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New Side-Chain Liquid Crystalline Polymer with Flexible Spacer Backbone

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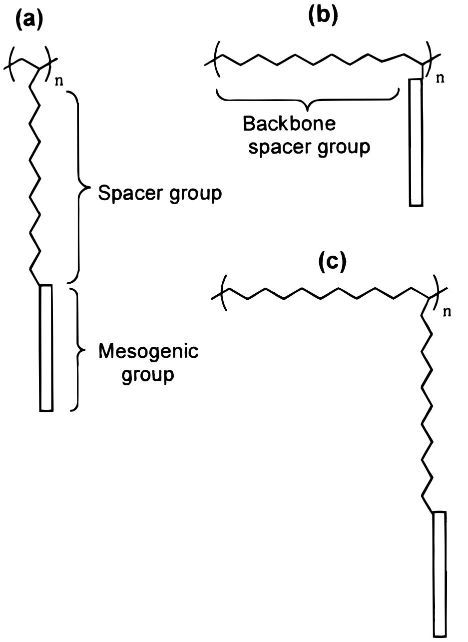
Introduction. Side-chain liquid crystalline polymers (SCLCPs) have attracted much attention of scientific and application research groups because of their possible application for electronic devices.[1] SCLCPs were disposed first by Ringsdorf[2] and Finkelmann, and it was enunciated that a flexible spacer should be inserted between the polymeric main chain and the mesogenic side groups to decouple the motions of side groups from that of the main chain in the liquid crystalline states.

As outlined below, three types of spacers are homologues of, respectively, (**a**) 1,2-type ordinary homopolymers containing spacers (most SCLCPs are included in this category), (**b**) copolymers of nonmesogenic monomers (e.g., ethylene) and monomers containing mesogens directly attached to the polymerizable group, and (**c**) copolymers of nonmesogenic monomers and monomers containing mesogens attached to the polymerizable group through a flexible spacer.[3]

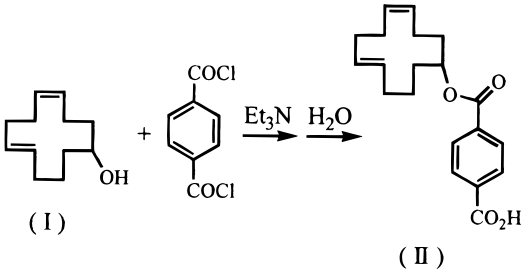


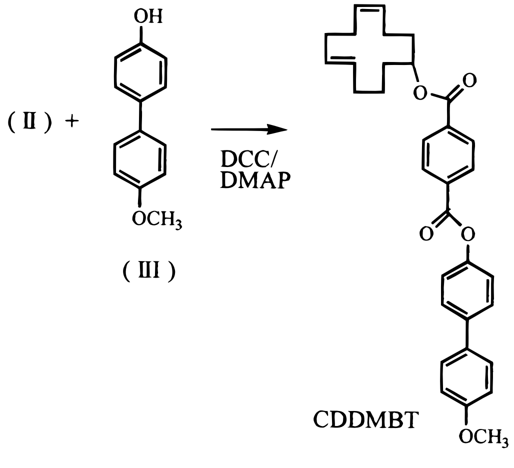
An example of a SCLCP, polymalonate containing flexible spacers in both the main chain and side groups, was first prepared by Ringsdorf.[4] However, a SCLCP with a pure methylene unit spacer (no polar functional group) in the backbone was not prepared yet.

The structures of **b** and **c** are unique in that the main chain spacer should be of exact length and conventional copolymerization with vinyl monomers are not adequate. We have been working on the synthesis of new cyclic monomer systems and their polymerization to obtain hydrocarbon copolymers of strict mer sequences[5−7] and application of this method to the synthesis of the present polymers **b** and **c** is rather unique.

We have synthesized a flexible polymer-backbone SCLCP system having a flexible spacer (12 methylenes per repeating unit) in the polymer backbone and no spacer in the side group. 4,8-Cyclododecadienyl 4′-methoxy-4-biphenyl terephthalate (CDDMBT) was prepared and polymerized by metathesis polymerization (PCDDMBT). Finally, double bonds in the polymer backbone were hydrogenated with H_2/Pd(C) to get SCLCP with a saturated and flexible backbone (PCDMBT).

Experimental Section. Synthesis of Monomer. 4,8-Cyclododecadienol (I). 9,10-Epoxy-1,5-cyclododecadiene was readily treated with conventional LAH reduction. Recrystallization from ether/*n*-pentane gave **I** as white crystals (91% yield). ^{1}H NMR (400 MHz in $CDCl_3$): δ =5.0−5.5(m, 4H), 3.6 (t, 1H), 1.0−2.2 (m, 15H). IR (KBr, cm^{-1}): 3252 (O−H), 2923 (C−H), 1449 (C=C). Mp: 68 °C.





