Poly(*p*-phenylene)s with Mesogenic Side Groups: A Potential Class of N_{II} Side Chain Liquid Crystalline Polymers?

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ABSTRACT: The synthesis and characterization of a series of *n*-[(4-cyano-4′-biphenylyl)oxy]alkyl-2,5-dichlorobenzoate monomers containing from $n = 2$ to 12 methylenic groups in the alkyl spacer and their Ni(0)-catalyzed polymerization to produce poly(*p*-phenylene)s (PPP) containing mesogenic side groups are described. The resulting side chain liquid crystalline polymers (SCLCPs) have both a rigid rodlike mesogenic backbone and rigid rodlike mesogenic side groups. All polymers display only a broad enantiotropic nematic phase and no side-chain crystallization. The isotropization temperature of these SCLCPs exhibits a steeper increase with the degree of polymerization (DP) than that observed for polymers with flexible or semiflexible backbones. Therefore, above plateau DPs their isotropization temperature is higher than that of polymers with flexible or semiflexible backbones, although it displays a classic odd−even dependence on the spacer length. These unusual trends may indicate that the director of the nematic phase of these SCLCPs is determined by the mesogenic backbone and not by the mesogenic side groups, and therefore, these polymers may provide the first examples of the N_{II} phase.

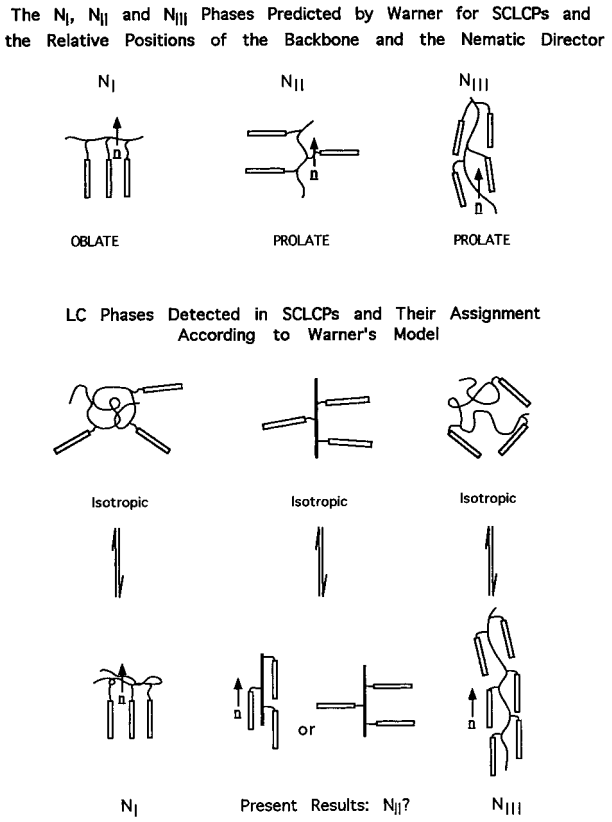
Introduction

The relative contributions of the order parameters associated with the main chain and with the side groups of side chain liquid crystalline polymers (SCLCP) (i.e., the relative positions of the nematic director vs the backbone and the side groups) to the order parameter of the polymer were used by Warner[1] to predict three potential liquid crystalline phases termed N_I, N_{II}, and N_{III}. They are shown on the first line of the top of Scheme 1.

X-ray diffraction[2a−c] and small-angle neutron scattering (SANS) experiments[2b,d−e] have demonstrated that in the N_I phase of SCLCPs the backbone adopts an oblate shape, and the nematic director (determined by the side group mesogen attached in an end-on fashion) is perpendicular to the backbone. In a smectic phase, X-ray and SANS[2b−e] experiments have shown that the backbone is confined in an oblate shape between the smectic layers generated by the mesogens. In this case, which also corresponds to the N_I model, the director is parallel to the mesogens (see left column of Scheme 1).

In the N_{III} phase, the nematic director is parallel both to the backbone and to the mesogens that are attached end-on or side-on and are jacketing the backbone. In these cases a prolate shape of the backbone was observed by X-ray and SANS experiments.[2c] The ordered LC arrangement of the mesogenic units in the nematic or smectic phase distorts the backbone from a random coil conformation into a prolate or oblate one. In both N_I and N_{III} phases the equilibrium situations for the backbone and mesogenic groups are different from those of the two individual systems (i.e., the backbone without mesogenic groups and the mesogenic groups without backbone). The nematic director *n* is primarily determined by the orientation of the mesogenic groups while the backbone is forced to adopt a distorted oblate or prolate conformation to accommodate the formation of the mesophase. This situation is characteristic for SCLCP with flexible or semiflexible backbones that are nonmesogenic.

Scheme 1. Theoretical Models of SCLCPs (M. Warner)



Examples of SCLCPs containing flexible or semiflexible backbones[3] or combinations of semiflexible main chain−side chain LCPs are available.[3a] The research in the field of SCLCPs with rigid backbones such as poly(1,6-heptadiyne),[4a] polyacetylene,[4b−d] poly(diacetylene),[4e]

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polythiophene,[4f−h] polypyrrole,[4i,j] poly(aryleneethynylene),[4k] polyaniline,[4l] polyglutamate,[4m] and polyesters[4n] was driven by their potential electrooptic properties that can be fine-tuned via the manipulation of the degree of order in the system. Nevertheless, none of these backbones are known to form nematic mesophases when only aliphatic spacers are attached as side groups. In addition, the investigations performed on these SCLCPs did not address the mechanism of the formation of their liquid crystalline phase.

In the N_{II} phase the nematic director is determined by the backbone and is parallel to it. While examples of SCLCP exhibiting N_I or N_{III} phase are available, according to our knowledge, attempts to produce polymers that exhibit the N_{II} phase were not reported. Such a polymer would require both mesogenic side groups and a mesogenic rigid rodlike backbone (i.e., a backbone that alone can generate a nematic phase). In addition, the contribution of the mesogenic backbone to the order parameter of the system would be greater than that for the N_I and N_{III} cases and would exceed that of the mesogenic side groups. Therefore, for suitable structural conditions, the backbone and not the mesogenic side groups would determine the nematic director of the SCLCP. In such a system, both the mesogenic groups and the backbone may be able to reach in their mesophase the equilibrium situation, which would correspond to that of the backbone without mesogenic groups and of mesogenic groups without a backbone. The dynamics of such a SCLCP should be different from that of polymers exhibiting N_I and N_{III} phases.

