Liquid Crystalline Features in a Polyolefin of Poly(methylene-1,3-cyclopentane)

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ABSTRACT: A liquid crystalline phase has been discovered in a polyolefin of poly(methylene-1,3-cyclopentane) (PMCP) having low molecular weight, which was obtained with cyclization polymerization of 1,5-hexadiene (HD) using a zirconocene catalyst in the presence of chain transfer reagents. PMCP clearly shows fluidity and birefringence above the glass transition temperature under the ambient conditions. Schlieren-like texture, which indicates nematic liquid crystalline phase, has been detected in places. Clear diffraction pattern is observed in wide-angle X-ray diffraction analysis below the isotropization temperature. The isotropization temperature decreases with decreasing of molecular weight of the PMCP. PMCP with the higher molecular weight takes the longer time for liquid crystallization from isotropic phase. Non-Newtonian viscosity region in the range of low share rate, which is a characteristic of liquid crystal, has been detected below the isotropization temperature.

Introduction

Polyolefin resins, such as polyethylene or polypropylene, are widely employed to make a variety of products due to their excellent properties. Recent development of transition metal catalysts, such as metallocene catalyst, for olefin polymerization has not only improved the properties of manufactured polyolefins but also made us possible to synthesize new types of polyolefins.[1] Because polyolefins are basically composed with carbon and hydrogen and C−C single bond backbone, the polymers have flexibility that causes folding and entanglement of the polymer chains under the ambient conditions,[2,3] as shown in a model of polyethylene, Figure 1a. Mesophase or liquid crystalline phase of ordinary polyolefins has been observed under the particular conditions. Ungar observed the liquid crystalline feature, hexagonal mesophase, of polyethylene under the conditions of high pressure and temperature, for example 280−307 °C at 8 kbar.[4] Recently, de Jeu et al. found out shear-induced smectic ordering in isotactic polypropylene at 200 °C.[5,6] The concept of these investigations is to line up the polymer chains with external force. While structures and features of polyolefins have been widely investigated, their liquid crystal properties have not been clearly observed under the mild conditions, at around room temperature and normal pressure. If the molecular design of polyolefins induced the liquid crystalline features under the ambient conditions, it would enable us to have new uses of polyolefins.

Over the past few decades, liquid crystalline polymers have been used in a variety of fields, and a large number of studies on their synthesis and characterization have been reported.[7] Most of liquid crystalline polymers have a rigid mesogenic group with a characteristic structure in their main chain or side chain. Inserting a rigid mesogenic core into the flexible chains of polyolefins should be a useful method to induce the liquid crystalline phase. Synthesis of such the polyolefins, however, are difficult because the transition metal catalysts, such as Ziegler−Natta catalyst or group 4 metallocene catalysts used in the synthesis, limit the applicable vinyl monomers. For example, functional groups in polar vinyl monomers inhibit the active site of the catalyst from insertion of the vinyl group in the monomer, or vinyl monomers with extremely bulky side chain are hard to be polymerized with the transition metal catalysts.

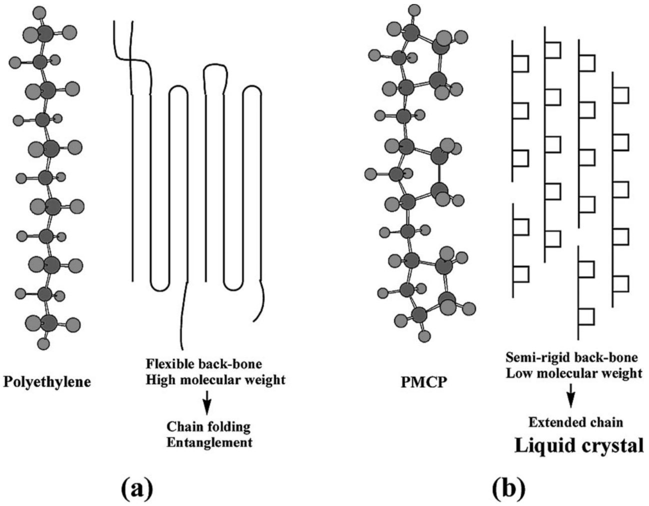

Figure 1. Molecular design of a liquid crystalline polyolefin.