4,8-Cyclododecadienoyl Terephthalic Acid (II). To a rapidly stirred solution of terephthaloyl chloride (73.1 g, 0.36 mol) in 200 mL of dry THF at 0 °C is added dropwise mixture of 4,8-cyclododecadienol (13 g, 72 mmol), triethylamine (9.5 g, 94 mmol), and THF (100 mL). The reaction mixture was then stirred for 1 h at room temperature. After salts were removed by filtration, sufficient distilled water was added to the stirred filtrate. The resulting solid, terephthalic acid, was removed by filtration, and washed with ethyl acetate. The filtrate was washed with 5% sodium carbonate solution and brine. The organic layer was dried over magnesium sulfate and solvent was evaporated with a rotary evaporator. Recrystallization of the crude solid

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Table 1. Polymerization of CDDMBT with Various Catalyst Systems[a]

expt no.	catalyst system (mole ratio)[b]	M/C[c]	conversion (%)[d]	GPC[e]	
				M_n	M_n/M_w
1	WCl_6/Et_2AlCl (1:4)	100			
2	$MoCl_5/Et_3Al$ (1:4)	100	trace		
3	$WCl_4(Oar)_2$[f]$/PbEt_4$ (1:2)	50	95	15 400	2.3
4	$WCl_4(Oar)_2/PbEt_4$ (1:2)	30	93	10 500	2.0

[a] Polymerization was carried out at 80 °C for 24 h. [b] A mixture of catalyst and cocatalyst in toluene or chlorobenzene was aged at 80 °C for 10 min before use as catalyst. [c] Monomer to catalyst mole ratio. [d] Methanol-insoluble polymer. [e] Values were obtained by GPC alaysis with polystyrene standards. [f] OAr was the 2,6-diphenylphenoxy group.

Table 2. Phase Transition Temperatures of CDDMBT, PCDDMBT, and PCDMBT (from Second Heating/Cooling Cycle)[a,b]

	phase transition in °C
CDDMBT	$K \underset{75}{\overset{82}{\rightleftharpoons}} S \underset{114}{\overset{149}{\rightleftharpoons}} N \underset{181}{\overset{186}{\rightleftharpoons}} I$
PCDDMBT	$G \underset{57}{\overset{62}{\rightleftharpoons}} S \underset{110}{\overset{116}{\rightleftharpoons}} I$
PCDMBT	$G \underset{56}{\overset{61}{\rightleftharpoons}} S \underset{100}{\overset{113}{\rightleftharpoons}} I$

[a] Key: K, crystalline; G, glassy; S, smectic; N, nematic; I, isotropic. [b] Heating/cooling rate = 10 °C/min.

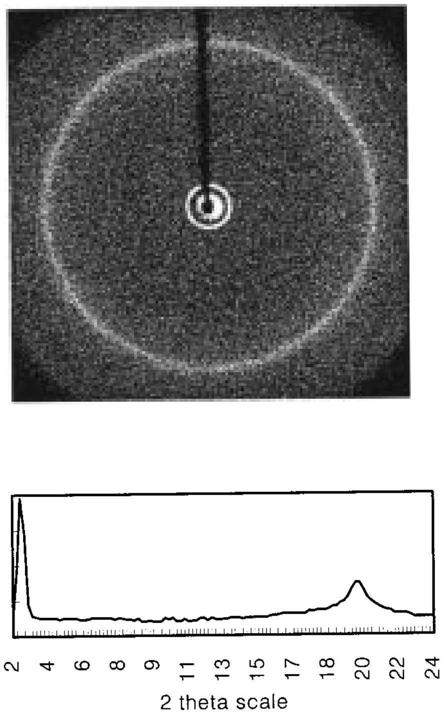


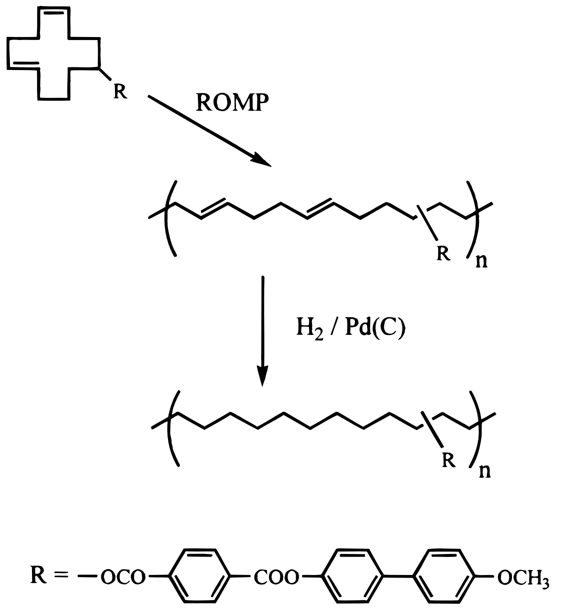
Figure 1. X-ray diffraction pattern of the unoriented PCDMBT film at 25 °C.