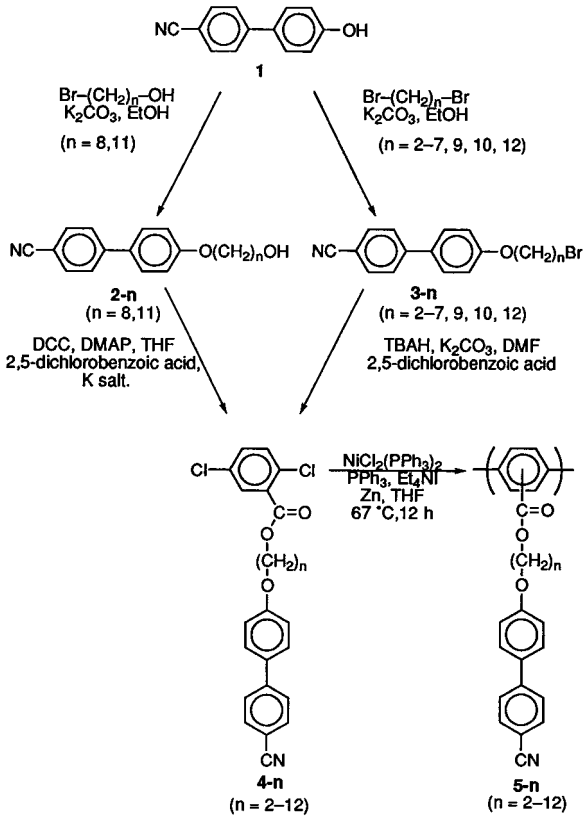
We have previously reported the synthesis and characterization of main chain LC poly(*p*-phenylene)s (PPPs).[5] This paper reports the synthesis and thermal characterization of a series of SCLCPs with a PPP backbone and [(4-cyano-4′-biphenylyl)oxy]alkyl side groups containing from 2 to 12 methylenic units in their alkyl spacer.

Results and Discussion

The synthesis of *n*-[(4-cyano-4′-biphenylyl)oxy]alkyl-2,5-dichlorobenzoates (**4-n)** with alkyl groups containing from $n = 2$ to $n = 12$ methylenic units is presented in Scheme 2. The alkylation of 4-hydroxy-4′-cyanobiphenylyl with α-bromo-*ω*-hydroxyalkanes ($n = 8$ and 11) or α,*ω*-dibromoalkanes ($n = 2-7$, 9, 10, and 12) generates the corresponding α-hydroxy-*ω*-[(4-cyano-4′-biphenylyl)-oxy]alkanes (**2-n**) and the α-bromo-*ω*-[(4-cyano-4′-biphenylyl)oxy]alkanes (**3-n**), respectively. The **2-n** series was esterified with 2,5-dichlorobenzoic acid while the **3-n** series was esterified using the potassium salt of the same acid to generate the corresponding **4-n** monomers. Polymerization of **4-n** in the presence of a Ni(0) catalyst using a procedure that we have previously developed in our laboratory for the synthesis of PPPs[5,6] afforded the corresponding side chain regioirregular PPPs with mesogenic side groups (**5-n**).

Tables 1 and 2 summarize the characterization of **5-n** by gel permeation chromatography (GPC) and differential scanning calorimetry (DSC) together with the polymerization yields and corresponding reaction times. Figure 1 presents the second heating and first cooling DSC scans of selected polymers. The DSC experiments in combination with thermal optical polarized microscopy demonstrated that all polymers exhibit only an enantiotropic nematic mesophase which expands over a very broad range of temperatures. This is an unexpected result since for conventional SCLCPs with flexible or semiflexible backbones only at short spacer length (i.e., containing two to four methylenic units) is a nematic phase observed while SCLCPs with longer spacers and 4-cyanobiphenyl side groups exhibit both smectic and crystalline phases.[3a−i]

Scheme 2. Monomer and Polymer Synthesis



The dependencies of T_g and of the isotropization temperature (T_i) of polymers containing respectively an even and odd number of methylenic groups (n) in the spacer on the degree of polymerization (DP) are shown in Figures 2 and 3. Two important results are generated by these figures. First, for any given n, the effect of DP is felt more strongly by T_i than it is by T_g. For example, ΔT_i ($\Delta T_i = T_{i,DPmax} - T_{i,DPmin}$) varies depending on n from 27 to 168 °C, while ΔT_g ($\Delta T_g = T_{g,DPmax} - T_{g,DPmin}$) varies from 8 to 86 °C. Consequently, since both T_i and T_g increase with DP, the breadth of the nematic phase increases with DP. Second, the slope of the increase of T_i as a function of DP is much larger than the corresponding slope observed for polymers with the same mesogen and spacer length but with flexible backbones.[3a−e] The plateau threshold for both T_i and T_g is reached at DP of about 15. Examples 12, 24, and 25 in Table 1 and examples 23 and 25 in Table 2 have broader polydispersities. The influence of polydispersity on the transition temperatures is smaller than that of DP,[3b] and therefore, these samples do not affect the T-DP trend. This result contrasts with the corresponding trend from SCLCPs with flexible or semiflexible backbones where the plateau is usually reached at larger values (i.e., DP = 25−50)[3a−d,j] and represents a remarkable difference between these two systems. Both these effects are more pronounced for shorter spacers. However, since both the present DP values and the ones for the SCLCPs with flexible and semiflexible backbones are relative to polystyrene standards, the present comparison is only qualitative.

Table 1. Ni(0)-Catalyzed Polymerization of 4-n with an Even Number of Methylenic Groups in the Spacer and Characterization of the Resulting Polymers

				GPC			transition temperature (°C) and corresponding enthalpy changes (kcal/mru)[a]	
entry	$(CH_2)_n$ *n*	reaction time (h)	yield (%)	$M_n \times 10^{-3}$	M_w/M_n	DP	heating	cooling
1	2	24	36	9.42	1.75	28	g 118 n 357 (0.08) i[b]	
2	4	24	93	9.61	2.24	26	g 91 n 271 (0.10) i i 264 (0.10) n 83 g	g 92 n 269 (0.10) i i 261 (0.11) n 81 g
3	6	0.25	29	3.36	1.35	8	g −6 n 73 (0.11) i i 69 (0.10) n −4 g	g −6 n 73 (0.11) i i 69 (0.10) n −4 g
4	6	0.50	79	4.85	1.73	12	g 66 n 210 (0.11) i i 207 (0.12) n 59 g	g 66 n 210 (0.15) i i 207 (0.14) n 61 g
5	6	4	82	5.89	2.18	15	g 73 n 216 (0.09) i i 205 (0.10) n 63 g	g 73 n 215 (0.11) i i 214 (0.13) n 62 g
6	6	24	93	10.5	2.50	26	g 76 n 219 (0.15) i i 217 (0.12) n 69 g	g 75 n 223 (0.16) i i 214 (0.11) n 67 g
7	6	24	94	13.8	2.06	35	g 72 n 234 (0.12) i i 222 (0.13) n 64 g	g 72 n 233 (0.12) i i 222 (0.13) n 65 g
8	6	24	79	14.2	2.12	36	g 79 n 240 (0.11) i i 237 (0.11) n 71 g	g 79 n 241 (0.12) i i 237 (0.11) n 71 g
11	8	24	84	7.83	2.39	18	g 58 n 185 (0.15) i i 180 (0.15) n 53 g	g 60 n 185 (0.15) i i 181 (0.16) n 54 g
12	8	24	99	8.43	3.07	20	g 64 n 188 (0.12) i i 181 (0.17) n 56 g	g 64 n 190 (0.14) i i 181 (0.16) n 57 g
13	8	24	91	15.7	2.61	37	g 66 n 212 (0.17) i i 205 (0.19) n 57 g	g 66 n 212 (0.19) i i 205 (0.18) n 58 g
14	10	0.25	31	1.30	1.24	3	g 6 n 70 (0.36) i i 65 (0.30) n −1 g	g 6 n 71 (0.32) i i 65 (0.30) n −2 g
15	10	0.50	92	1.33	1.29	3	g 12 n 79 (0.28) i i 68 (0.19) n 7 g	g 12 n 75 (0.21) i i 68 (0.19) n 7 g
16	10	1.0	93	4.00	1.29	9	g 42 n 131 (0.14) i i 129 (0.16) n 35 g	g 42 n 132 (0.15) i i 129 (0.16) n 35 g
17	10	24	95	7.41	2.45	16	g 51 n 154 (0.24) i i 154 (0.19) n 45 g	g 51 n 154 (0.19) i i 154 (0.19) n 45 g
18	10	24	93	7.59	1.90	17	g 51 n 156 (0.21) i i 155 (0.19) n 43 g	g 51 n 156 (0.21) i i 155 (0.19) n 43 g
19	10	24	99	8.51	1.87	19	g 51 n 154 (0.21) i i 153 (0.18) n 42 g	g 51 n 154 (0.19) i i 152 (0.16) n 42 g
20	10	24	99	9.52	2.04	21	g 49 n 164 (0.20) i i 160 (0.21) n 43 g	g 51 n 163 (0.19) i i 160 (0.20) n 43 g
21	12	0.25	17	1.46	1.20	3	g 10 n 75 (0.57) i i 71 (0.55) n 2.7 g	g 10 n 75 (0.55) i i 71 (0.55) n 2.9 g
22	12	0.50	42	1.75	1.41	4	g 16 n 89 (0.21) i i 80 (0.21) n 9 g	g 16 n 89 (0.21) i i 79 (0.20) n 10 g
23	12	12	84	5.10	1.75	11	g 46 n 126 (0.10) i i 121 (0.10) n 40 g	g 47 n 129 (0.11) i i 121 (0.10) n 40 g
24	12	24	94	7.91	3.10	16	g 44 n 139 (0.28) i i 132 (0.22) n 36 g	g 44 n 138 (0.31) i i 132 (0.25) n 38 g
25	12	24	89	9.55	3.50	20	g 45 n 142 (0.12) i i 133 (0.15) n 38 g	g 45 n 141 (0.15) i i 132 (0.12) n 37 g
26	12	24	92	14.3	2.18	30	g 44 n 154 (0.26) i i 144 (0.25) n 36 g	g 47 n 154 (0.24) i i 144 (0.25) n 37 g
27	12	24	97	15.4	2.9	32	g 48 n 160 (0.20) i i 152 (0.24) n 39 g	g 48 n 159 (0.23) i i 151 (0.21) n 40 g