We extensively investigated a new concept for designing mesomorphic polyolefins in which the topology of methylene linkage is controlled by inserting small cyclic units into the main chain of polyethylene.[8,9] We discovered that inserting 1,3-cyclopentane units into the main chain of polyethylene transformed the orthorhombic crystals into hexagonal crystals.[10,11]

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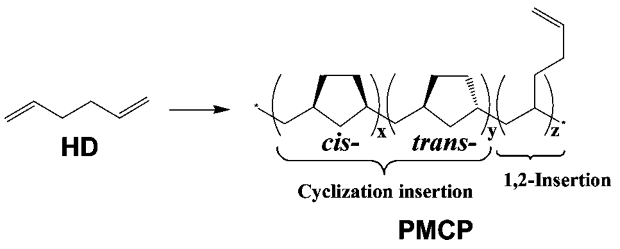
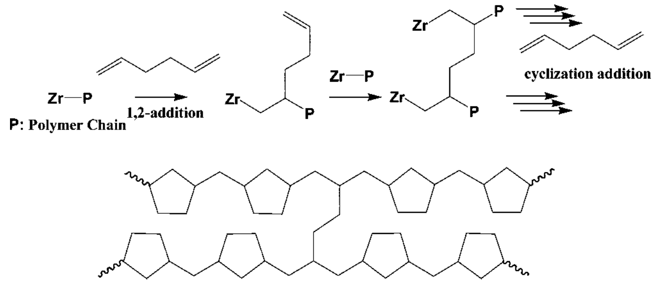
Scheme 1. Structure of PMCP Prepared by Cyclization Polymerization of HD



Scheme 2. Cyclopolymerization of HD without Chain Transfer Reagent



We expect that this observation should be relevant to the formation of mesophase, that is to say, the 1,3-cyclopentane units in the methylene linkage should give rigidity into the polymer chains and reduce entanglement and folding of polymer chains.[12] This led us to focus on the characteristic structure of poly(methylene-1,3-cyclopentane) (PMCP), which also forms hexagonal crystals and is produced by cyclization polymerization of 1,5-hexadiene (HD) with various transition metal catalysts,[13−16] as shown in Scheme 1. The 1,3-cyclopentane units in PMCP may play a role of like a rigid mesogen in the main chain of the methylene linkage that dose not deform the *trans*-zigzag conformation of polyethylene. PMCP has been widely considered to be a crystalline polymer, whose melting point ranged from 70 to 190 °C, which increased with increasing *cis*-content of the 1,3-cyclopentane structure.[16,17] We have found a mesophase in high molecular weight PMCP with high cyclization selectivity and high *trans*-content.[18] The PMCP sample showed elastomeric shape and birefringence and indicated formation of liquid crystalline phase. It was difficult, however, to show characteristic features of liquid crystal due to their high viscosity. The viscosity derived from the high molecular weight and cross-linking structure formed in the polymerization, as shown in Scheme 2, may be sufficiently large to lose the obvious fluidity and the birefringence dose not always show the well-known liquid crystalline texture.[19] If control of 1,3-cyclopentane structure without cross-linking and decreasing molecular weight of PMCP would be effective to prevent the polymer chains from forming entanglement and folding with maintaining the linearity of the polymer chain, then it would be possible to invest polyolefin with clear features of mesophase or liquid crystal, as shown in Figure 1b. This paper examines the synthesis of low molecular weight PMCP, and reports the characteristic features of mesophase of PMCP under the ambient conditions.

Scheme 3. Chain Transfer Reaction in Cyclopolymerization of HD in the Presence of Al(C$_2$H$_5$)$_3$ (a) and H$_2$ (b)

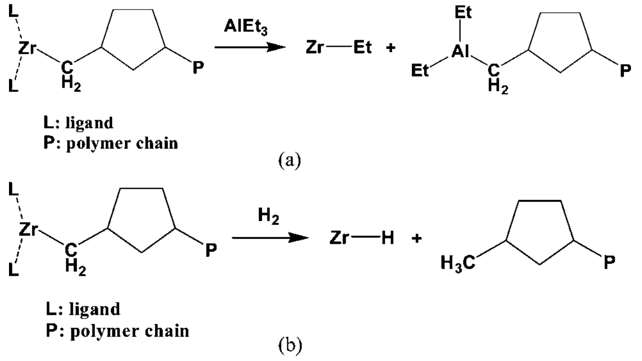


Table 1. Structures and Thermal Properties of PMCP Obtained with Catalyst 1[a]

