relationship between molecular weight and phase behavior and elucidated the chain length at which the phase transitions no longer vary as additional monomer units are added. Some of these studies also revealed the effect of spacer length on the thermotropic behavior of the SCLCPs.<sup>21–25</sup>

Similar data for other types of polymers should help establish trends in structure/property relationships of SCLCPs and build up knowledge concerning how to prepare novel macromolecules with specific phases and transition temperatures. The polynorbornene backbone should provide some interesting new information. Since polynorbornene has a glass transition temperature of approximately 40 °C, the new SCLCPs should have a flexibility between that of poly(vinyl ethers) (poly(methyl vinyl ether),  $T_g = -31$  °C) and polyacrylates (poly(methyl acrylate),  $T_g = 5$  °C) or polymethacrylates (poly(methyl methacrylate),  $T_g = 100$  °C).<sup>29</sup> In this paper we report the living ring-opening metathesis polymerization of mesogenic norbornene derivatives using  $\text{Mo}(\text{CH-}t\text{-Bu})$ -

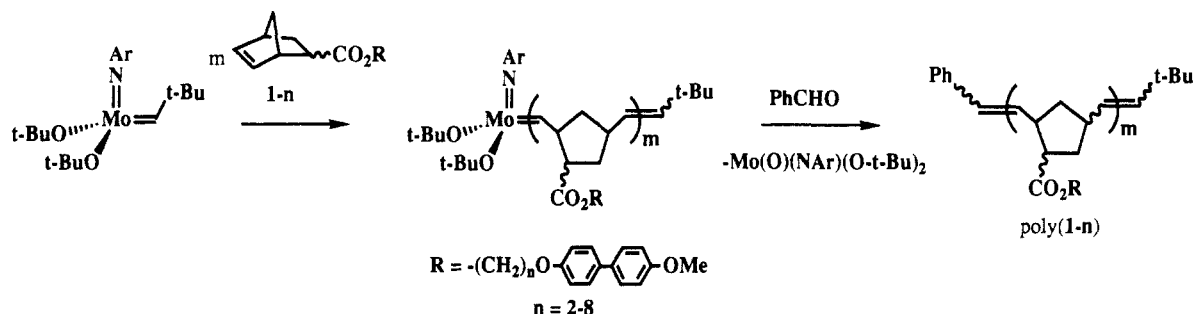
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Scheme I



Scheme II



(NAr)(O-*t*-Bu)<sub>2</sub> as the initiator and describe the influence of spacer length, of molecular weight, and of molecular weight distribution on the phase behavior of the resulting polymers. The norbornene monomer series 5-[[*n*-[(4'-methoxy-4-biphenyl)oxy]alkyl]carbonyl]bicyclo[2.2.1]hept-2-ene (1-*n*) with spacer lengths *n* of 2–8 methylene units will be discussed. The synthesis and thermotropic behavior of compounds with *n* = 9–12 will be presented in a subsequent paper.

## Results and Discussion

**Synthesis of Monomers.** The monomers were synthesized as shown in Scheme I. The first step consisted of nucleophilic displacement of the halide of an *n*-haloalkanol with 4-methoxy-4'-hydroxybiphenyl under basic conditions.<sup>30</sup> However, in the case of 4-chlorobutanol, even under very mild conditions the tetrahydrofuran was formed exclusively via intramolecular cyclization. Therefore it was necessary to protect the hydroxy group of 4-chlorobutanol with tetrahydropyran before reaction with 4-methoxy-4'-hydroxybiphenyl. The resulting mesogenic alcohols were then treated with an isomeric mixture of bicyclo[2.2.1]hept-2-ene-5-carboxyl chloride (exo:endo = 1:3). Monomer 1-6 was also synthesized using a higher concentration of the endo isomer (exo:endo = 1:9).

All monomers are crystalline and melt into the isotropic state. However, less stable crystalline modifications are obtained from the melt than from solution, but the most thermodynamically stable crystalline form also can be obtained from the melt by annealing at the appropriate temperature.

**Polymerization of 1-*n*.** As outlined in Scheme II, *n* equivalents of 1-*n* were added to Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)<sub>2</sub><sup>7,31</sup> in THF. After 1 h at room temperature, benzaldehyde was added to give a benzylidene-terminated polymer. The molecular weight of poly(1-*n*) was controlled by varying the molar ratio of the monomer to the initiator ([M]/[I]). The polymer yields were quantitative in all cases, and the polymers were purified by at least one precipitation. The results of polymer characterizations are presented in Table I and Figure 1. A linear relationship is obtained by plotting the number-average molecular weight (*M<sub>n</sub>*) of poly(1-4) and poly(1-6) as a function of [M]/[I] for ratios up to 100 (Figure 1). Molecular weights were determined by gel permeation chromatography (GPC) versus polystyrene standards. Figure 1b includes the results of polymerization of monomer 1-6 (both ratios of exo:endo isomers). Similar plots were obtained for all

other monomers. The fact that these plots are linear and that the molecular weight distributions (PDI = *M<sub>w</sub>*/*M<sub>n</sub>*) are narrow and independent of molecular weight demonstrates that the polymerizations are living. However, the lines do not extrapolate to the origin, indicating that the true molecular weights differ slightly from those determined by comparison with polystyrene standards. The molecular weights of the 100-mers tend to deviate more from theory than shorter polymers because of increased sensitivity of the catalytic intermediates to trace impurities, to experimental error in measuring small amounts of catalyst, and perhaps also to slow reaction of catalytic intermediates with the ester functionality. Although 100-mers of 1-*n* (*n* = 6, 8) sometimes showed a small double molecular weight peak by GPC analysis, the PDIs are still lower than 1.24. The GPC traces of poly(1-6) and poly(1-7) are presented in Figure 2, along with GPC traces of some polymer blends (vide infra).