[a] Heating and cooling rates are 20 °C/min. [b] Sample decomposed after the first heating scan.

Figure 4 shows the dependence of the isotropic to nematic (T_{in}) and of T_g on the number of methylenic groups in the spacer (*n*) for polymers with DP = 29. These values were obtained by extrapolation from the data available in Figures 2 and 3. A continuous decrease in T_g with *n* (albeit with a weak odd−even dependence on *n*) and a decrease in T_{in} with *n* via a strong odd−even dependence on the spacer parity are observed. This dependence is induced by the mesogenic side groups and weakens with increasing spacer length.

General thermodynamic considerations[7] on the effect of various structural factors on the generation and stabilization of LC phases have predicted that SCLCPs with more rigid backbones should display higher isotropization temperatures and lower entropy changes (ΔS_i). However, experimental results[3c−k] have demonstrated that for a given spacer length and mesogen pair, with increasing flexibility of the backbone of SCLCPs, T_g decreases while both the melting and isotropization temperatures increase**.** Also, for a given backbone, as the spacer length increases,[3a−g,k] more ordered (i.e., smectic or crystalline) phases form. In the case of SCLCPs with flexible backbones, T_i is higher for the polymers containing the most flexible backbones. At the same time, ΔS_i values are larger for the SCLCPs with the most rigid backbones that exhibit the lowest transition temperatures. While this experimental trend seems to be against thermodynamic intuition[3a−g,7] we have explained it[3h] by the difference between the mechanisms of chain distortion (by the mesogenic side groups) of backbones with different flexibilities. Flexible backbones are more easily distorted to accommodate mesophases with higher order parameter and consequently generate higher T_i than more flexible backbones. Therefore, thermally less stable (monotropic vs enantiotropic) and higher ordered (smectic or crystalline vs nematic)

Table 2. Ni(0)-Catalyzed Polymerization of 5-n with an Odd Number of Methylenic Groups in the Spacer (*n*) and Characterization of the Resulting Polymers

				GPC			transition temperature (°C) and corresponding enthalpy changes (kcal/mru)[a]	
entry	$(CH_2)_n$ *n*	reaction time (h)	yield (%)	$M_n \times 10^{-3}$	M_w/M_n	DP	heating	cooling
1	3	24	86	10.2	1.95	29	g 99 n 218 (0.12) i	g 98 n 219 (0.051) i
							i 211 (0.049) n 92 g	i 212 (0.047) n 92 g
2	5	0.25	34	1.06	1.15	3	g 35 n 81 (0.13) i	g 35 n 81 (0.13) i
							i 74 (0.10) n 27 g	i 74 (0.12) n 27 g
3	5	0.50	90	5.33	1.70	14	g 75 n 195 (0.063) i	g 75 n 198 (0.038) i
							i 195 (0.049) n 68 g	i 196 (0.056) n 67 g
4	5	24	87	10.6	2.40	28	g 75 n 207 (0.050) i	g 76 n 206 (0.066) i
							i 196 (0.075) n 69 g	i 196 (0.075) n 69 g
5	5	12	97	16.0	1.90	42	g 83 n 208 (0.066) i	g 84 n 208 (0.071) i
							i 196 (0.060) n 78 g	i 196 (0.055) n 77 g
6	5	24	98	18.6	2.28	49	g 83 n 228 (0.082) i	g 83 n 230 (0.085) i
							i 218 (0.063) n 72 g	i 218 (0.061) n 75 g
7	5	6	99	20.5	1.82	53	g 80 n 223 (0.073) i	g 80 n 223 (0.083) i
							i 218 (0.062) n 72 g	i 217 (0.072) n 72 g
8	5	24	92	23.8	1.83	62	g 78 n 232 (0.080) i	g 79 n 233 (0.078) i
							i 224 (0.067) n 71 g	i 223 (0.072) n 72 g
9	7	0.25	39	1.06	1.19	3	g 12 n 57 (0.078) i	g 12 n 57 (0.078) i
							i 51 (0.072) n 7 g	i 51 (0.095) n 7 g
10	7	0.50	18	1.70	1.26	4	g 40 n 100 (0.19) i	g 40 n 100 (0.19) i
							i 94 (0.17) n 32 g	i 94 (0.18) n 32 g
11	7	24	93	12.7	2.08	31	g 58 n 190 (0.057) i	g 59 n 190 (0.061) i
							i 188 (0.005) n 51 g	i 188 (0.005) n 52 g
12	7	24	97	12.7	1.82	31	g 56 n 191 (0.087) i	g 58 n 191 (0.085) i
							i 188 (0.074) n 50 g	i 188 (0.070) n 52 g
13	7	24	91	13.0	1.66	32	g 61 n 197 (0.09) i	g 59 n 199 (0.09) i
							i 192 (0.090) n 51 g	i 190 (0.090) n 52 g
14	7	24	93	13.9	1.62	34	g 58 n 205 (0.061) i	g 58 n 205 (0.064) i
							i 200 (0.065) n 52 g	i 200 (0.053) n 52 g
15	7	24	94	18.3	1.65	44	g 63 n 216 (0.044) i	g 63 n 216 (0.063) i
							i 211 (0.064) n 56 g	i 211 (0.063) n 56 g
16	9	0.25	22	1.70	1.26	4	g 26 n 94 (0.28) i	g 26 n 94 (0.28) i
							i 88 (0.23) n 19 g	i 88 (0.23) n 19 g
17	9	0.50	23	1.96	1.38	5	g 22 n 89 (0.11) i	g 22 n 89 (0.10) i
							i 81 (0.10) n 14 g	i 81 (0.10) n 16 g
18	9	4	96	9.90	2.13	23	g 47 n 176 (0.078) i	g 50 n 176 (0.081) i
							i 171 (0.040) n 41 g	i 173 (0.057) n 43 g
19	9	24	91	12.3	1.89	28	g 55 n 177 (0.098) i	g 55 n 177 (0.082) i
							i 170 (0.090) n 47 g	i 170 (0.088) n 47 g
20	9	24	94	13.2	1.93	30	g 49 n 173 (0.041) i	g 49 n 172 (0.064) i
							i 171 (0.041) n 42 g	i 171 (0.064) n 43 g
21	9	24	89	14.2	1.87	32	g 53 n 184 (0.10) i	g 53 n 184 (0.082) i
							i 176 (0.10) n 43 g	i 176 (0.11) n 45 g
22	11	6	99	2.45	1.4	5	g 32 n 67 (0.59) i	g 32 n 67 (0.59) i
							i 59 (0.58) n 25 g	i 59 (0.58) n 25 g
23	11	6	93	3.88	3.8	8	g 32 n 66 (0.082) i	g 32 n 66 (0.082) i
							i 89 (0.17) n 24 g	i 89 (0.17) n 25 g
24	11	24	94	8.57	1.72	18	g 41 n 133 (0.13) i	g 41 n 132 (0.13) i
							i 124 (0.13) n 35 g	i 123 (0.11) n 34 g
25	11	24	96	9.19	2.85	20	g 47 n 139 (0.077) i	g 46 n 139 (0.10) i
							i 133 (0.089) n 40 g	i 133 (0.089) n 40 g
26	11	24	96	13.9	1.66	30	g 49 n 155 (0.10) i	g 49 n 156 (0.10) i
							i 147 (0.093) n 41 g	i 147 (0.089) n 41 g
27	11	1	92	14.9	1.73	32	g 43 n 158 (0.11) i	g 44 n 158 (0.10) i
							i 153 (0.11) n 37 g	i 152 (0.10) n 37 g

