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Liquid Crystalline Features of Optically Active Poly(methylene-1,3-cyclopentane)

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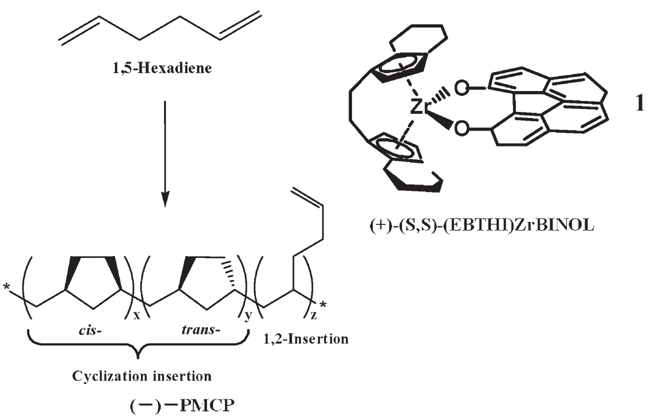
Because the main chain of the polyolefin is formed by carbon–carbon single bonds, the polymers have flexibility that causes folding and entanglement of the polymer chains.[1,2] Mesophase and liquid crystalline phase were observed in the conventional polyolefins, such as polyethylene and isotactic polypropylene, under the conditions of high temperature with high pressure or shearing.[3–5] We have investigated induction of the liquid crystalline features in polyolefin by means of molecular design. It was found out the clear liquid crystalline phase in a polyolefin of poly(methylene-1,3-cyclopentane) (PMCP), which is composed with alternating linkage of methylene and 1,3-cyclopentane unit. PMCP was synthesized by cyclization polymerization of 1,5-hexadiene (HD) with various metallocene catalysts.[6–10] PMCP has been widely considered to be a crystalline polymer.[9,10] We investigated control of microstructure of PMCP and have found a clear liquid crystalline phase in the PMCP samples with high cyclization ratio of the HD units, *trans*-rich structures of the 1,3-cyclopentane units, and low molecular weight.[11] The PMCP samples showed Schlieren-like texture indicating nematic liquid crystal.[11,12]

Waymouth and co-workers reported synthesis of an optically active PMCP by cyclization polymerization of HD using an optically active zirconocene catalyst and its optical rotation in chloroform solution due to their one side helical structure.[7,8] In this study, we dealt with the liquid crystalline features of optically active PMCP and reported the formation of cholesteric liquid crystal in some PMCP samples with low molecular weight. In particular, the effect of molecular weight on molar optical rotation and natures of liquid crystalline phase of the optically active PMCP had been described.

The optically active PMCP samples were prepared by cyclization polymerization of HD with an optically active zirconocene catalyst, [(+)-(*S*,*S*)-ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl)-1,1′-bi-2-naphtholate], **1**, combined with methylaluminoxane (MAO) as a cocatalyst in the presence of triethylaluminum ($AlEt_3$) as a chain transfer reagent to control the molecular weight in toluene at room temperature (Scheme 1).[11,13] The structure and properties of the obtained the PMCP samples are summarized in Table 1. The molecular weight of the PMCP decreased with increasing molar ratio of $[AlEt_3]/[Zr]$ due to the chain transfer reaction of the active sites at propagating chain ends to $AlEt_3$. The cyclization ratios of HD units, [x] + [y] in Scheme 1, were more than 97%. The *trans*-ratios of 1,3-cyclopenatene units ([x] in Scheme 1) ranged from 68 to 74%.

The PMCP samples obtained with the optically active zirconocene catalyst show optical rotation in chloroform solution, as reported by Waymouth.[7,8] A relationship between number-averaged molecular weight (M_n) and molar optical rotation of the PMCP samples in chloroform solution at room temperature is shown in Figure 1. The M_ns of the PMCP samples were measured by gel-permeation chromatography and relatively calibrated with standard polystyrene samples. The PMCP samples whose molecular weights were more than 4000 showed the molar optical rotation about −21°. The result was in agreement with the previous report by Waymouth, which was the molar optical rotations of the PMCP samples with high molecular weight were relatively insensitive to the molecular weight.[8] On the other hand, there was a rapid decrease in the molar optical rotation of the PMCP samples with molecular weights less than 4000. These results indicated that PMCP samples with relatively high molecular weight form stable helix, whereas the helix formation of the low molecular weight samples was unstable in chloroform solution at room temperature.[8]