Proton NMR spectra of poly(1-*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 the ring-opened structure. We presume the detailed polymer structure is complex, consisting of cis and trans double bonds and head-to-head, head-to-tail, and tail-to-tail arrangements of the repeat units.<sup>32,33</sup> In contrast, the resonances due to the aromatic protons of the mesogenic biphenyl group are relatively sharp.

**Thermal Characterization of Polymers.** Poly(1-*n*) was characterized by a combination of differential scanning calorimetry (DSC) and thermal polarized optical microscopy. The first and subsequent DSC heating scans were essentially identical, and all heating and cooling scans were completely reproducible. Figures 3 and 4 show the second heating and first cooling scans of poly(1-6) and poly(1-7) with theoretical degrees of polymerization of approximately 5 to 100; they are typical of the scans obtained for polymers with other spacer lengths. The complete thermal transitions from the second heating and first cooling scans of all polymers are summarized in Table I.

With the exception of oligomers of 1-5, poly(1-*n*) (*n* = 2–8) displays only an enantiotropic nematic mesophase over the entire range of molecular weights and flexible spacer lengths. The textures observed by polarized optical microscopy and the small enthalpy changes are characteristic of nematic mesophases. Figure 5 is a representative polarized optical micrograph showing the schlieren texture of poly(1-4). The presence of a nematic mesophase

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

monomer	[1- <i>n</i> ]/[Mo] (mol/mol)	theor <i>M<sub>n</sub></i>	<i>M<sub>n</sub></i>	GPC PDI	DP	phase transition (°C) and corresponding enthalpy changes (kJ/mru) <sup>a</sup>	
						heating	cooling
1-2	100	36444	37306	1.05	102	g 74 n 93 (0.65) i	i 80 (0.59) n 66 g
1-2	50	18222	15225	1.07	42	g 71 n 91 (0.62) i	i 77 (0.63) n 64 g
1-2	20	7289	6799	1.09	19	g 69 n 87 (0.76) i	i 76 (0.73) n 62 g
1-2	10	3644	4310	1.14	12	g 63 n 78 (0.29) i	i 66 (0.29) n 55 g
1-2	5	1822	2782	1.14	8	g 57 n 69 (0.08) i	i 57 (0.07) n 50 g
1-3	100	37847	43993	1.20	116	g 61 n 88 (0.64) i	i 80 (0.56) n 55 g
1-3	50	18924	20172	1.08	53	g 61 n 86 (0.56) i	i 78 (0.62) n 54 g
1-3	20	7569	7633	1.12	20	g 57 n 79 (0.61) i	i 72 (0.53) n 52 g
1-3	10	3784	4224	1.13	11	g 53 n 71 (0.48) i	i 63 (0.58) n 46 g
1-3	5	1892	2663	1.16	7	g 48 n 62 (0.22) i	i 51 (0.25) n 41 g
1-4	100	39249	52857	1.05	135	g 51 n 96 (1.13) i	i 91 (1.24) n 45 g
1-4	50	19625	21800	1.05	56	g 50 n 93 (1.10) i	i 88 (1.13) n 43 g
1-4	20	7850	9376	1.09	24	g 43 n 85 (0.95) i	i 80 (0.98) n 37 g
1-4	10	3925	5804	1.11	15	g 42 n 78 (0.90) i	i 73 (0.94) n 34 g
1-4	5	1963	3755	1.14	10	g 34 n 67 (0.75) i	i 61 (0.75) n 27 g
1-5	100	40652	61247	1.12	151	g 44 n 88 (1.34) i	i 82 (1.27) n 37 g
1-5	50	20326	26386	1.06	65	g 43 n 87 (1.39) i	i 81 (1.27) n 37 g
1-5	20	8130	8185	1.11	20	g 40 n 80 (1.16) i	i 74 (1.07) n 34 g
1-5	10	4065	4963	1.12	12	g 51 k 74 (-3.64) k 90 (5.93) i	i 78 (1.09) n <sup>b</sup> 43 g
1-5	5	2033	3490	1.12	9	g 46 k 66 (-1.92) k 87 (6.85) i	i 65 n <sup>b</sup> 59 k (3.08) <sup>c</sup> g
1-6	100	42055	61022	1.17 <sup>d</sup>	145	g 43 n 95 (1.43) i	i 88 (1.47) n 37 g
1-6	50	21028	24067	1.15	57	g 42 n 93 (1.42) i	i 88 (1.47) n 35 g
1-6 <sup>e</sup>	50	21028	23383	1.13	56	g 38 n 92 (1.39) i	i 86 (1.48) n 29 g
1-6	20	8411	6739	1.16	16	g 35 n 87 (1.43) i	i 81 (1.48) n 28 g
1-6 <sup>e</sup>	20	8411	9690	1.20	23	g 34 n 86 (1.23) i	i 79 (1.21) n 26 g
1-6	15	6308	5165	1.17	12	g 33 n 84 (1.17) i	i 77 (1.31) n 26 g
1-6	10	4206	3962	1.16	9	g 31 n 80 (1.31) i	i 74 (1.15) n 25 g
1-6	5	2103	2663	1.20	6	g 28 n 72 (1.19) i	i 66 (0.92) n 22 g
1-6	blend <sup>f</sup>		9741	2.50	23	g 37 n 89 (1.41) i	i 83 (1.55) n 30 g
1-7	100	43457	34089	1.17	78	g 38 n 95 (2.12) i	i 89 (1.90) n 30 g
1-7	50	21729	15326	1.05	35	g 36 n 93 (1.94) i	i 86 (1.88) n 28 g
1-7	20	8961	7257	1.09	17	g 31 n 85 (1.60) i	i 79 (1.73) n 23 g
1-7	10	4346	4254	1.11	10	g 28 n 79 (1.28) i	i 73 (1.63) n 20 g
1-7	5	2173	2817	1.16	6	g 24 n 71 (1.18) i	i 64 (1.30) n 17 g
1-7	blend <sup>f</sup>		7546	4.78	17	g 28 n 83 (1.63) i	i 76 (1.81) n 21 g
1-8	100	44861	46386	1.23 <sup>d</sup>	103	g 30 n 91 (1.86) i	i 83 (1.76) n 21 g
1-8	50	22430	17498	1.11	39	g 27 n 87 (1.83) i	i 82 (1.75) n 21 g
1-8	20	8972	6846	1.12	15	g 26 n 84 (1.60) i	i 78 (1.67) n 19 g
1-8	10	4486	4082	1.14	9	g 23 n 79 (1.48) i	i 73 (1.75) n 17 g
1-8	5	2243	2791	1.17	6	g 20 n 73 (1.41) i	i 67 (1.53) n 13 g