sample	AlEt$_3$/Zr mol/mol	H$_2$ MPa	T_p[b] °C	[C][c] %	*trans*[d] %	M_n[e] ($\times 10^{-3}$)	M_w/M_n[e]	T_g[f] °C	T_i[f] °C
1	0	0	23	99.9	68.6	42.7	9.6	39.3	
2	200	0	23	99.6	74.1	6.9	5.6	9.3	73.1
3	400	0	23	99.6	71.6	5.9	4.4	−7.3	65.0
4	800	0	23	99.0	72.6	3.0	4.0	−12.7	59.3
5	1500	0	23	99.6	71.8	2.4	3.2	−14.8	46.4
6	2500	0	23	99.8	70.5	2.1	2.3	−18.0	42.7
7	0	0.1	23	98.3	72.3	5.6	3.8	2.2	65.4
8	0	0.5	23	99.5	73.2	3.0	7.4	0.3	55.0
9	0	0	−25	87.8	75.0	11.8	2.5		

[a] Polymerization conditions; [**1**] = 0.1 (mmol/L), MAO[Al]/[**1**] = 2000 (mol/mol), HD = 0.2 mol/L. [b] Polymerization temperature (rt: room temperature). [c] Cyclization ratio of polymerized HD units, [C] = {[x] + [y]}/{[x] + [y] + [z]} in Scheme 1, determined by ^{1}H NMR spectroscopy. [d] Content of *cis* and *trans* units in the cyclic units determined by ^{13}C NMR spectroscopy. [e] 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. [f] Glass transition (T_g) and isotropization temperature (T_i) determined by DSC at a heating rate of 10 °C/min after previous heating to 150 °C and cooling to −50 °C (second heating process).

Results and Discussion

PMCP samples were synthesized cyclization polymerization of HD using a zirconocene catalyst *rac*-dimethylsilylenebis(indenyl)zirconium dichloride **1**, using methyaluminoxane (MAO) as a cocatalyst in toluene with triethylaluminum (AlEt$_3$) or hydrogen as chain transfer reagents to decrease the molecular weight of the resulting polymer, as shown in Scheme 3. The polymerization without chain transfer reagent was also conducted as a reference (sample 1). The structure and properties of PMCP are summarized in Table 1, and the corresponding structures are shown in Scheme 1. Molecular weight of PMCP decreased with increasing of [AlEt$_3$]/[Zr] molar ratio or H$_2$ pressure, indicating that AlEt$_3$ and hydrogen effectively played a role of chain transfer reagent in the polymerization.[20−29] Although the polymerization was conducted with a homogeneous catalyst, molecular weight distributions of PMCP, especially that which was synthesized without chain transfer reagent (sample 1), was somewhat broad. The broad molecular weight distribution of PMCP should be derived from the cross-linking structure, as shown in Scheme 2. The molecular weight distribution has become narrow with the increasing of chain transfer reagents. Furthermore, no gel fraction (highly cross-linked part) was yielded in the polymerization with the chain transfer reagents. The chain transfer reagents have an effect on preventing from the cross-linking formation. The cyclization ratio of HD unit, [C] = {[x] + [y]}/{[x] + [y] + [z]} in Scheme 1, and *trans*-ratio of 1,3-cyclopenatene unit were almost independent of the amount of the chain transfer reagents.

The texture of PMCP was observed using a polarized optical microscope 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 PMCP samples with the high cyclization ratio (samples 2−8) showed birefringence not a part but throughout the soft and sticky specimens. Any spherulites, which are usually observed in crystalline

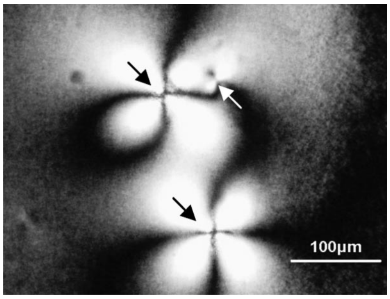


Figure 2. Polarized optical micrograph of PMCP (sample 4) at room temperature.

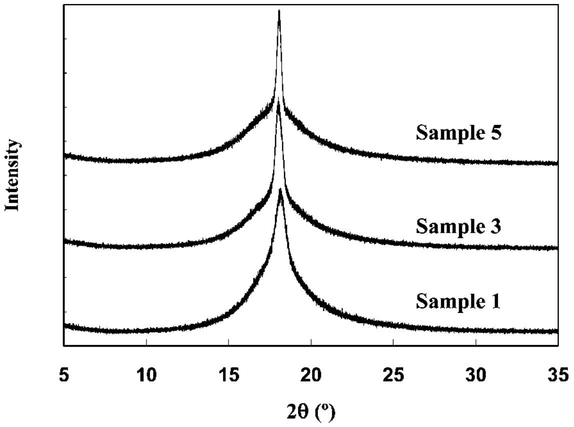


Figure 3. WAXD patterns of PMCP samples; samples, 1, 3, and 5 recorded at 25 °C.