Scheme 1. Synthesis of Optically Active PMCP Prepared by Cyclization Polymerization of HD with an Optically Active Zirconocene Catalyst 1



All the PMCP samples were soft and sticky and showed birefringent textures which indicated liquid crystalline phases in the observations of polarized optical micrograph at room temperature. The PMCP samples for optical micrographs were prepared after previous heating to 150 °C and cooling to room temperature on a slide glass with cover glass and taking care to get rid of shear. The polarized optical micrographs of PMCP samples with different molecular weights are shown in Figure 2. The birefringent texture of PMCP with relatively high molecular weight (sample 2, M_n = 6300) showed the fingerprint texture indicating cholesteric liquid crystal. The PMCP samples with molecular weights more than 3000 showed the similar fingerprint texture. Both the fingerprint texture and Schliere-like texture derived from cholesteric liquid crystal and Schliere-like texture, which indicate nematic liquid crystal, respectively, were observed in the micrograph of PMCP with M_n = 2700 (sample 6). The coexistence of both the nematic and cholesteric phases in a sample is not observed in small liquid crystal molecule until now. In the case of sample 6, the distribution of the molecular weight, which was coexistence of relatively high and low molecular weights samples which show cholesteric and nematic liquid crystal phases, respectively, should induce the characteristic texture. The micrograph of the low molecular weight PMCP (sample 8, M_n = 2100) shows the sanded, featureless texture indicating nematic liquid crystal.

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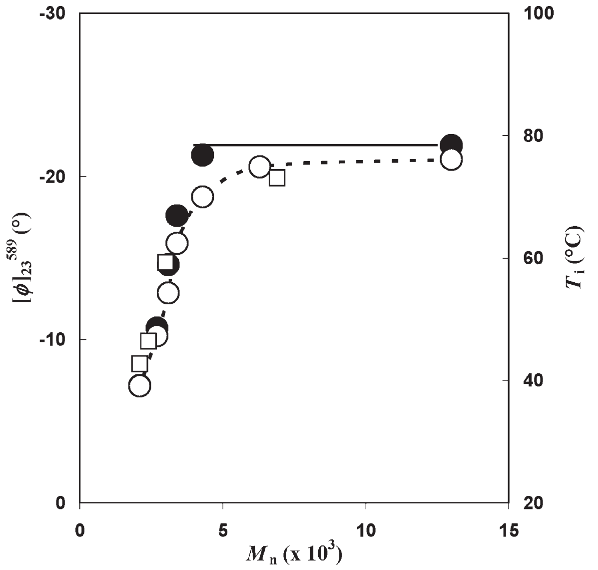

Figure 1. Relationship between number-average molecular weight (M_n) and molar optically rotation (●) or liquid crystal−isotropic transition temperature (T_i) (○) of PMCP obtained with the catalyst **1** and T_i of achiral PMCP (□) for a reference.[11]

Differential scanning calorimetry (DSC) measurement of the PMCP samples was made at a cooling or heating rate of 10 °C/min from 125 °C to −50 °C (cooling process) and −50 to 125 °C (second heating process), previously heating to 125 °C to determine liquid crystal−isotropic transition temperature (T_i). The T_i denoted the endothermic peak top in DSC chart on the second heating process. A relationship between molecular weight and T_i of optically active PMCP is also plotted in Figure 1. The T_i showed curved increase with increasing of the molecular weight of PMCP. The results of the previously reported achiral PMCP samples, which were obtained with an achiral metallocene catalyst (*rac*-dimethylsilylenebis(indenyl)zirconium dichloride),[11] were also plotted in Figure 1. Both the optically active and achiral PMCP samples showed the same profile because there was no thermodynamically difference between cholesteric and nematic liquid crystals.

It was found out a cholesteric liquid crystal phase in the optically active PMCP samples whose molecular weights were more than 3000. The PMCP samples formed stable one-side helical structure not only in the chloroform solution but also in the bulk and induce the cholesteric liquid crystal phase.[14] It has been also investigated that the molecular structure of the optically active PMCP in the bulk and mechanism which induced the cholesteric liquid crystal phase by solid-state NMR and simulation study, and the results will be reported elsewhere.