<sup>a</sup> Data from second heating and first cooling scans. <sup>b</sup> Monotropic. <sup>c</sup> Overlapped with previous transition. <sup>d</sup> A small double molecular weight peak was present. <sup>e</sup> Exo/endo = 10:90. <sup>f</sup> See text.

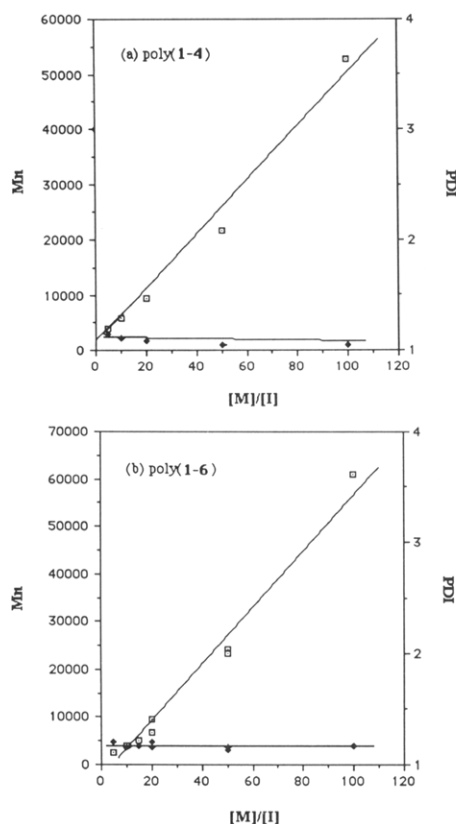
contrasts with the crystalline nature of the corresponding monomers. Although stabilization of a liquid crystalline mesophase by polymerization is traditionally explained as a "polymer effect", the structures of the norbornene monomer and the resulting polymer repeat unit are substantially different and therefore are not directly comparable.

Poly(1-5), containing at least 20 repeat units, also displays an enantiotropic nematic mesophase. However, the nematic mesophase of the two lower molecular weight oligomers is monotropic and observable only on cooling, while a melting point is observed on heating, in addition to the glass transition. As shown in Figure 6, a transition ascribable to recrystallization overlaps with one ascribable to vitrification of the 9-mer on cooling. Therefore, the sample undergoes continued recrystallization upon heating through the glass transition, followed by melting. The same is true of the 12-mer except that recrystallization is not detected on cooling. However, the fact that the enthalpy of the recrystallization endotherm is only 60% of that of melting demonstrates that some recrystallization did take place on cooling. Crystallization evidently is suppressed below the glass transition temperature at higher

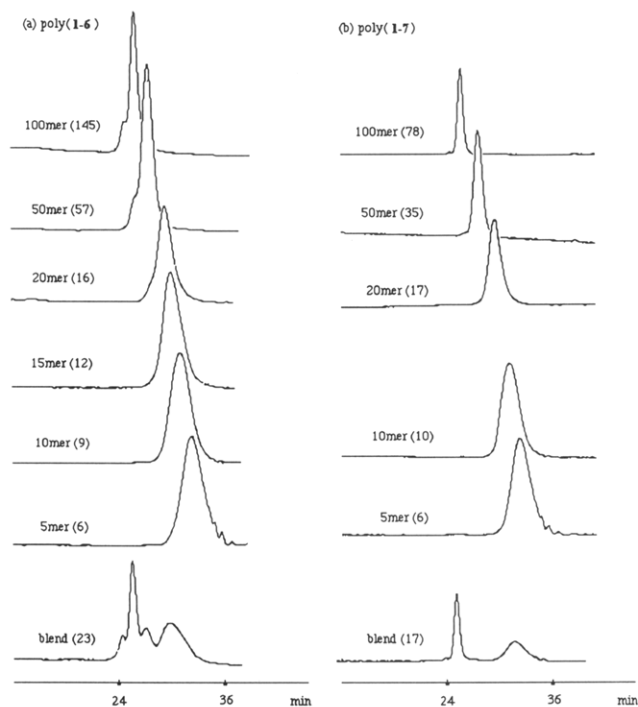
molecular weights. We cannot explain why only the oligomers of the 5-spacer are crystalline.

