Macromolecules **2007,** *40,* 6859−6862

Novel Liquid Crystalline Polyrotaxane with Movable Mesogenic Side Chains

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Received April 3, 2007; Revised Manuscript Received July 15, 2007

ABSTRACT: A novel side-chain liquid crystalline polyrotaxane (LCPR) whose mesogenic side chains can slide and rotate on the linear backbone was first developed. To obtain the LCPR, 6-(4′-cyanobiphenyl-4″-yloxy)hexanoyl chloride was prepared and reacted with a polyrotaxane consisting of α-cyclodextrin, poly(ethylene glycol) ($M_w = 35\,000$), and adamantane end groups. The molecular characterization of the LCPR was performed with FT-IR, ^{1}H NMR, and gel permeation chromatography analysis. Its phase structures and transitions were investigated by differential scanning calorimetry, wide-angle X-ray diffraction, and polarized light microscopy experiments. The experimental results shows that the LCPR has glass transition at 70 °C and mesomorphic−isotropic transition at 129 °C.

Introduction

Diverse structures of liquid crystalline polymers (LCPs) have been prepared by incorporating mesogenic molecular structures into their main and side chains.[1] In such cases, covalent bonds are generally used to achieve the desired molecular structure. On the other hand, supramolecular architectures through mechanical bonding have generated great interest in recent years due not only to their structures and properties but also to their potential applications as smart and stimuli-responsive materials.[2−6] Polyrotaxanes (PRs) are supramolecular polymers in which a number of cyclic molecules are threaded onto a linear polymer chain and are mechanically interlocked in the polymer chain by bulky end groups.[7−14] The most characteristic feature of PRs is that each macrocycle slides and rotates on the polymer chain. This feature enables the preparation of fascinating molecular materials such as molecular tubes formed by cross-linking macrocycles in a single PR,[15] insulated molecular wires incorporating conductive polymers,[16,17] and drug delivery systems.[18,19] We have also reported a novel gel, called a topological gel or a slide-ring gel, which has movable figure-of-eight cross-links formed by cross-linking cyclic molecules on different PRs.[20]

In particular, PRs comprised of α-cyclodextrin (α-CD) and poly(ethylene glycol) (PEG) have been studied extensively due to their facile synthesis and biocompatibility.[4,18−23] Additionally, the α-CD moiety is very convenient for functionalization because it has 18 hydroxyl groups that can be subjected to chemical modification with a variety of functional groups. Modification of the CD provides the PR with fascinating properties such as useful solubility,[26] fluorescence,[24,27] biological functionality,[28,29] and stimuli responsivity.[30−33] For instance, methylation of CD provides the PR with a thermoreversible sol−gel transition property as well as with water solubility.[30−33] We extend this modification concept to LCPs, creating new side-chain LCPs with mobile mesogens along the polymer main chain that can rotate around the chain, as shown in Figure 1.

In this study, we report the first example of a liquid crystalline PR (CB5PR) built by mesogen-substituted cyclodextrins and PEG, which provides new liquid crystalline polymers with high-mobility mesogenic side chains, as compared to conventional LCPs having covalently bonded mesogenic side chains.

Experimental Section

Materials. All the materials used in this study were commercial samples and were used as supplied, unless otherwise stated. The polyrotaxane used in this study was prepared from α-CD, poly(ethylene glycol) of average molecular weight 35 000, and 1-adamantanamine, according to the previously reported method.[25] The number of α-CD in the polyrotaxane was estimated to be ca. 110 from the ^{1}H NMR signals, which corresponds to 28% coverage of the PEG chain by α-CDs, assuming that a α-CD molecule can perfectly cover two PEG monomer units. 6-(4′-Cyanobiphenyl-4″-yloxy)hexanoic acid was prepared from 6-bromohexanoic acid according to a procedure described in the literature.[34]