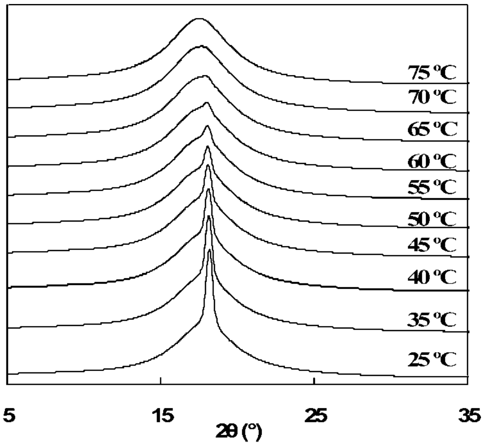


Figure 4. WAXD patterns of PMCP sample 3 recorded at 25−75 °C in heating process.

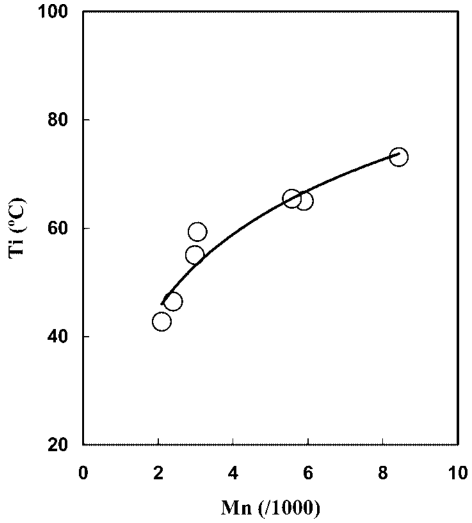


Figure 5. Relationship between number average molecular weight (M_n) and T_i of PMCP prepared in the presence chain transfer reagents.

polyolefin, were not detected in the present PMCP samples. These results indicate that the PMCP samples were not composed by mixture of amorphous domain and (micro)crystalline domain. While the greater part of the PMCP samples showed featureless texture, Schlieren-like structures were observed in places in sample 4, as shown in Figure 2. The textures pointed black or white arrows should be derived from disclination of $s = \pm 1$ or $\pm 1/2$, respectively. PMCP with the low molecular weight (samples 2−8) showed the similar optical texture, indicating nematic liquid crystalline phase. PMCP with high molecular weight (sample 1, M_n = 44700) showed birefringence, however, no characteristic optical texture, such as Schlieren structure due to their fairly high viscosity, as previously reported. PMCP, which was prepared at −25 °C, had low cyclization selectivity (87.8%) and did not show any optical textures (sample 9).

WAXD profiles of PMCP samples at room temperature are shown in Figure 3. Intense diffraction was observed at $2\theta = 18.1°$, and the diffraction corresponds to the lateral interchain packing distance, 4.9 Å, of mesophase. Peak width of the diffraction decreased with decreasing of the molecular weight of the PMCP samples. These WAXD patterns look like those of highly crystalline polymer, and many researchers believe that PMCP is a crystalline polymer as previously reported.[14] However, the form of PMCP for WAXD analysis is surely soft and sticky even at the room temperature.[30] WAXD profiles of sample 3 were recorded on the heating process from 25 to 75 °C (Figure 4). Intensity of the diffraction decreased from 35 °C with increasing of the acquired temperature and disappeared over 70 °C, which corresponds to the temperature of completion of isotropization detected with DSC measurement.[31]