The phase transition temperatures of each polymer obtained on heating are plotted in Figure 7 as a function of the degree of polymerization obtained by GPC analysis. Regardless of the length of the spacer, the glass transition and isotropization temperatures of all polymers become independent of molecular weight at approximately 30–50 repeat units. These results are analogous to those reported for mesogenic polysiloxanes (DP ~ 12),<sup>34</sup> poly(vinyl ethers) (DP ~ 10–20),<sup>20–25</sup> polyacrylates (DP ~ 12–40),<sup>35,36</sup> and polymethacrylates (DP ~ 12).<sup>19</sup> There are a few examples using less well-defined systems which report unexpectedly high values of a few hundred repeat units.<sup>37–39</sup>

Table I also lists the change in enthalpy of isotropization for all polymers at each molecular weight and all spacer lengths. Because the enthalpy change of the nematic-isotropic transition is so small and therefore subject to experimental error, the data are scattered as a function of molecular weight. In general, however, the enthalpy change is relatively independent of molecular weight, except for the lowest degree of polymerization.

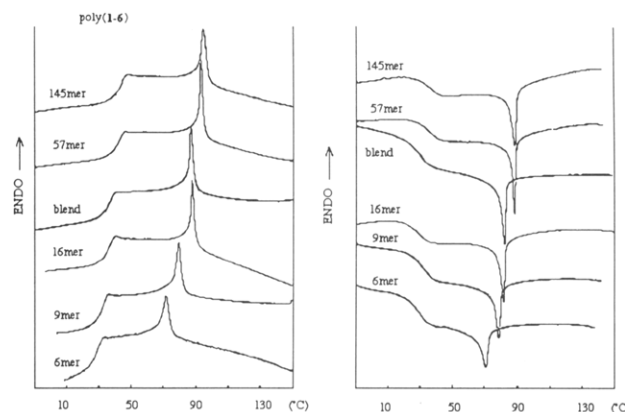


**Figure 1.** Plots of the number-average molecular weight ( $M_n$ ) and the polydispersity ( $PDI = M_w/M_n$ ) of (a) poly(1-4) and (b) poly(1-6) versus the molar ratio of monomer to initiator ( $[M]/[I]$ ).

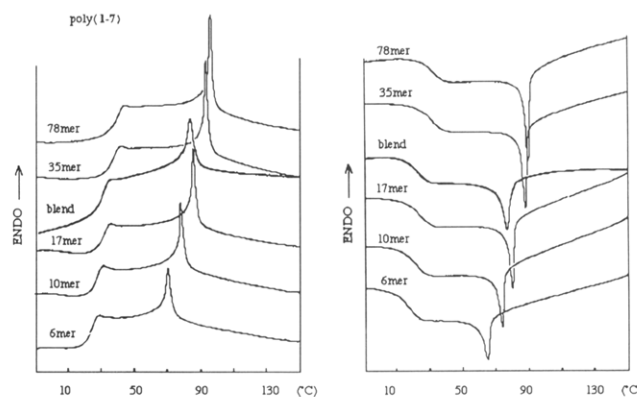


**Figure 2.** GPC traces of (a) poly(1-6) and (b) poly(1-7), including blends. The theoretical and observed (in parentheses) degrees of polymerization (DP) are shown on each trace.

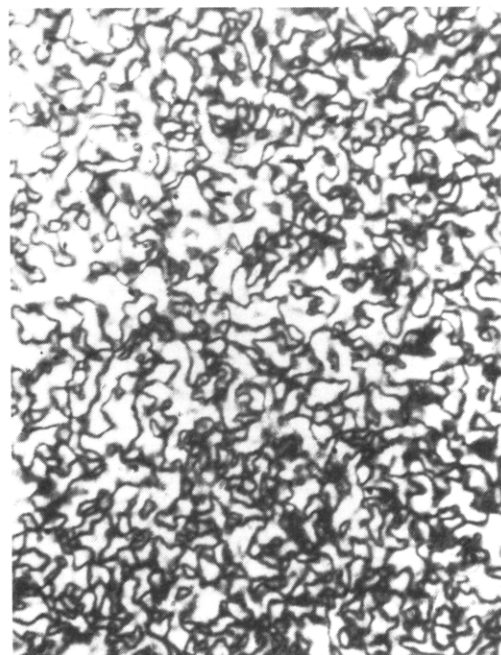
The peak width of transitions involving liquid crystalline mesophases as a function of molecular weight is also of interest. Because the transition temperatures of oligomers depend on the chain length, we might expect that the widths of oligomerics should be broader than those of high molecular weight polymers with the same polydis-