Table 1. Structure and Thermal Properties of Optically Active PMCP Obtained with Catalyst 1[a]

sample	$AlEt_3$/Zr (mol/mol)	trans[b] (%)	cis[b] (%)	1,2-[b] (%)	M_n[c] × 10^{-3}	M_w/M_n[c]	$[\phi]^{23}_{589}$[d] (deg)	T_g[e] (°C)	T_i[e] (°C)
1	0	67	31	2	13.0	3.4	−21.9	−3.6	76.1
2	250	69	29	2	6.3	3.6		−7.1	74.9
3	500	68	30	2	4.3	3.0	−21.2	−13.6	70.0
4	750	69	29	2	3.4	2.3	−17.6	−20.0	62.4
5	1000	70	27	3	3.1	2.5	−14.6	−17.2	54.3
6	1500	72	25	3	2.7	2.0	−10.7	−22.1	47.3
7	2000	72	25	2	2.1	2.1		−23.8	39.2
8	2500	71	26	3	2.1	2.0		−24.9	39.1

[a] Polymerization conditions; [**1**] = 0.1 (mmol/L), MAO[Al]/[**1**] = 1000 (mol/mol), HD = 0.2 mol/L, polymerization temperature: room temperature. [b] Ratios of *trans*-, *cis*-, and 1,2-units, [x], [y], and [z] in Scheme 1, respectively, determined by ^{1}H and ^{13}C NMR spectroscopy. [c] Number-average molecular weight and molecular weight distribution of PMCP determined by GPC at 40 °C using chloroform as a solvent and calibrated with standard polystyrene samples. [d] Optical rotation of PMCP detected in chloroform solution using polarized light of 589 nm at room temperature (23 °C). [e] Glass transition (T_g) and isotropization temperature (T_i) determined by DSC at a heating rate of 10 °C/min after previous heating to 125 °C and cooling to −50 °C (second heating process).

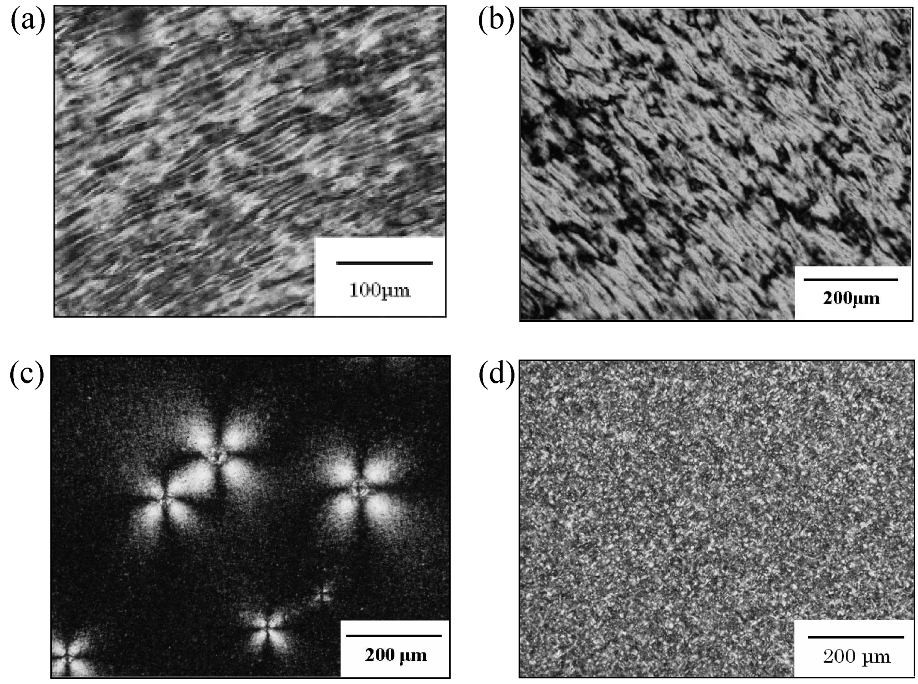

Figure 2. Polarized optical micrographs of PMCP samples: sample 2 (a), sample 6 (b, c), and sample 8 (d).

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Supporting Information Available: Experimental details and DSC profiles. This material is available free of charge via the Internet at http://pubs.acs.org.

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