Synthesis. Ethyl 6-(4′-Cyanobiphenyl-4″-yloxy)hexanoate. Ethyl 6-bromohexanoate (54.6 g, 0.245 mol), 4-cyano-4′-hydroxybiphenyl (40.0 g, 0.205 mol), anhydrous potassium carbonate (30.0 g, 0.218 mol), and a small amount of potassium iodide were stirred in DMF (100 mL) for 48 h at 50 °C in a flask under an argon atmosphere. Subsequently, 300 mL of ethyl acetate was added to the reaction mixture, and it was washed with 300 mL of water three times. After the organic phase was dried over anhydrous magnesium sulfate and filtered off, the ethyl acetate was removed by evaporation. The obtained solid was purified by recrystallization from ethanol, giving ethyl 6-(4′-cyanobiphenyl-4″-yloxy)hexanoate as a white powder (80.0 g, 80%); mp 88−89 °C (lit.[34] 88−89 °C). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): $\delta = 1.26$ (t, 3H, $J = 7.1$ Hz, $-CH_3$), 1.46−1.92 (m, 6H, $-CH_2-$) 2.35 (t, 2H, $J = 7.4$ Hz, $-CH_2COO-$), 4.01 (t, 2H, $J = 6.3$ Hz, $-OCH_2-$), 4.14 (q, 2H, $J = 7.1$ Hz, $-CH_2OCO-$), 6.98 (d, 2H, $J = 9.0$ Hz, ArH), 7.53 (d, 2H, $J = 9.0$ Hz, ArH), 7.64 (d, 2H, $J = 8.5$ Hz, ArH), and 7.69 (d, 2H, $J = 8.5$ Hz, ArH).

6-(4-Cyanobiphenyl-4′-yloxy)hexanoic Acid. The ester (80.0 g, 0.237 mol) and potassium hydroxide (20.0 g, 0.356 mol) were stirred in ethanol (500 mL) for 3 h at 80 °C in a flask under an argon atmosphere. The resultant yellow slurry was poured into iced

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10.1021/ma070785u CCC: \$37.00

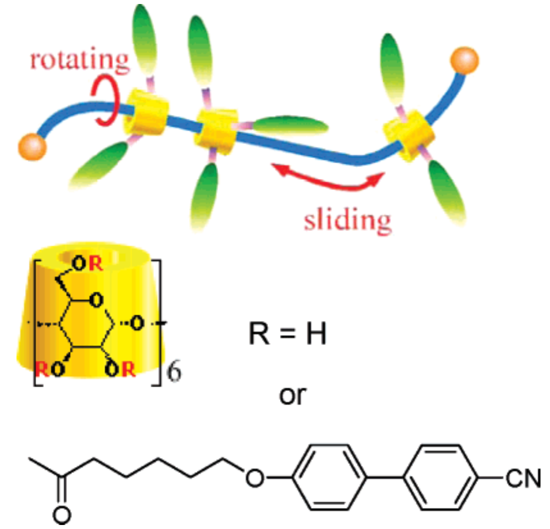

Figure 1. Structure of mesogen-substituted polyrotaxane.

water (700 mL) and then neutralized with concentrated hydrochloric acid. The white precipitate was filtered off, washed with water, and dried under vacuum. Recrystallization from ethanol (700 mL) provided 6-(4′-cyanobiphenyl-4″-yloxy)hexanoic acid as a white powder (58.7 g, 80%), K 163.7 °C I 157.1 °C N 134.3 °C (from DSC) (lit.[34] K 163.7 °C I 157.1 °C N 134.3 °C from DSC). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): $\delta = 1.28-1.80$ (m, 6H, $-CH_2-$), 2.24 (t, 2H, $J = 7.3$ Hz, $-CH_2COO-$), 4.01 (t, 2H, $J = 6.3$ Hz, $-OCH_2-$), 7.03 (d, 2H, $J = 8.8$ Hz, ArH), 7.66 (d, 2H, $J = 8.8$ Hz, ArH), 7.70 (d, 2H, $J = 8.3$ Hz, ArH), 7.93 (d, 2H, $J = 8.3$ Hz, ArH), and 12.02 (s, 1H, COOH).

6-(4′-Cyanobiphenyl-4″-yloxy)hexanoyl Chloride. The acid (4.29 g, 13.9 mmol) was added to thionyl chloride (26 mL) in an iced bath and stirred for 15 h at room temperature in a flask under an argon atmosphere, giving a clear yellow solution. This solution was then gently heated to 50 °C for 60 min to expel any remaining gases from solution. The excess thionyl chloride was then removed under reduced pressure, and the oily residue coevaporated several times with dry diethyl ether. The acid chloride was then used in the next step without further purification.