**Figure 3.** Normalized DSC thermograms of poly(1-6): (a, left) second heating scan; (b, right) first cooling scan.

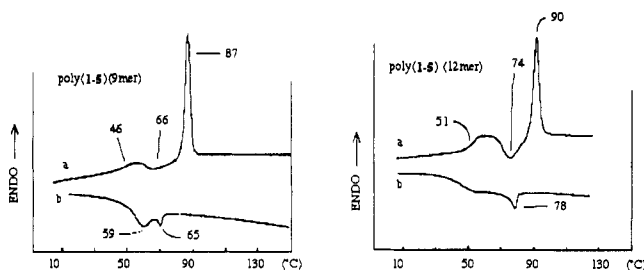


**Figure 4.** Normalized DSC thermograms of poly(1-7): (a, left) second heating scan; (b, right) first cooling scan.

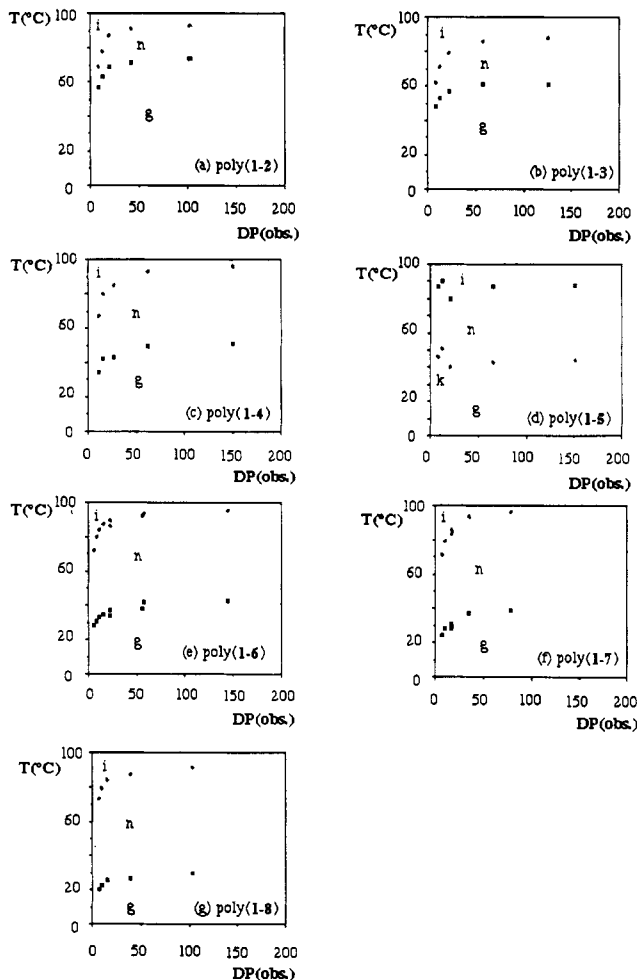


**Figure 5.** Polarized optical micrograph (magnification 120 $\times$ ) of the nematic schlieren texture observed on cooling poly(1-4) 16-mer from the isotropic state; 77  $^{\circ}\text{C}$ .

persity. In addition, polydisperse oligomers would then be expected to exhibit broader peaks than essentially monodisperse oligomers and polymers. This trend has been observed both for main-chain LCPs<sup>40</sup> and for some mesogenic polysiloxanes<sup>41</sup> and poly(vinyl ethers).<sup>21-25</sup> However, this argument assumes that each chain length melts independently, even when the different chain lengths are isomorphic. An alternative argument is that since the



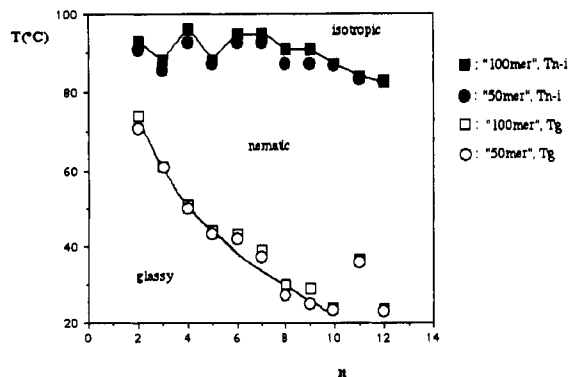
**Figure 6.** Normalized DSC thermograms of poly(1-5) 9-mer and 12-mer: (a) second heating scan; (b) first cooling scan.



**Figure 7.** Dependence of the phase transition temperatures on the GPC-determined degree of polymerization of (a) poly(1-2), (b) poly(1-3), (c) poly(1-4), (d) poly(1-5), (e) poly(1-6), (f) poly(1-7), and (g) poly(1-8). All data are from the second heating scans.

rate of formation of each phase decreases with increasing molecular weight due to increasing viscosity, transitions of higher molecular weight polymers should be slower than those of lower molecular weight polymers, with the result that the transition occurs over a broader temperature range. Indeed, the peak width of isotropization also has been observed to increase with increasing molecular weight over the range of molecular weights where the transition temperatures depend on molecular weight.<sup>20</sup>

With the exception of the poly(1-6) 145-mer, it appears that the isotropization transitions plotted in Figure 3 may become slightly sharper as molecular weight increases. The peak width also can be qualitatively observed by polarized optical microscopy, since it corresponds to the amount of biphasic material (anisotropic and isotropic) present at the transition. To determine whether polydispersity affects the sharpness of the nematic-isotropic



**Figure 8.** Dependence of the phase transition temperatures on the flexible spacer length ( $n$  methylene units) of the 100-mers and 50-mers of poly(1- $n$ ).

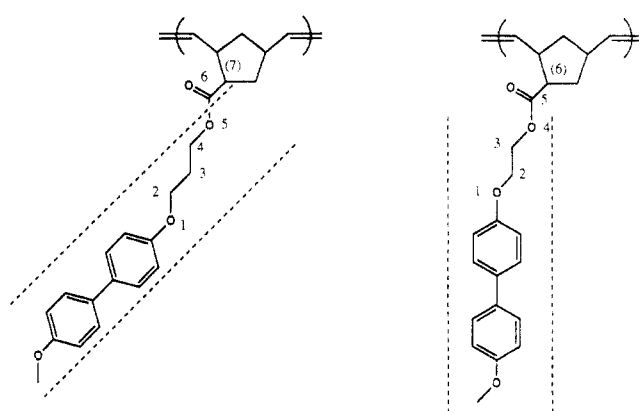
transition of these polymers, we prepared the multimodal blend of poly(1-6) shown in Figure 2a using low-PDI 9-, 16-, 57-, and 145-mers in a ratio of 15:15:15:55. The resulting blend has a number-average molecular weight of 9741 ( $DP = 23$ ) and a polydispersity of 2.5. Even this multimodal sample undergoes a sharp transition from the nematic to the isotropic state (Figure 4), and the glass transition and isotropization temperatures of this blend correspond to those of a monomodal/monodisperse 23-mer (Table I).