phases as well as faster dynamics are obtained for SCLCPs with flexible backbones.[3a−g,k] In line with this experimental trend,[3h,i] if the backbone conformation continues to be distorted by the mesogenic side groups, one should expect that SCLCPs with even more rigid backbones such as PPP display higher T_g, *lower* melting and isotropization temperatures, and narrower mesophase temperature range. Thermodynamically more stable (enantiotropic vs monotropic) but thermally less stable (i.e., of lower isotropization temperatures) LC phases should be exhibited by the SCLCPs with more rigid backbones when their conformation is distorted.

The unexpected differences between the experimental trends observed for conventional SCLCPs and the behavior of these side chain polymers are now obvious. A significant difference is that while the values of T_{in} and T_g are lower than those of our previously reported model main chain PPPs,[5] the isotropization temperatures are unexpectedly much *higher* than of any of the similar SCLCPs with flexible or semiflexible backbones.[3a−e,4] This higher isotropization temperature is in line with thermodynamic predictions[7] that do not require a distortion of the backbone conformation during the formation of the mesophase. Another difference is the fact that while the side chains of SCLCPs with flexible backbones are able to crystallize even at small *n*,[3a−i,k] the rigid PPP backbone prevents side chain crystallization or the formation of smectic phases even for spacers containing 12 methylenic units.

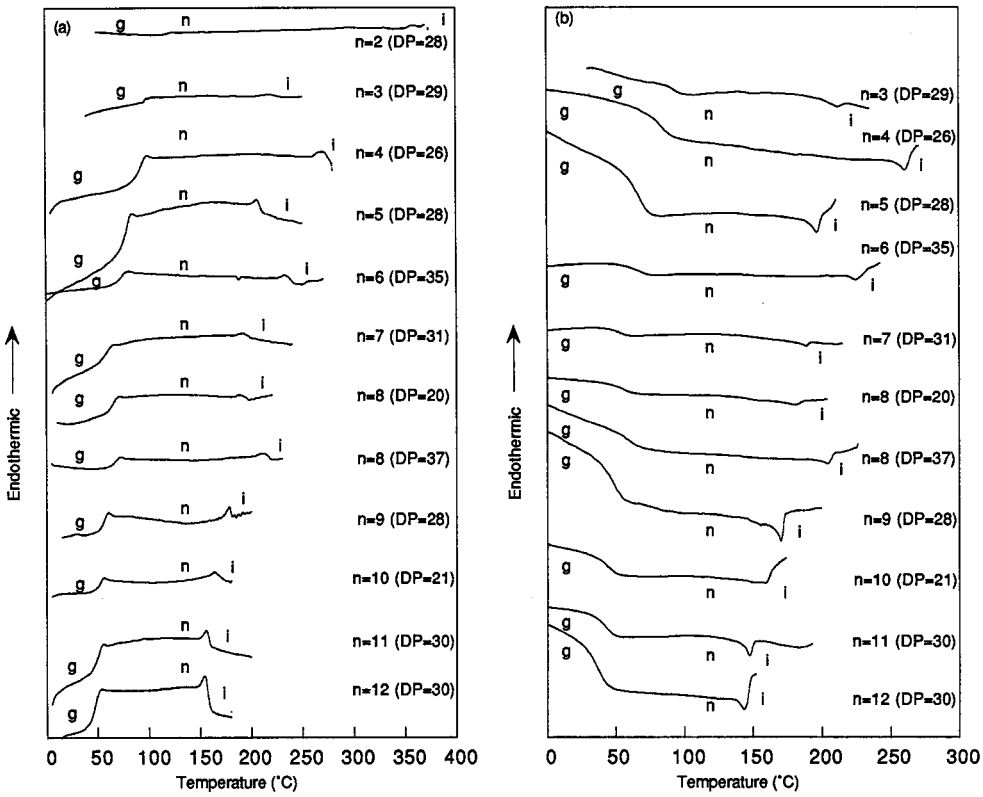


Figure 1. DSC thermograms (20 °C/min) of **5-n** with $n = 2-12$: (a) second heating scan and (b) first cooling scans. Thermogram for $n = 2$ is first heating scan; sample decomposed above ≈370 °C on first heating scan.

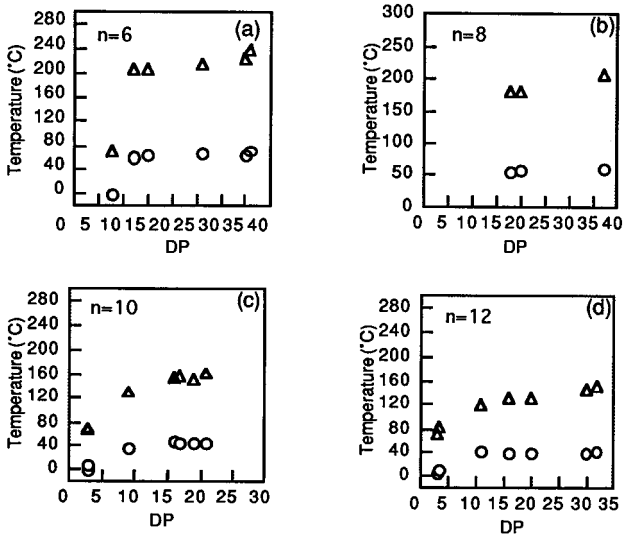


Figure 2. Dependence of isotropic−nematic (△) and the nematic−glass (○) transition temperatures of **5-n** (n = even) on the degree of polymerization (DP). (a) $n = 6$; (b) $n = 8$; (c) $n = 10$; (d) $n = 12$.