Relationship between the molecular weight and isotropization temperature (T_i), where T_i denotes the endothermic peak top in the DSC chart of the second heating process[31] of PMCP, which is shown in Figure 5. The T_i showed a curved increase with an increasing of the molecular weight of PMCP, as reported in some liquid crystalline polymers.[32,33] PMCP with high molecular weight (sample 1) did not show clear transition temperature in the DSC analysis.[31] An exothermic peak, which corresponded to a mesophase from isotropic phase, was detected in the cooling process of the DSC analysis of PMCP.[33] Both the DSC analysis and optical microscope observation confirmed enantiotropy of the mesophase. The isothermal mesophase formation process of PMCP (samples 2 and 5) from isotropic phase at room temperature (25 °C between T_i and T_g), rapidly cooled from 150 °C to room temperature, was studied with a polarized optical microscope by measuring the intensity of depolarized light passing through the samples.[34−40] Time dependence on the weight fraction of mesophase formable polymer, which formed mesophase at time *t* (X_t), is illustrated in Figure 6. The profiles showed that the formation of mesopahse started immediately at 25 °C without an induction period, which was ordinarily detected in crystalline polymer. Half-time of the formation of mesophase ($t_{1/2}$) of samples 2 and 5 were 1930 and 470 s, respectively. The results clearly show that PMCP, with a higher molecular weight, takes a longer time for the formation of mesophase from the isotropic phase due to its higher viscosity. Although a long period of annealing of high molecular weight PMCP (sample 1) at a little higher temperature than the T_g did not induce the formation of Schlieren-like structures, the treatment was effective for the increase of the intensity of depolarized light, that is to say, liquid crystallinity.

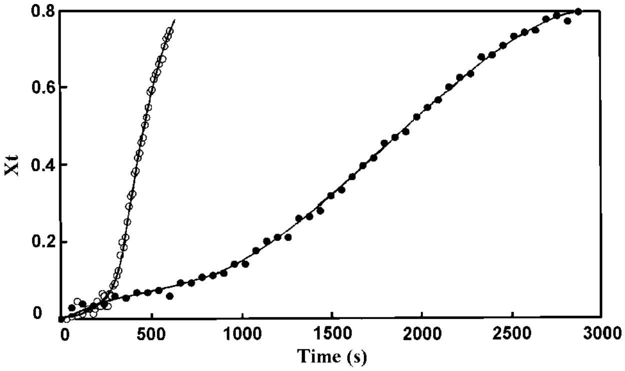


Figure 6. Time dependence on the weight fraction of mesophase formable polymer that formed mesophase at time *t* (X_t); sample 2 (black circle), sample 5 (white circle).

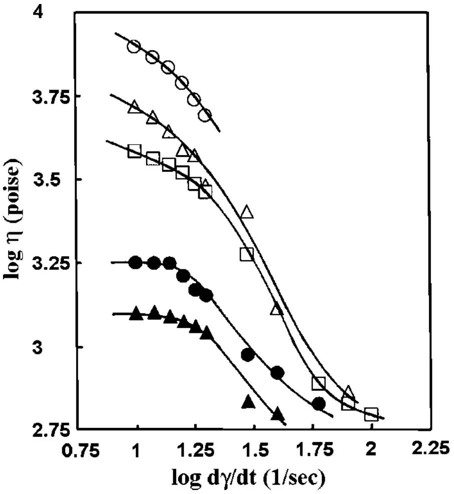


Figure 7. Relationship between share rate ($d\gamma/dt$) and viscosity (η) of PMCP (sample 8) at 75 °C (white circle), 80 °C (white triangle), 85 °C (white square), 90 °C (black circle), and 100 °C (black triangle).

The PMCP samples are enough fluid to measure viscosity with a cone and plate viscometer. Figure 7 shows effect of temperature and shear rate on viscosity of PMCP (sample 8). Viscosity of PMCP drastically decreased over the temperature of completion of isotropization (85.2 °C detected with DSC). A Newtonian viscosity region, which indicated isotropic fluid, was observed in the range of low share rate over the temperature of completion of isotropization (at 90 and 100 °C). On the other hand, the measurements below the temperature of completion of isotropization did not exhibit a Newtonian viscosity region even in the range of low share rate ($d\gamma/dt < 1.25$). This observation is a characteristic feature of liquid crystalline polymers.[40−48]

Precise molecular design of a PMCP produced the first example of a polyolefin with a mesophase under the ambient conditions. Both high cyclization selectivity of the inserted HD units and a high *trans*-content of the 1,3-cyclopentane units are required to induce the mesophase in PMCP. Lowering the molecular weight is also effective to induce the clear mesomorphic features. Both the results of the microscopic Schlirene-like optical texture and the lateral interchain distance would reflect the nematic character of the mesophase. We also tried to find the mesophase of poly(1,3-cyclopentane) (PCPE), which is composed of a rigid 1,3-cyclopentane segment (with no methylene unit). The mesophase, however, has not been observed in PCPE. PMCP is a semirigid polymer composed of a rigid 1,3-cycloetane unit and a flexible methylene unit. The 1,3-cyclopentane unit provides linearity in the polymer chain and should influence the interchain packing and interaction to form the mesophase. In addition, decreasing the molecular weight of PMCP should prevent from forming the entanglement of the polymer chains. The T_i was controllable with control of PMCP molecular weight and decreased with decreasing molecular weight.