We also prepared the bimodal blend of the 6- and 78-mers of poly(1-7) shown in Figure 2b. This blend has a number-average degree of polymerization of 22 and a polydispersity of 4.78. The nematic-isotropic transition of this extremely polydisperse sample is also sharp (Figure 4), and the transition temperatures again correspond to those of a monodisperse 17-mer (Table I). Therefore, the peak width is *not* affected by polydispersity if the component polymers are isomorphic over the temperature range at which the transition occurs.

As discussed earlier, the spacer length does not affect the molecular weight at which the phase transitions become independent of molecular weight. However, the spacer length does affect the temperature of the transitions. The transition temperatures determined on heating are plotted in Figure 8 as a function of the number of methylene units in the flexible spacer, including poly(1- $n$ ) with  $n = 9$ –12.<sup>42</sup> To avoid errors ascribable to the theoretical and/or experimentally determined molecular weights, the transition temperatures are plotted only for the 50-mers and 100-mers, since the temperatures of these transitions are independent of molecular weight. The glass transition temperature decreases rapidly with increasing spacer length as a consequence of decreased packing density of the chains. Those compounds with  $n \geq 9$  exhibit side chain crystallization; melting/crystallization overlaps  $T_g$  when  $n = 10$ –12. In general, the isotropization temperatures decrease slightly as the spacer length increases, with an odd-even alternation. This alternation is observable only for spacer lengths up to  $n = 6$ . Polymers that contain even spacers display higher isotropization temperatures than those that contain the odd spacers.

Since the glass transition temperatures decrease rapidly with increasing spacer length while isotropization decreases only slightly, the temperature window of the mesophase is broader for the longer spacers. Figure 8 also demonstrates that the temperature window broadens as spacer length and molecular weight increase. This is generally true for SCLCPs, except that an increase in the isotropization temperature with increasing spacer length may also contribute to stabilization of the mesophase.<sup>21–25,43–45</sup>

Scheme III



With SCLCPs, there has been some discrepancy as to whether even- or odd-member spacers result in higher isotropization temperatures. This discrepancy was resolved for polysiloxanes, polyacrylates, and polymethacrylates by considering the total number of atoms between the backbone and mesogen as part of the "spacer", including the interconnecting units.<sup>18</sup> In this case, even-spacer lengths result in higher smectic-isotropic transition temperatures because they place the mesogen perpendicular to rather than at an angle to the polymer backbone. Consequently, the anisotropy and linearity of the mesogenic side chains are enhanced and the formation of layers is favored. In contrast, the nematic-isotropic transition temperatures of poly(vinyl ethers) containing 4-cyano-4'-biphenyloxy mesogens and short spacers are higher for the odd spacers than for the even spacers.

As shown in Scheme III, similar arguments can be applied to this mesogenic polynorbornene system. However, in order to compare it with the above acyclic polymer backbones, the substituted carbon atom of the cyclopentane ring may also be considered as part of the spacer. If this is so, then even spacers are more linear and anisotropic, and our data agree with those obtained for polysiloxanes, polyacrylates, and polymethacrylates. On the other hand, if the substituted carbon of the cyclopentane ring is not considered part of the spacer, then odd-spacer lengths are more anisotropic and should have the higher transition temperatures corresponding to the poly(vinyl ethers). Therefore, these results do not resolve the confusion; results from additional well-defined systems exhibiting nematic-isotropic and smectic-isotropic transitions will be required. However, the relative anisotropy and placement of the mesogen relative to the backbone may not dictate the stability of nematic mesophases, or the orientation of the backbone and mesogen may not be comparable in these two poly(vinyl ether) and polynorbornene systems. That is, since there are three nematic mesophases possible in SCLCPs which are defined by the relative orientations of the mesogenic side chain and polymer backbone,<sup>46</sup> the nematic mesophases of the poly(vinyl ether) system and this polynorbornene system may be different and therefore not comparable.

## Conclusions

5- $\{[n-[(4'\text{-Methoxy-4-biphenyl)oxy]alkyl}]\text{carbonyl}\}$ -bicyclo[2.2.1]hept-2-enes with  $n = 2\text{--}8$  were polymerized by ring-opening metathesis polymerization in a living manner to provide a complete series of well-defined SCLCPs with systematically varying molecular weights. All polymers exhibit an enantiotropic nematic mesophase which is stabilized by both increasing molecular weight and increasing spacer length. Because of the simplicity

of the mesomorphic behavior of this system, it was possible to determine the effect of polydispersity on the transition temperatures by blending monodisperse polymers. The isotropization temperature of polydisperse and multimodal blends corresponds to that predicted by the number-average molecular weight. In addition, the range over which this transition occurs is not influenced by the polydispersity. In this system, the transitions become independent of molecular weight when chains contain 30–50 repeat units, and polymers with an odd number of methylene units in the spacer display higher transition temperatures than those with an even number. This alternation vanishes when the spacer length is greater than  $n = 6$ .