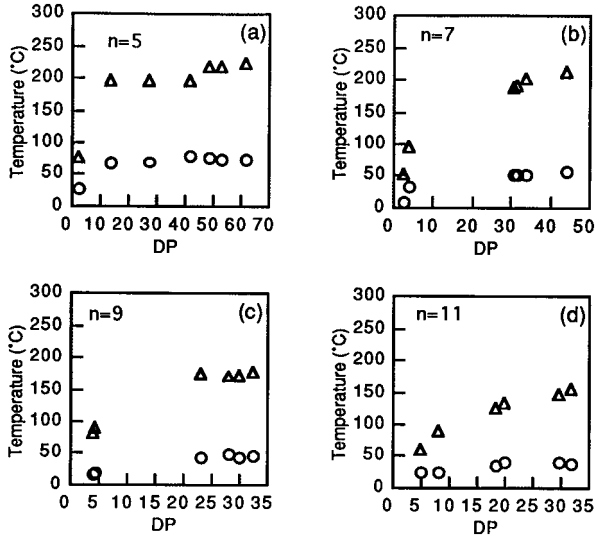


Figure 3. Dependence of isotropic−nematic (△) and the nematic−glass (○) transition temperatures of **5-n** (n = odd) on the degree of polymerization (DP). (a) $n = 5$; (b) $n = 7$; (c) $n = 9$; (d) $n = 11$.

The dependence of the enthalpy (ΔH) and entropy (ΔS) changes at the isotropic−nematic transition for these polymers is presented in Figure 5. Both ΔS and ΔH increase continuously in an odd−even fashion with increasing the spacer length. This increase is due to the increased contributions from the methylenic units with n.[7a] The values of the entropy change at the isotropization ($\Delta S_i = 0.1-0.6$ cal/(mru K)) are however smaller than those associated with the isotropization of SCLCPs with flexible or semiflexible backbones[3a−h,j] ($\Delta S_i = 0.5-3$ cal/(mru K), where mru stands for mole repeat unit).

We believe that the formation of the mesophase displayed by these SCLCPs is determined by their DP. Below a certain DP, the nematic director is determined by the side groups. Above this critical DP, the major contribution to the nematic director comes from the backbone. At least two architectures are possible for SCLCPs whose nematic director is determined by their backbone: (a) one in which the mesogens are jacketing the PPP backbone are parallel to it and (b) one in which the mesogens are perpendicular to the PPP backbone. Both models are schematically shown on the bottom of the middle column of Scheme 1. The model in which the backbone and the mesogens are parallel to each other

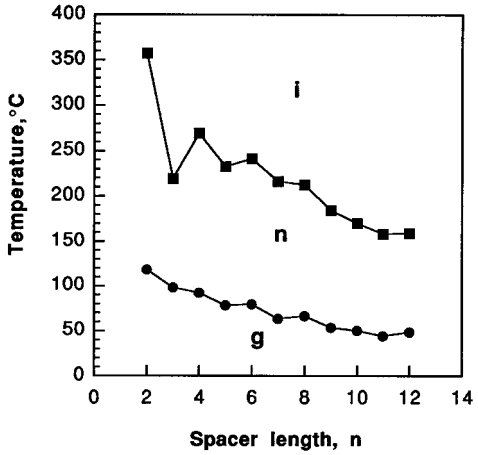


Figure 4. Dependence of the isotropic−nematic (■) and the nematic−glass (●) transition temperatures on the number of methylene units (*n*) in the flexible spacer of **5-n** with DP = 29.

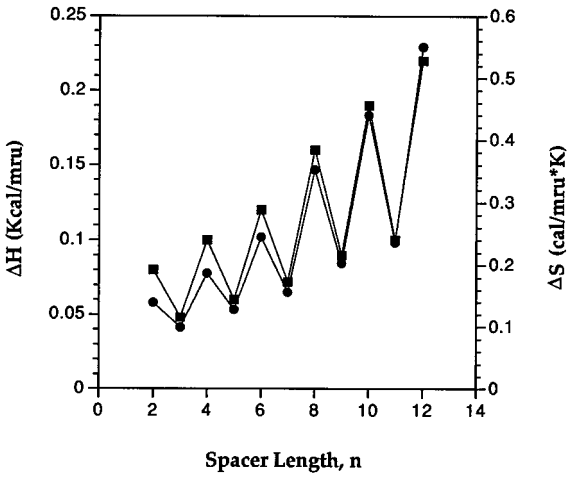


Figure 5. Dependence of the enthalpy (■) and entropy (●) changes at the isotropic−nematic transition of **5-n** on the number of methylene units (*n*) in the flexible spacer for DP = 29.

is supported by the lack of side chain crystallization in these polymers. Nevertheless, detailed structural investigations are required to discriminate between these two and eventually other alternative models. Regardless of the molecular architecture in the phase nematic of these SCLCPs, we believe that for large DPs they may correspond to Warner's[1] N_{II} phase.

The structural differences between these SCLCPs with a rigid-rod-like backbone and SCLCPs with flexible and semiflexible backbones explain the differences in their phase behavior. As the main chain is more rigid, the value of the order parameter is reached much faster than in the case of flexible backbones, and consequently the slope from Figures 2 and 3 is higher for these polymers. The higher isotropization temperatures of the PPP-based SCLCPs from Figure 4 are due to the cooperative effect of the order parameters of the mesogenic backbone and of the mesogenic side groups. In conventional SCLCPs the contribution of the main chain is negligible. The more rigid PPP backbone also drives mesophase formation and suppresses side chain crystallization. The inability of the side chains to crystallize also reveals the strong nematic coupling between the rigid mesogenic backbone and the mesogenic side groups. The higher values of ΔH and ΔS (Figure 5) for the polymers in which the side groups are connected to the backbone via even number of methylenic units than in the case of odd number of methylenic units reflect the higher degree of order in the corresponding nematic phases which most probably was brought about by a better parallel alignment between the mesogenic side groups and the rigid main chain. The fact that these values are smaller than those corresponding to SCLCPs with more flexible backbones[3j] is a consequence of the fact that the rigid PPP backbone maintains an extended chain conformation both in the LC and in the isotropic phase. Therefore, the term associated with the distortion of the backbone by the side groups in the LC phase and which makes a large contribution in the expressions of ΔH and ΔS in the case of SCLCPs with flexible backbones is absent for the PPP-based SCLCPs.

The results presented here actually fall in line with our original thermodynamic assessment[7] that SCLCPs with more rigid backbones should display higher transition temperatures and lower entropy changes associated with the isotropization transition as well as less ordered mesophases.