Preparation of Cyanobiphenyl-Substituted Polyrotaxane (CB5PR). Polyrotaxane (1.0 g), dried under vacuum at 80 °C for 1 h, was dissolved in 20 mL of dry *N,N′*-dimethylacetamide (DMAc) with 8% lithium chloride. To the solution, triethylamine (1.8 mL, 12 mmol) and a dry DMAc solution of the above-prepared acid chloride (1.0 equiv to OH groups of polyrotaxane) was slowly added under an argon atmosphere in an iced bath and then stirred for 24 h at room temperature. The reaction mixture was poured into water (350 mL), and the precipitate was collected by filtration. The obtained solid was dissolved in DMAc and precipitated from methanol and ethanol several times and then collected by centrifugation. The precipitate was dried under vacuum at 50 °C to give 2.0 g of CB5PR as a pale yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): $\delta = 1.0-2.5$ (CH_2 of alkyl spacer), $2.8-6.2$ (Ph−O−CH_2, H of CD, and CH_2 of PEG), $6.6-8.2$ (H of biphenyl). FTIR-ATR (ν_{max}, cm^{-1}): 3399, 2936, 2871, 2225, 1732, 1603, 1495, 1249, 1180, 1032, and 822. Anal. Calcd for $((C_{36}H_{52.4}O_{30})\text{-}(C_2H_4O)_{7.4}(C_{19}H_{18}NO_2)_{7.6}(H_2O)_4)_n$: C, 65.40; H, 6.38; N, 2.97. Found: C, 65.21; H, 6.08; N, 2.82.

Characterization. FTIR spectra were recorded on a Nicolet 4700 FT-IR spectrophotometer equipped with a DuraSamplIR diamond ATR accessory (SENSIR Technologies). The spectral resolution was maintained at 2 cm^{-1}. The obtained spectra were corrected by using the Advanced ATR correction of the OMNIC software with the following parameters: crystal is diamond, number of reflections is one, angle of reflection is 45°, and the refractive index of the sample is 1.5. NMR spectra were recorded on a JEOL JNM-AL400 spectrometer. Gel permeation chromatography: (GPC) was carried out on a TOSOH GPC system HLC-8220, equipped with a refractive index detector (two TSK-GEL SUPER AWM-H columns; eluent: DMSO/0.01 M lithium chloride; flow rate: 0.5 mL min^{-1}; temperature: 50 °C). Differential scanning calorimetry (DSC) measurements were carried out using a Seiko Instruments Inc. EXTAR SII-6000 DSC system. Each sample was encapsulated in a silver pan (5 mm in diameter) and heated from 20 to 200 °C at a heating rate of 10 °C min^{-1} in a nitrogen flow. Polarized optical microscopy was performed on an Olympus CH-2 microscope fitted with a Linkam TH600 hot stage and a Linkam PR600 thermal controller. A photomicrographic attachment was used to take images under cross-polarized light. To obtain micrographs, a powder sample was placed between two glass slides. The X-ray diffraction patterns were measured using a diffractometer (type 4037, Rigaku) with graded *d*-space elliptical side-by-side multilayer optics, monochromatic Cu Kα radiation (40 kV, 30 mA, $\lambda = 1.542$ Å), and an imaging plate (R-Axis IV) in a flat camera. The samples were sealed in quartz capillary tubes (1.5 mm diameter; 0.01 mm wall thickness) and positioned on a hot stage (Mettler FP82HT). The powders were exposed to radiation for 10 min with a camera length of 150 mm.

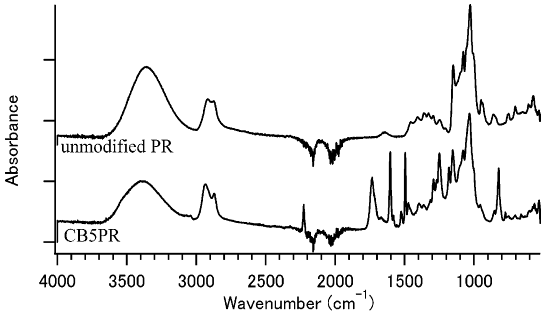

Figure 2. FTIR-ATR spectra of CB5PR (bottom) and unmodified PR (upper).

Results and Discussion

Synthesis and Characterization of CB5PR. The PR comprising PEG (average molecular weight = 35 000) and α-CD was prepared by a previously reported method.[25] The number of α-CDs in a single PR is estimated at ca. 110, which corresponds to 28% coverage of the PEG chains with α-CDs. The controlled coverage is important to our molecular design because the α-CDs should have enough space to move along the PEG chain. A mesogenic group based on biphenyl was employed because it has been extensively studied in both low-molecular-mass materials and in polymers and is reasonably stable under a variety of conditions. 6-(4′-Cyanobiphenyl-4″-yloxy)hexanoic acid was prepared from 6-bromohexanoic acid according to a procedure described in the literature.[34] In the key step of the synthesis, the acid chloride of biphenyl was coupled selectively to the hydroxyl group on the cyclodextrin, the ring molecule of PR, because the PEG has no functional groups on its chain.