product from ethanol gave **II** as white crystals: 9 g (27.4 mmol, 38% yield). ^1H NMR (400 MHz in $CDCl_3$): δ =10.2 (s, 1H), 8.1 (m, 4H), 5.6 (m, 1H), 5.4 (m, 2H), 5.2 (m, 2H), 1.8−2.4 (m, 8H), 1.2−1.8 (m, 6H). IR (KBr, cm^{-1}): 3600 (COO−H), 1708 (C=O in ester), 1684 (C=O in acid). Mp: 140−145 °C.

4,8-Cyclododecadienyl-4′-methoxy-4-biphenyl Terephthalate (CDDMBT). 4,8-Cyclododecadienoyl terephthalic acid(II) (1.76 g, 5.37 mmol), (dimethylamino)pyridine (0.52 g, 4.3 mmol), 50 mL of methylene chloride and methoxybiphenol (**III**) (1.07 g, 5.37 mmol) were placed in 100 mL flask. The flask was surrounded by an ice bath, and DCC (1.22 g, 5.9 mmol) was added for 5 min. The reaction mixture was then stirred for 8 h at room temperature. After conventional workup, recrystallization from ethanol gave CDDMBT as white crystals: 1.5 g (2.9 mmol, 54.7% yield). ^1H NMR (400 MHz in $CDCl_3$): δ = 8.3 (d, 2H), 8.2 (d, 2H), 7.6 (d, 2H), 7.5 (d, 2H), 7.3 (d, 2H), 7.0 (d, 2H), 5.4−5.7 (m, 4H), 5.1 (m, 1H), 3.9 (s, 3H), 1.8−2.4 (m, 8H), 1.2−1.8 (m, 6H). IR (KBr, cm^{-1}): 2923 (C−H), 1731 (C=O).

Polymerization. To a polymerization ampule sealed with rubber septum, degassed with argon were injected the prepared 0.1 N catalyst solution and 0.1 N cocatalyst solution with a syringe sequentially into the ampule. After the mixed catalyst solution was activated at 80 for 10 min, 0.5 g of monomer in 2 mL toluene was introduced into the ampule with syringe and polymerization was carried out at 80 °C. The polymerization was terminated by pouring the reaction into a large amount of methanol. The resulting polymerized products were precipitated and filtered. The crude products were dissolved by chloroform and precipitated into methanol to complete remove of the residual monomer and catalyst. Polymers were separated by filtration, thoroughly washed with methanol, and vacuum-dried.

Hydrogenation. To a pressure reactor were introduced 0.5 g of polymer, 0.5 g of Pd(C), and 20 mL of THF. The reactor was filled with hydrogen gas and then stirred for 48 h at room temperature. After Pd(C) was removed by filtration, the resulting filtrate was concentrated to 5 mL and precipitated with a large amount of methanol. The polymer precipitates were collected and dried in a vacuum oven.



Results and Discussion. In Table 1 the results for the ring opening metathesis polymerization of the monomer by various catalyst systems are listed. The Basset catalyst system[8] gave high molecular weight polymer in high conversion, whereas other catalyst systems showed little or no catalytic activity. The number average molecular weight of the polymer was 1.1×10^4 to 1.5×10^4 and polydispersity was 2.00−2.30 in high conversion.

The chemical structures of the monomers and the polymers were confirmed by IR, ^1H NMR, and ^{13}C NMR spectra. The IR spectrum of PCDDMBT exhibits ab-