## Experimental Section

**Materials and Methods.** All polymers were prepared in THF under a nitrogen atmosphere in a Vacuum Atmospheres drybox. Tetrahydrofuran 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 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%), 2-chloro-1-ethanol (99%), 3-chloro-1-propanol (98%), 6-chloro-1-hexanol (97%), 7-bromo-1-heptanol (95%), and 8-bromo-1-octanol (95%) were used as received from Aldrich. 4-Chloro-1-butanol (Aldrich, 85%) was washed with aqueous  $\text{NaHCO}_3$ , dried with  $\text{MgSO}_4$ , and distilled. 5-Chloro-1-pentanol (95%) was used as received from Lancaster Synthesis Inc. 2-Norbornene-5-carboxylic acid chloride (exo/endo = 1/3)<sup>47</sup> and 4'-methoxy-4-hydroxybiphenyl<sup>48</sup> were prepared as described in the literature. endo-2-Norbornene-5-carboxylic acid was synthesized by hydrolysis of the corresponding endo-methyl ester obtained by the Lewis acid catalyzed Diels-Alder addition of cyclopentadiene and methyl acrylate.<sup>49</sup> endo-2-Norbornene-5-carboxylic acid chloride was prepared by treatment of the carboxylic acid with  $\text{PCl}_5$  under standard conditions. All other reagents and solvents were commercially available and used as received.

The catalyst was synthesized in four steps from  $[\text{NH}_4][\text{Mo}_2\text{O}_7]$ ;<sup>51</sup> the intermediates are  $\text{Mo}(\text{NAr})_2\text{Cl}_2$  (dimethoxyethane),  $\text{Mo}(\text{NAr})_2(\text{CH}_2\text{-}t\text{-Bu})_2$ , and  $\text{Mo}(\text{CH-}t\text{-Bu})(\text{NAr})_2(\text{triflate})_2$  (dimethoxyethane).<sup>7</sup> It is very important to remove all  $\text{ArNH}_3\text{OTf}$  from  $\text{Mo}(\text{CH-}t\text{-Bu})(\text{NAr})_2(\text{triflate})_2$  (dimethoxyethane) before adding lithium *tert*-butoxide. All steps must be carried out under a dinitrogen atmosphere, and the catalyst must be stored and used under dinitrogen or other inert gas in the absence of water and other potentially reactive protic impurities in the monomer (e.g., carboxylic acid or alcohol). The catalyst used in these studies was stored as a solid at  $-40^\circ\text{C}$  under dinitrogen.

Polymer blends were prepared by coprecipitation in methanol of the appropriate amount of each component from THF (0.05 g/mL); the yield of the blend of poly(1-6) was 76%, while the yield of poly(1-7) was 77%.

300-MHz  $^1\text{H}$  NMR spectra were recorded on a Varian XL-300 spectrometer. All spectra were recorded in  $\text{CDCl}_3$  with TMS as internal standard. Obvious multiplicities and routine coupling constants are usually not listed. Molecular weight was determined by gel permeation chromatography (GPC) at room temperature using a set of Shodex KF802.5, 803, 804, 805, and 800P columns (700 Å,  $2 \times 10^3$  Å,  $2 \times 10^4$  Å,  $1 \times 10^5$  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) samples in THF. GPC columns were calibrated using polystyrene standards (Polymer Laboratories Ltd.) ranging from 1206 to  $1.03 \times 10^6$  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  $20^\circ\text{C}/\text{min}$ . Glass transition temperatures ( $T_g$ 's) were assumed to be the temperature at the middle of the change in the heat capacity. All second and subsequent heating scans were



identical. A Nikon optical polarized microscope (magnification 160 $\times$ ) equipped with a Mettler FP82 hot stage and a Mettler FP800 central processor was used to observe the thermal transitions and to analyze anisotropic textures.

**Synthesis of *n*-(4'-Methoxy-4-biphenyl)oxy]alkyl-1-ol (*n* = 2–8).** All of the compounds except *n* = 4 were synthesized by a modified literature procedure<sup>30</sup> as in the following example. 5-Chloro-1-pentanol (3.8 g, 0.031 mol) was added to a solution of 4'-methoxy-4-hydroxybiphenyl (6 g, 0.03 mol) and NaOH (1.2 g, 0.03 mol) in ethanol (50 mL) and water (3 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 and water. Recrystallization from ethanol yielded 3.9 g (45%) of colorless crystals. Higher yields (>80%) were obtained using bromo alcohols.

**2-[(4'-Methoxy-4-biphenyl)oxy]ethanol.** <sup>1</sup>H NMR  $\delta$  2.10 (t, 1 H, OH), 3.90 (s, 3 H, CH<sub>3</sub>O), 4.05 (m, 2 H, CH<sub>2</sub>OH), 4.18 (dd, 2 H, CH<sub>2</sub>OAr), 7.01 (dd, 4, H<sub>aryl</sub>), 7.53 (dd, 4, H<sub>aryl</sub>).

**3-[(4'-Methoxy-4-biphenyl)oxy]-1-propanol.** <sup>1</sup>H NMR  $\delta$  1.72 (t, 1 H, OH), 2.03 (q, 2 H, CH<sub>2</sub>CH<sub>2</sub>OH), 3.80 (s, 3 H, CH<sub>3</sub>O), 3.86 (dt, 2 H, CH<sub>2</sub>OH), 4.13 (t, 2 H, CH<sub>2</sub>OAr), 6.92 (dd, 4, H<sub>aryl</sub>), 7.44 (dd, 4, H<sub>aryl</sub>).

**4-[(4'-Methoxy-4-biphenyl)oxy]-1-butanol** was synthesized from the tetrahydropyranyl ether of 4-chloro-1-butanol prepared by a standard procedure.<sup>50</sup> The chloro ether was reacted with 4'-methoxy-4-hydroxybiphenyl, and the resulting substituted tetrahydropyranyl ether was hydrolyzed without separation: <sup>1</sup>H NMR  $\delta$  1.56 (br t, 1 H, OH), 1.85 (m, 2 H, CH<sub>2</sub>CH<sub>2</sub>OAr), 1.97 (m, 2 H, CH<sub>2</sub>CH<sub>2</sub>OH), 3.80 (dt, 2 H, CH<sub>2</sub>OH), 3.90 (s, 3 H, CH<sub>3</sub>O), 4.10 (t, 2 H, CH<sub>2</sub>OAr), 7.00 (dd, 4, H<sub>aryl</sub>), 7.52 (dd, 4, H<sub>aryl</sub>).