Figure 2 shows the FTIR-ATR spectra for CB5PR and the unmodified PR. The most typical peak is observed for CB5PR at 2225 cm^{-1}, assigned to the stretching absorption of the cyano groups of biphenyls. Another significant peak is the C=O stretching of the esters at 1733 cm^{-1}. The peaks at 1603 and 1495 cm^{-1} indicate the existence of para-substituted aromatic hydrocarbons: cyanobiphenyl side chains.[35]

The ^{1}H NMR spectra for CB5PR with a side-chain unit and the unmodified PR are shown in Figure 3. The peaks of the PR are broadened after modification. However, peaks originating from the side chain are distinctly observed in the regions of 6.6−8.2 and 2.8−6.2 ppm. The modification ratio of the products was estimated to be 42% of the OH groups of the PR, which implies that ca. 7.6 cyanobiphenyls were introduced per α-CD by comparing the integrations between the regions at 6.6−

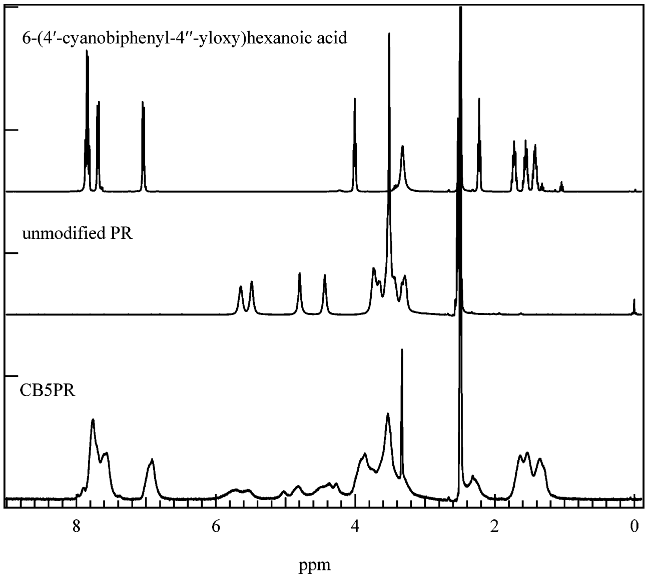

Figure 3. 400 MHz ^{1}H NMR spectra of CB5PR (bottom), 6-(4′-cyanobiphenyl-4″-yloxy)hexanoic acid (upper), and the unmodified PR (middle) in DMSO-d_6.

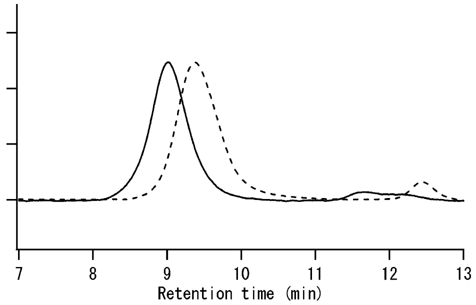

Figure 4. GPC chromatograms for CB5PR (solid line) and the unmodified PR (broken line).

8.2 ppm (biphenyl rings) and at 2.8−6.2 ppm (CH_2 of Ph−O−CH_2, H of CD, and CH_2 of PEG other protons). The ratio was also confirmed by using 1,3,5-benzenetricarboxylic acid as a internal standard for integration.

The purity of biphenylated polyrotaxane was examined by GPC. Figure 4 shows the chromatograms for CB5PR and the unmodified PR. A large peak assigned to the CB5PR is observed at around 9 min. The position of the peak is shifted to a higher-molecular-weight region, as compared with that of the unmodified PR, indicating an increase in molecular weight due to the addition of side chains. Impurity in the low-molecular-weight region is hardly observed. These results indicate that modification of the PR with cycanobiphenyl successfully occurs with this synthetic scheme.

Phase Transitions and Phase Structures. Figure 5 shows the differential scanning calorimetry (DSC) thermograms of CB5PR. On heating, an endothermic peak is observed at 136 °C. Upon cooling, two transitions are observed at 129 and 70 °C. The transition at 70 °C probably resulted from a glass transition because the transition curve depends on the thermal history of the sample. The transition at 129 °C is not observed for the unmodified PR; therefore, the transition must originate from the modification with mesogenic side chains. The temperature at 129 °C corresponds to a mesomorphic-to-isotropic transition, as observed with a polarizing optical microscope.