The mesomorphic features of PMCP have applications in polymer science as well as in the development of high-performance polyolefins.

Experimental Section

Materials. *rac*-Dimethylsilylenebis(indenyl)zirconium dichloride, **1**, was commercially obtained from Boulder Science Co., Ltd., and used without further purification. A toluene solution of MAO was commercially obtained from Albemare Co., Ltd., and used as solid after evaporation of toluene. A toluene solution of $AlEt_3$ was commercially obtained from Kanto Chemical Co., Inc., and used as received. HD (Tokyo Kasei) was dried with CaH_2 and distilled under a nitrogen atmosphere. Toluene (Kanto Chemical Co., Inc.) was dried with CaH_2 and distilled under a nitrogen atmosphere.

Synthesis of PMCP. The polymerization of HD was carried out in a 100 mL glass reactor equipped with a magnetic stirrer. MAO, toluene, and HD were added to the reactor under a nitrogen atmosphere. A toluene solution of $AlEt_3$ was used as a chain transfer reagent to control the molecular weight of PMCP. The polymerization was started by introducing a toluene solution of a zirconocene catalyst **1** to the reactor and terminated by adding a small amount of methanol. The polymerization was also conducted in a 100 mL stainless steel auto clave with hydrogen as a chain transfer reagent instead of $AlEt_3$. The polymer was precipitated in a large excess of methanol and recovered by filtration. The polymer obtained was extracted with boiling *o*-dichlorobenzene (ODCB) to remove the catalyst residues and gel fraction of the polymer. The gel fraction, a highly crosslinking polymer that was insoluble in boiling ODCB, was obtained only in PMCP sample 1 obtained without any chain transfer reagents. The solution of extracted polymer was concentrated by evaporation, and the polymer was reprecipitated in a large excess of methanol. The precipitate was recovered by filtration or decantation and dried in vacuo at 60 °C for 6 h.

Analytical Procedures. ^{1}H and ^{13}C NMR spectra of the PMCP were recorded at 100 °C on a JEOL Alpha-300 spectrometer in pulse Fourier transform mode. The sample solution was made in 1,2,4-trichlorobenzene/C_6D_6 (9/1 v/v) or $CDCl_3$ as solvents and the resonance of C_6D_6 (7.15 ppm, 128.03 ppm) or $CDCl_3$ (7.24 ppm, 77.03 ppm) was used as an internal reference. Molecular weight and molecular weight distribution of the PMCP were measured at 40 °C by means of gel permeation chromatography (GPC), Shimadzu Prominence GPC System, using chloroform as a solvent and calibrated with standard polystyrene samples. The samples for optical micrographs, DSC measurement, and WAXD were prepared after previous heating to 150 °C and cooling to room temperature. The polarized optical micrographs of the PMCP were observed using an optical microscope (Olympus BX50). The weight fraction of mesophase formable polymer that formed mesophase at time *t* (X_t) was calculated from depolarized light, which was measured with the optical microscope equipped with a CdS light sensor with fixed electrical current as an analyzer, using the following equation; $X_t = 1 - (V_\infty - V_t)/(V_\infty - V_0)$, where V_∞, V_t, and V_0 are output voltage of CdS sensor after the liquid-crystallization at time *t* and at time 0, respectively.[38−40] DSC measurement was made on a Rigaku DSC-8230 at a heating or cooling rate of 10 °C/min from −50 to 150 °C, previously heating to 150 °C and cooling to −50 °C. WAXD patterns of PMCP were recorded on Rigaku RAD-C or *R*-AXIS RAPID equipped with controlled heater, using Cu Kα radiation. Viscosity of PMCP was measured with a cone and plate viscometer (Brookfield CAP Viscometer, Model CAP 2000+).

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Supporting Information Available: A movie of handling of PMCP sample 5 at room temperature and DSC charts of samples 3, 5, and 6. This information is available free of charge via the Internet at http://pubs.acs.org.

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(30) A movie of handling of PMCP sample 5 at room temperature is available in Supporting Information.

(31) DSC charts of samples 3, 5, and 6 are available in Supporting Information.

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