Conclusions

The first examples of liquid crystalline side chain polymers based on a PPP rigid-rod-like mesogenic backbone and containing mesogenic side groups were presented. These polymers display several remarkable differences from conventional SCLCPs based on flexible or semiflexible backbones and may provide a synthetic model for the preparation of SCLCPs exhibiting the N_{II} mesophase. While X-ray and SANS documentation of this aspect is still in progress, fine-tuning of mesophase properties as well as of the transitions between various types of nematic phases and chain conformations in the LC phases exhibited by these systems can be achieved via a careful control of the structural parameters of the backbone, mesogen, and spacer. The PPP-based SCLCPs described in this work represent a novel class of side chain LCPs with nondistorted backbones that deserve very careful consideration and further investigation.

Experimental Section

Techniques. Melting points are uncorrected and were determined with a Thomas-Hoover Uni-Melt capillary melting point apparatus. ^{1}H NMR (200 MHz) and $^{13}C\{^1H\}$ (50 MHz) NMR spectra were recorded on a Varian Gemini-200 spectrometer, in $CDCl_3$. Chemical shifts (δ) are reported in parts per million (ppm) downfield from tetramethylsilane (TMS) and are referenced relative to the ^{1}H resonance of TMS or ^{13}C resonance of $CDCl_3$ (77.0 ppm). GC analyses were performed on a Hewlett-Packard 5890 using a flame ionization detector and a 10% SP-2100 column. Thin-layer chromatography (TLC) analyses were performed on polyester sheets precoated with 0.25 mm thick silica gel containing a 254 nm indicator (Kodak 13181). Column chromatographic purifications were performed with 32−63 mesh ICN silica gel or activated basic Al_2O_3 (Brockmann I, 150 mesh). A Perkin-Elmer DSC-7 differential scanning calorimeter (DSC), equipped with a TAC 7/DX thermal analysis controller, was used to determine the thermal transitions which were reported as the maxima and minima of their endothermic and exothermic peaks, respectively. In all cases, heating and cooling rates were 20 °C/min. Glass transition temperatures (T_g) were read at the middle of the change in the heat capacity. Optical polarized microscopy was performed using an Olympus BX40 optical microscope. Molecular weights were determined by gel permeation chromatography (GPC) with a Perkin-Elmer series 10 LC instrument equipped with an LC-100 column oven and Nelson analytical 900 series integrator data station. The measurements were made at 40 °C using the UV detector set at 254 nm using THF as solvent (1 mL/min). A set of Phenomenex Phenogel columns

(5×10^4 and 500 Å) and a calibration plot constructed with polystyrene standards were used to determine the molecular weights. Therefore, all molecular weights determined by GPC are relative to polystyrene. Elemental analyses were carried out at M-H-W Laboratories in Phoenix, AZ, and agreed with theoretical values.

Materials. Unless noted otherwise, all reagents were purchased from commercial sources (Aldrich or Lancaster) and used without further purification. *N*-Methyl-2-pyrrolidone (NMP) was distilled under reduced pressure. Tetrahydrofuran (THF) was distilled over sodium/benzophenone. Zinc dust was stirred in acetic acid, washed with water, and dried in vacuo at 120 °C. $NiCl_2(PPh_3)_2$,[8] 4-bromo-4′-acetoxybiphenyl,[9] 4-bromo-4′-hydroxybiphenyl,[9] and 4-cyano-4′-hydroxybiphenyl[9] were prepared according to published procedures. Unless otherwise noted, all compounds synthesized were purified until their 200 MHz ^{1}H NMR spectra corresponded to the expected structure, and the purity was established by comparison with published melting points or found to be higher than 99.5% by GC, HPLC, and TLC.

α-Bromo-ω-[(4-cyano-4′-biphenylyl)oxy]alkanes and α-hydroxy-ω-[(4-cyano-4′-biphenylyl)oxy]alkanes were prepared according to published methods,[3j,10] the analytical data are listed below.

1-Bromo-2-[(4-cyano-4′-biphenyl)oxy]ethane: white crystals; mp 77−78 °C °C; ^{1}H NMR ($CDCl_3$) δ 7.73 (d, J = 8.2 Hz, 2H), 7.61 (d, J = 8.2 Hz, 2H), 7.55 (d, J = 8.5 Hz, 2H), 7.02 (d, J = 8.5 Hz, 2H), 4.36 (t, J = 6.2 Hz, 2H), 3.68 (t, J = 6.2 Hz, 2H).

1-Bromo-3-[(4-cyano-4′-biphenylyl)oxy]propane: white crystals; mp 100.5−101.0 °C; ^{1}H NMR ($CDCl_3$) δ 7.72 (d, J = 8.6 Hz, 2H), 7.62 (d, J = 8.6 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H), 7.02 (d, J = 8.8 Hz, 2H), 4.17 (t, J = 5.8 Hz, 2H), 3.64 (t, J = 6.4 Hz, 2H), 2.36 (quintet, J = 6.1 Hz, 2H).

1-Bromo-4-[(4-cyano-4′-biphenylyl)oxy]butane: white crystals; mp 62−63 °C; ^{1}H NMR ($CDCl_3$) δ 7.72 (d, J = 8.5 Hz, 2H), 7.62 (d, J = 8.5 Hz, 2H), 7.53 (d, J = 8.7 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 4.06 (t, J = 5.9 Hz, 2H), 3.51 (t, J = 6.4 Hz, 2H), 2.04 (br m, 4H).

1-Bromo-5-[(4-cyano-4′-biphenylyl)oxy]pentane: white crystals; mp 72−74 °C; ^{1}H NMR ($CDCl_3$) δ 7.72 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.6 Hz, 2H), 6.99 (d, J = 8.6 Hz, 2H), 4.03 (t, J = 6.1 Hz, 2H), 3.46 (t, J = 6.7 Hz, 2H), 1.96 (quintet, J = 7.0, 2H), 1.86 (quintet, J = 7.0 Hz, 2H), 1.65 (quintet, J = 7.0 Hz, 2H).

1-Bromo-6-[(4-cyano-4′-biphenylyl)oxy]hexane: white crystals; mp 68−70 °C; ^{1}H NMR ($CDCl_3$) δ 7.71 (d, J = 8.5 Hz, 2H), 7.62 (d, J = 8.5 Hz, 2H), 7.53 (d, J = 8.7 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 4.02 (t, J = 6.4 Hz, 2H), 3.44 (t, J = 6.7 Hz, 2H), 1.87 (br m, 4H), 1.57−1.35 (br m, 4H).

1-Bromo-7-[(4-cyano-4′-biphenylyl)oxy]heptane: white crystals; mp 43 °C (DSC); ^{1}H NMR ($CDCl_3$) δ 7.72 (d, J = 8.6 Hz, 2H), 7.62 (d, J = 8.6 Hz, 2H), 7.53 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 4.02 (t, J = 6.4 Hz, 2H), 3.43 (t, J = 6.7 Hz, 2H), 1.85 (br m, 4H), 1.55−1.29 (br m, 6H).

1-Bromo-9-[(4-cyano-4′-biphenylyl)oxy]nonane: white crystals; mp 63 °C (DSC); ^{1}H NMR ($CDCl_3$) δ 7.71 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.7 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 4.01 (t, J = 6.5 Hz, 2H), 3.41 (t, J = 6.8 Hz, 2H), 1.84 (br m, 4H), 1.54−1.28 (br m, 10H).

1-Bromo-10-[(4-cyano-4′-biphenylyl)oxy]decane: white crystals; mp 144 °C (DSC); ^{1}H NMR ($CDCl_3$) δ 7.71 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.7 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 4.01 (t, J = 6.4 Hz, 2H), 3.41 (t, J = 6.8 Hz, 2H), 1.82 (Br m, 4H), 1.54−1.25 (br m, 12H).