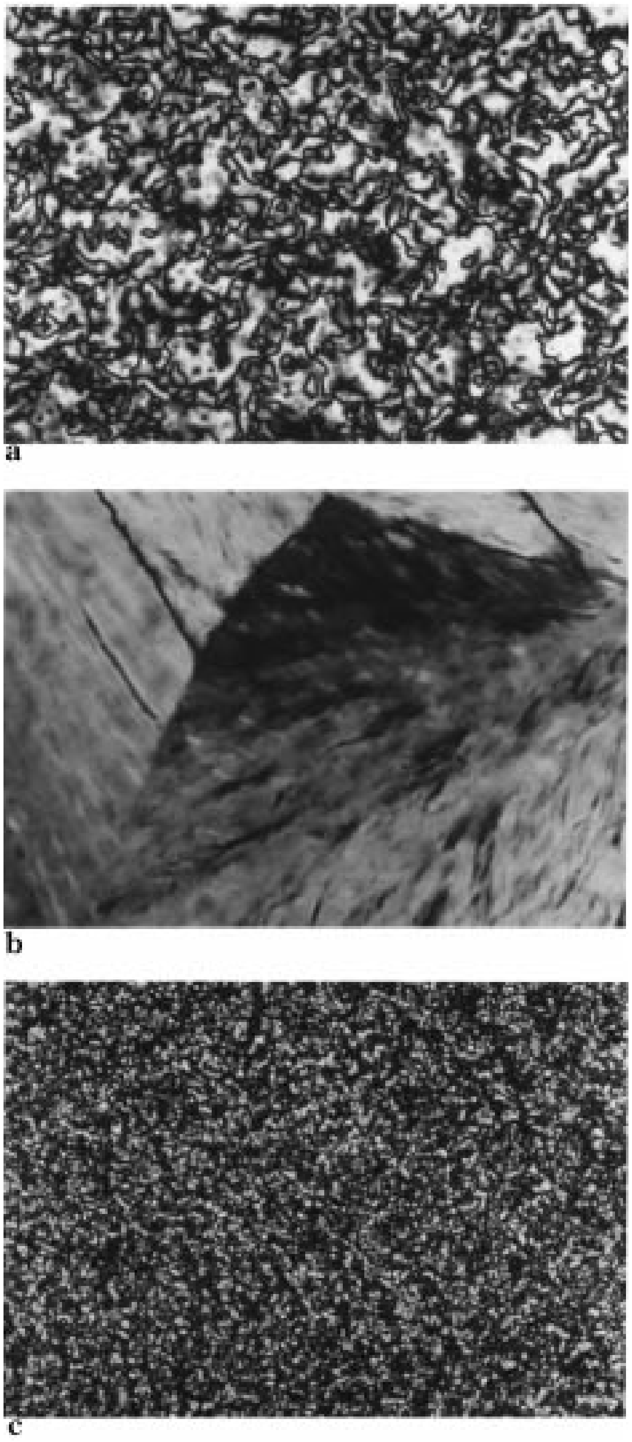


Figure 2. Optical polarization micrographs (×200) of CDDMBT (a) taken at 160 °C, (b) taken at 102 °C, and (c) PCDMBT taken at 70 °C.

sorption bands at 720 and 968 cm^{-1} attributable to =CH out of plane bending of cis and trans double bonds, respectively. The ^{1}H NMR spectrum of PCDDMBT shows aromatic protons (7.0−8.2 ppm), double bond protons (5.3−5.5 ppm), an oxy proton in the ring (5.2 ppm), methoxy protons (3.8 ppm), allyl protons (1.9−2.1 ppm), and alkyl protons (1.4−1.9 ppm) in the correct proportion of ring-opened mers. As the hydrogenation proceeded, the double bond proton peaks at 5.3−5.5 ppm disappeared and alkyl proton peak grew up at 1.4 ppm. The 720 and 968 cm^{-1} bands of the IR spectrum clearly disappeared. These spectral data indicate that the ring-opening metathesis polymerization and hydrogenation occurs cleanly and the final polymers are 5:1 copolymers of ethylene and vinyl mesogenic ester.

Resulting polymers PCDDMBT and PCDMBT were readily soluble in common solvents such as chloroform or THF. When solution cast, the polymers gave turbid white films.

We summarized the phase transition temperatures of CDDMBT, PCDDMBT, and PCDMBT in Table 2 from the DSC thermogram. In general, polymers exhibit higher phase transition temperatures than their monomers. However, in this case, the phase transition temperature of PCDDMBT or PCDMBT is much lower than that of the monomer, CDDMBT. On the other hand, the phase transition temperature of PCDMBT is slightly lower than PCDDMBT. It is thought to be due to easier free rotation of the main chain.

To investigate the phase, PCDDMBT and PCDMBT were measured with a thin film X-ray diffractometer as shown in Figure 1. It was found that sharp diffraction maxima in the low-angle range($2\theta = 2.5$) and narrow peak in the wide angle region ($2\theta = 20$) result from the smectic order. Figure 2 shows the (a) nematic and (b) smectic textures of CDDMBT and (c) grained smectic texture of PCDMBT obtained from optical microscopy with a crossed polarizer.

Further research on the changes of the mesogenic group of the cyclododecadienyl monomers and the copolymerization is now in progress.

References and Notes

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