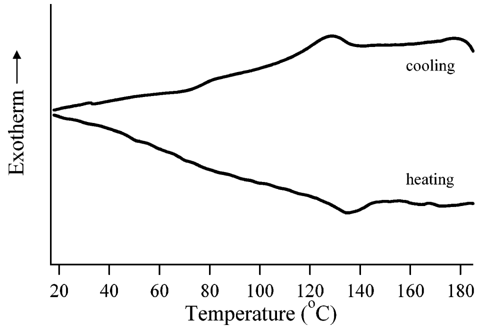

Figure 5. DSC thermograms of CB5PR on heating and cooling at 10 °C/min.

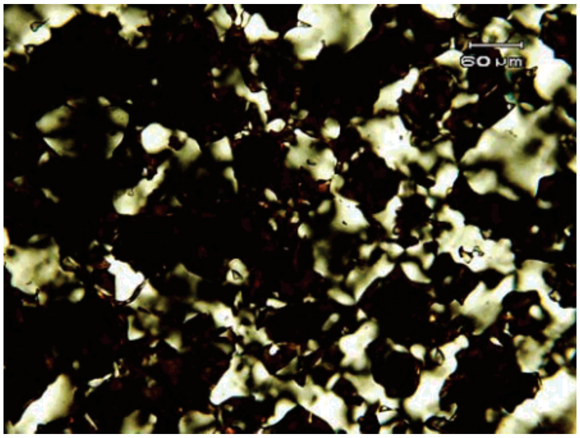

Figure 6. Polarizing optical micrograph of CB5PR at 100 °C.

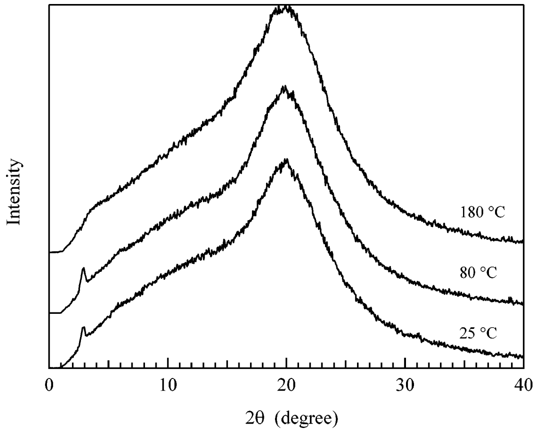

Figure 7. XRD patterns of CB5PR at 25, 80, and 180 °C.

Figure 6 shows a polarizing optical microphotograph of CB5PR at 100 °C. A schlieren-like texture, identified as a nematic or smectic phase, is observed. The brightness of the view field gradually increases with decreasing temperatures, and the texture is maintained up to room temperature. This result indicates that CB5PR forms a liquid crystalline glass state at room temperature.

X-ray diffraction (XRD) patterns of CB5PR measured at 25, 80, and 180 °C are shown in Figure 7. Two diffraction peaks are observed—at $2\theta = 2.9°$ (30 Å) and 20.0° (4.4 Å)—at 25 and 80 °C, whereas the small-angle peak disappears at 180 °C. According to the literature,[36] the typical XRD pattern of a nematic liquid crystal is characterized by (i) a diffuse peak in the high-angle region and (ii) a broad peak (rarely visible due to its low intensity) in the low-angle region. The XRD diagram of the LCPR actually has these two features: it exhibits a diffuse halo at $2\theta = 20.0°$ and a small peak at $2\theta = 2.9°$. Therefore, CB5PR seems to have a nematic mesophase at temperatures below 130 °C.

Conclusions

Liquid crystalline polyrotaxane with movable mesogenic side chains was first synthesized. 6-(4′-Cyanobiphenyl-4″-yloxy)-hexanoyl chloride was reacted with a polyrotaxane consisting of α-CD, PEG, and adamantane end groups. The chemical structures of the monomers and polymer were confirmed by various characterization techniques. Their phase structures and transitions of the polymers were investigated with DSC, POM, and WAXD. The LCPR shows glass transition at 70 °C and mesomorphic−isotropic transition at 129 °C. Further experiments including systematic synthesis and measurements are in progress to investigate the type of mesophase and pattern of the molecular packing in more detail. We believe that the potential of LCPRs with movable mesogenic side chains as a new system of LCP needs to be explored by researchers in search of the ways of making new specialty materials.

Acknowledgment. The authors thank Dr. Hiroyuki Minamikawa (National Institute of Advanced Industrial Science and Technology (AIST)) for the XRD measurements.

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MA070785U