1-Bromo-12-[(4-cyano-4′-biphenylyl)oxy]dodecane (74%): white crystals; mp 77−78 °C; ^{1}H NMR ($CDCl_3$) δ 7.71 (d, J = 8.6 Hz, 2H), 7.62 (d, J = 8.6 Hz, 2H), 7.53 (d, J = 8.7 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 4.01 (d, J = 6.5 Hz, 2H), 3.41 (d, J = 6.8 Hz, 2H), 1.82 (br m, 4H), 1.53−1.10 (br m, 16H).

8-[4-Cyano-4′-biphenylyl)oxy]octanol: white crystals; mp 84−86 °C; ^{1}H NMR ($CDCl_3$) 7.71 (d, J = 8.6 Hz, 2H), 7.62 (d, J = 8.6 Hz, 2H), 7.53 (d, J = 8.7 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 4.01 (t, J = 6.4 Hz, 2H), 3.66 (t, J = 5.5 Hz, 2H), 1.81 (br m, 4H): 1.65−1.29 (br m, 8H).

11-[(4-Cyano-4′-biphenylyl)oxy]undecanol (78%): white crystals; mp 87−89 °C; ^{1}H NMR ($CDCl_3$) δ 7.71 (d, J = 8.7 Hz, 2H), 7.52 (d, J = 8.7 Hz, 2H), 7.02 (d, J = 8.7 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 4.00 (t, J = 6.4 Hz, 2H), 3.65 (t, J = 5.5 Hz, 2H), 1.81 (br m, 4H), 1.50−1.02 (br m, 14H).

Monomers: The α-hydroxy-ω-[(4-cyano-4′-biphenylyl)oxy]-alkanes (**2-n**: n = 8, 11) and α-bromo-ω-[(4-cyano-4′-biphenylyl)oxy]alkanes (**3-n**: n = 2−7, 9, 10, 12) were esterified with 2,5-dichlorobenzoic acid and the potassium salt of 2,5-dichlorobenzoic acid, respectively.

2-[(4-Cyano-4′-biphenylyl)oxy]ethyl-2,5-dichlorobenzoate: (78%): white crystals; mp 123−124 °C; ^{1}H NMR ($CDCl_3$) δ 7.81 (s, 1H), 7.72 (d, J = 8.5 Hz, 2H), 7.62 (d, J = 8.5 Hz, 2H), 7.53 (d, J = 8.7 Hz, 2H), 7.39 (s, 1H), 7.38 (s, 1H), 6.99 (d, J = 8.7 Hz, 2H), 4.44 (t, J = 6.0 Hz, 2H), 4.09 (t, J = 6.0 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 164.16, 158.93, 144.95, 132.68, 132.51, 132.24, 132.06, 131.33, 130.69, 128.40, 127.08, 118.99, 115.18, 110.17, 65.73, 63.91.

3-[(4-Cyano-4′-biphenylyl)oxy]propyl-2,5-dichlorobenzoate: white crystals; mp 91−93 °C; ^{1}H NMR ($CDCl_3$) δ 7.81 (s, 1H), 7.72 (d, J = 8.5 Hz, 2H), 7.62 (d, J = 8.5 Hz, 2H), 7.53 (d, J = 8.7 Hz, 2H), 7.39 (s, 1H), 7.38 (s, 1H), 6.99 (d, J = 8.7 Hz, 2H), 4.44 (t, J = 6.0 Hz, 2H), 4.09 (t, J = 6.0 Hz, 2H), 2.00 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 164.36, 159.22, 145.01, 132.53, 132.47, 132.17, 131.91, 131.56, 131.21, 131.16, 128.30, 126.99, 119.00, 114.98, 110.01, 64.40, 62.69, 28.42.

4-[(4-Cyano-4′-biphenylyl)oxy]butyl-2,5-dichlorobenzoate: white crystals; mp 84 °C; ^{1}H NMR ($CDCl_3$) δ 7.80 (s, 1H), 7.72 (d, J = 8.5 Hz, 2H), 7.62 (d, J = 8.5 Hz, 2H), 7.53 (d, J = 8.7 Hz, 2H), 7.39 (s, 2H), 6.99 (d, J = 8.7 Hz, 2H), 4.44 (t, J = 6.0 Hz, 2H), 4.09 (t, J = 6.0 Hz, 2H), 2.00 (br m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 164.54, 159.47, 145.19, 132.62, 132.56, 132.48, 132.24, 132.99, 131.52, 131.38, 131.22, 128.36, 127.08, 119.09, 115.03, 110.09, 67.33, 65.57, 25.91, 25.41.

5-[(4-Cyano-4′-biphenylyl)oxy]pentyl-2,5-dichlorobenzoate: white crystals; mp 129 °C; ^{1}H NMR ($CDCl_3$) δ 7.81 (s, 1H), 7.72 (d, J = 8.5 Hz, 2H), 7.62 (d, J = 8.5 Hz, 2H), 7.53 (d, J = 8.7 Hz, 2H), 7.39 (s, 1H), 7.38 (s, 1H), 6.99 (d, J = 8.7 Hz, 2H), 4.39 (t, J = 6.4 Hz, 2H), 4.05 (t, J = 6.1 Hz, 2H), 1.99−1.80 (m, 4H), 1.75−1.59 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 164.56, 159.58, 144.19, 132.60, 132.53, 132.41, 132.21, 131.97, 131.48, 131.37, 131.18, 128.31, 127.05, 119.08, 115.02, 110.03, 67.68, 65.75, 28.76, 28.28, 22.64.

6-[(4-Cyano-4′-biphenylyl)oxy]hexyl-2,5-dichlorobenzoate: white crystals; mp 75 °C; ^{1}H NMR ($CDCl_3$) δ 7.79 (s, 1H), 7.71 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 8.8 Hz, 2H), 7.39 (s, 1H), 7.38, s, 1H), 6.99 (d, J = 8.8 Hz, 2H), 4.37 (t, J = 6.6 Hz, 2H), 4.02 (t, J = 6.3 Hz, 2H), 2.11−1.70 (br m, 4H), 1.65−1.30 (br m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 164.40, 159.64, 145.16, 132.54, 132.45, 132.27, 132.12, 131.58, 131.28, 131.09, 128.23, 126.97, 126.91, 118.96, 115.02, 110.02, 67.84, 65.79, 28.99, 28.40, 25.67, 25.62.

7-[(4-Cyano-4′-biphenylyl)oxy]heptyl-2,5-dichlorobenzoate: white crystals; mp 97 °C (DSC); ^{1}H NMR ($CDCl_3$) δ 7.80 (s, 1H), 7.72 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 8.8 Hz, 2H), 7.53 (d, J = 8.8 Hz, 2H), 7.39 (s, 2H), 6.99 (d, J = 8.8 Hz, 2H), 4.37 (t, J = 6.4 Hz, 2H), 4.03 (t, J = 6.4 Hz, 2H), 1.90−1.77 (br m, 4H), 1.65−1.40 (br m, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 164.57, 159.76, 145.25, 132.59, 132.51, 132.32, 132.18, 131.95, 131.68, 131.30, 131.15, 128.28, 127.04, 119.03, 115.09, 110.07, 68.03, 65.97, 29.10, 28.91, 28.47, 25.91.