***n*-(4'-Methoxy-4-biphenyl)oxy]-1-alkanol (*n*  $\geq$  5).** The <sup>1</sup>H NMR spectra of the *n*-(4'-methoxy-4-biphenyl)oxy]-1-alkanols (*n*  $\geq$  5) are identical:  $\delta$  1.25 (t, 1 H, OH), 1.3–1.7 (m, 2 [*n* – 3]H, [CH<sub>2</sub>]<sub>*n*-3</sub>), 1.83 (q, 2 H, CH<sub>2</sub>CH<sub>2</sub>OAr), 3.65 (q, 2 H, CH<sub>2</sub>OH), 3.85 (s, 3 H, CH<sub>3</sub>O), 4.00 (t, 2 H, CH<sub>2</sub>OAr), 6.96 (dd, 4, H<sub>aryl</sub>), 7.46 (dd, 4, H<sub>aryl</sub>).

**Synthesis of 5-{*n*-(4'-Methoxy-4-biphenyl)oxy]alkyl]-carbonyl]bicyclo[2.2.1]hept-2-enes (1-*n*, *n* = 2–8).** The 1-*n* monomers were prepared in 70–80% yield as in the following example. A solution of 2-norbornene-5-carboxylic acid chloride (1.56 g, 9.96 mmol) in THF (5 mL) was added dropwise to a refluxing slurry of 7-[(4'-methoxy-4-biphenyl)oxy]-1-heptanol (3.0 g, 9.54 mmol) and triethylamine (1.01 g, 9.98 mmol) in THF (40 mL). The solution was refluxed and stirred for 24 h. The mixture was cooled and the solvent was removed on a rotary evaporator. The residue was dissolved in chloroform, and the solution was washed with aqueous K<sub>2</sub>CO<sub>3</sub> and water and then dried over anhydrous MgSO<sub>4</sub>. Concentration of the filtered chloroform solution yielded 3.31 g (80%) of 1-7.

All monomers were purified by column chromatography using Al<sub>2</sub>O<sub>3</sub> 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. The monomers were recrystallized until no improvement was seen in the polydispersity of polymers prepared using 100 equiv of monomer: <sup>1</sup>H NMR resonances at  $\delta$  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;  $\delta$  5.95 (dd) and 6.21 (dd) are due to the endo olefinic protons, and  $\delta$  6.15 (m) is due to the exo olefinic protons;  $\delta$  1.2–2.0 (m, 2 [*n* – 2]H, [CH<sub>2</sub>]<sub>*n*-2</sub>), 3.86 (s, 3 H, OCH<sub>3</sub>), 4.07 (t, 2 H, CH<sub>2</sub>OAr), 4.18 (m, 2 H, CH<sub>2</sub>OOC). Melting points (by DSC): 1–2, 94 °C; 1–3, 91 °C; 1–4, 77 °C; 1–5, 98 °C; 1–6, 72 °C; 1–7, 86 °C; 1–8, 60 °C.

**Polymerization Procedure.** A solution of Mo(CH<sub>3</sub>-*t*-Bu)(NAr)(O-*t*-Bu)<sub>2</sub> (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 mixture was then stirred for 1 h. The polymerization was quenched by adding 20  $\mu$ L of benzaldehyde (0.19 mmol). 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 >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: <sup>1</sup>H NMR  $\delta$

1.0 (m, terminal *t*-Bu), 1.2–2.2 (br), 2.2–3.2 (br), 3.85 (s, OCH<sub>3</sub>), 4.07 (br, CH<sub>2</sub>OAr), 4.26 (br, CH<sub>2</sub>OOC), 5.15–5.55 (br, olefinic H), 6.97 (br d, H<sub>aryl</sub>), 7.51 (br d, H<sub>aryl</sub>).

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**Registry No.** 1-2, 141484-44-8; 1-2 (homopolymer), 141484-55-1; 1-3, 141484-45-9; 1-3 (homopolymer), 141484-56-2; 1-4, 141484-46-0; 1-4 (homopolymer), 141484-57-3; 1-5, 141484-47-1; 1-5 (homopolymer), 141484-58-4; 1-6, 141484-48-2; 1-6 (homopolymer), 141484-59-5; 1-7, 141484-49-3; 1-7 (homopolymer), 141484-60-8; 1-8, 141484-50-6; 1-8 (homopolymer), 141484-61-9; MeO-(C<sub>6</sub>H<sub>4</sub>-p-)O(CH<sub>2</sub>)<sub>5</sub>OH, 141484-51-7; MeO-(C<sub>6</sub>H<sub>4</sub>-p-)O(CH<sub>2</sub>)<sub>2</sub>OH, 103594-19-0; MeO-(C<sub>6</sub>H<sub>4</sub>-p-)O(CH<sub>2</sub>)<sub>3</sub>OH, 141484-52-8; MeO-(C<sub>6</sub>H<sub>4</sub>-p-)O(CH<sub>2</sub>)<sub>4</sub>OH, 141484-53-9; MeO-(C<sub>6</sub>H<sub>4</sub>-p-)O(CH<sub>2</sub>)<sub>7</sub>OH, 141484-54-0; HO(CH<sub>2</sub>)<sub>5</sub>Cl, 5259-98-3; MeO-(C<sub>6</sub>H<sub>4</sub>-p-)OH, 16881-71-3; 2-norbornene-5-carboxylic acid chloride, 27063-48-5.