8-[(4-Cyano-4′-biphenylyl)oxy]octyl-2,5-dichlorobenzoate: 8-(4-Cyano-4′-biphenylyl)oxy]octanol (3.0 g, 8.2 mmol), 2,5-dichlorobenzoic acid (2.9 g, 15 mmol), 1,3-dicyclohexyl carbodiimide (DCC) (3.1 g, 15 mmol), and 4-(dimethylamino)-pyridine (DMAP) (0.12 g, 1.0 mmol) were stirred in THF (20 mL) at 22 °C for 24 h. After removing the THF under reduced pressure, the residue was purified by flash column chromatography (CH_2Cl_2). The product containing CH_2Cl_2 fraction was poured into MeOH to precipitate white crystals; mp 78 °C (DSC); ^{1}H NMR ($CDCl_3$) 7.80 (s, 1H), 7.71 (d, J = 8.7 Hz, 2H), 7.62 (d, J = 8.7 Hz, 2H), 7.53 (d, J = 8.7 Hz, 2H), 7.39 (s, 1H), 7.38 (s, 1H), 6.99 (d, J = 8.7 Hz, 2H), 4.34 (t, J = 6.6 Hz, 2H),

4.01 (t, J = 6.4 Hz, 2H), 1.90−1.70 (br m, 4H), 1.65−1.35 (br m, 8H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 164.55, 159.71, 145.20, 132.49, 132.31, 132.16, 131.93, 131.58, 131.18, 131.13, 128.25, 126.99, 119.06, 115.02, 109.96, 68.02, 66.00, 29.14, 29.11, 29.06, 28.45, 25.89, 25.84.

9-[(4-Cyano-4′-biphenylyl)oxy]nonyl-2,5-dichlorobenzoate: white crystals; mp 96 °C (DSC); ^1H NMR ($CDCl_3$) δ 7.80 (s, 1H), 7.71 (d, J = 8.5 Hz, 2H), 7.62 (d, J = 8.5 Hz, 2H), 7.53 (d, J = 8.7 Hz, 2H), 7.39 (s, 1H), 7.38 (s, 1H), 6.99 (d, J = 8.7 Hz, 2H), 4.34 (t, J = 6.6 Hz, 2H), 4.01 (t, J = 6.5 Hz, 2H), 1.85−1.75 (br m, 4H), 1.57−1.20 (br m, 10H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 164.61, 159.83, 145.31, 132.62, 132.54, 132.32, 132.20, 131.99, 131.75, 131.31, 131.18, 128.31, 127.07, 119.06, 115.12, 110.10, 68.14, 66.05, 29.37, 29.25, 29.21, 29.10, 28.53, 25.99, 25.94.

10-[(4-Cyano-4′-biphenylyl)oxy]decyl-2,5-dichlorobenzoate: white crystals; mp 77 °C (DSC); ^1H NMR ($CDCl_3$) δ 7.80 (s, 1H), 7.72 (d, J = 8.7 Hz, 2H), 7.62 (d, J = 8.7 Hz, 2H), 7.53 (d, J = 8.7 Hz, 2H), 7.39 (s, 2H),6.99 (d, J = 8.7 Hz, 2H), 4.34 (t, J = 6.6 Hz, 2H), 4.01 (t, J = 6.5 Hz, 2H), 1.95−1.65 (br m, 4H), 1.60−1.25 (br m, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 164.57, 159.81, 145.27, 132.58, 132.52, 132.30, 132.17, 131.27, 131.16, 128.27, 127.04, 119.04, 115.10, 110.07, 68.15, 66.07, 29.40, 29.36, 29.29, 29.19, 29.13, 28.52, 25.99, 25.92.

11-[(4-Cyano-4′-biphenylyl)oxy]undecyl-2,5-dichlorobenzoate: white crystals; mp 110 °C (DSC); ^1H NMR ($CDCl_3$) δ 7.80 (s, 1H), 7.71 (d, J = 8.7 Hz, 2H), 7.62 (d, J = 8.7 Hz, 2H), 7.53 (d, J = 8.7 Hz, 2H), 7.38 (s, 2H), 6.99 (d, J = 8.7 Hz, 2H), 4.34 (t, J = 6.6 Hz, 2H), 4.01 (t, J = 6.5 Hz, 2H), 1.92−1.68 (br m, 4H), 1.60−1.20 (br m, 14H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 164.59, 159.83, 145.28, 132.59, 132.53, 132.30, 132.18, 131.98, 131.74, 131.26, 131.17, 128.28, 127.05, 119.05, 115.12, 110.08, 68.18, 66.09, 29.48, 29.43, 29.33, 29.21, 29.16, 28.53, 26.01, 25.94.

12-[(4-Cyano-4′-biphenylyl)oxy]dodecyl-2,5-dichlorobenzoate: 1-Bromo-12-[(4-cyano-4′-biphenylyl)oxy]dodecane (2.00 g, 4.52 mmol), the potassium salt of 2,5-dichlorobenzoic acid (1.55 g, 6.77 mmol), and tetrabutylammonium hydrogen sulfate (TBAH) (0.1 g) were stirred in DMF (20 mL) at 60 °C under N_2 for 24 h. The mixture was poured in water (200 mL), and the resulting precipitate was isolated by filtration. Recrystallization (2 times in CH_3OH) afforded 2.40 g (4.34 mmol, 96%) of white crystals; mp 84−86 °C, ^1H NMR ($CDCl_3$) δ 7.80 (s, 1H), 7.71 (d, J = 8.6 Hz, 2H), 7.62 (d, J = 8.6 Hz, 2H), 7.53 (d, J = 8.7 Hz, 2H), 7.39 (s, 2H), 6.99 (d, J = 8.7 Hz, 2H), 4.33 (t, J = 6.8 Hz, 2H), 4.01 (t, J = 6.6 Hz, 2H), 1.89−1.68 (br m, 4H), 1.55−1.20 (br m, 16H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 164.55, 159.74, 145.20, 132.49, 132.29, 132.15, 131.92, 131.58, 131.14, 128.24, 126.99, 119.06, 115.01, 109.94, 68.10, 66.07, 29.47, 29.41, 29.32, 29.16, 29.13, 28.47, 25.97, 25.90.

Polymers: In a typical polymerization,[5] a 125 mL Schlenk tube was charged with $NiCl_2(PPh_3)_2$ (65.42 mg, 0.1 mmol), Zn (458 mg, 7.0 mmol), Et_4Ni (386 mg, 1.5 mmol), PPh_3 (157 mg, 0.6 mmol), and 5-[(4-cyano-4′-biphenylyl)oxy]pentyl-2,5-dichlorobenzoate (455 mg, 1 mmol). The tube was capped with a rubber septum, and the contents were repeatedly vacuumed and then flushed with argon. Dry THF (1 mL) was than added via a syringe, and the mixture was stirred at 65 °C for 24 h. The dark red-brown product was precipitated from $CHCl_3$ solution (2 mL) into a mixture of MeOH (100 mL) and HCl (25 mL). The resulting precipitate was filtered dried and reprecipitated one more time from $CHCl_3$ solution into acetone and one time from $CHCl_3$ solution into MeOH. The final precipitate was filtered and dried to yield 395 mg (87%) of polymer. ^1H and ^{13}C NMR spectra ($CDCl_3$) were used to demonstrate the regioirregular[5,6] structure of these polymers. Elemental analyses agreed with the calculated values.

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References and Notes

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