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Communications to the Editor

Synthesis and Liquid Crystalline Behavior of Stereoregular Polyketones with Mesogenic Side Chains

Kyoko Nozaki,*,[†,‡] Yasutoyo Kawashima,[†] Takuro Oda,[†] and Tamejiro Hiyama*,[†]

Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan, and Conversion and Control by Advanced Chemistry, PRESTO, Japan Science and Technology Corporation (JST)

Kiyoshi Kanie and Takashi Kato*

Department of Chemistry & Biotechnology, Graduate School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

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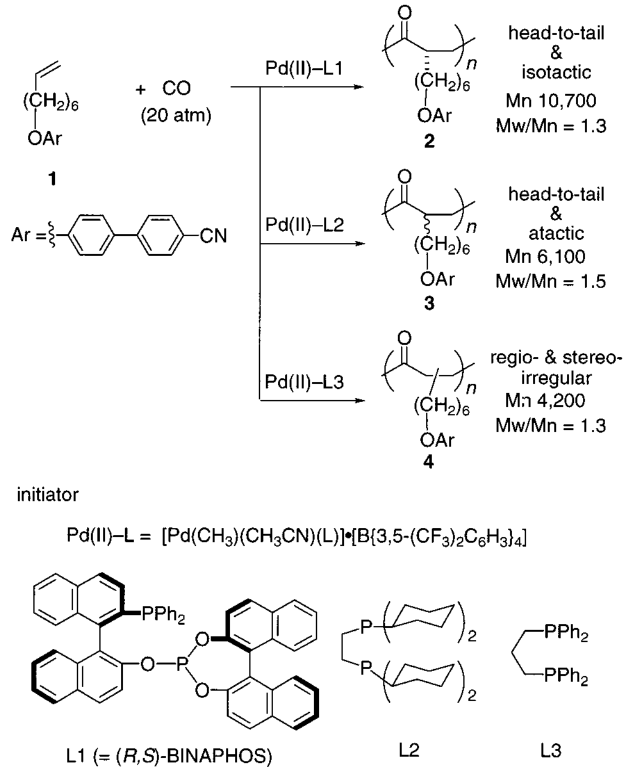
Although a large number of side-chain liquid crystalline polymers (SCLCP) have been developed in the past two decades, only a few reports concern the effects of backbone stereoregularity.[1,2] Lenz and Spassky synthesized backbone−chiral SCLCPs by ring-opening polymerization of optically active monomers.[3,4] The chirotopic centers in the backbone derived the formation of the chiral nematic phase. As an alternative synthetic route toward backbone chiral SCLCPs, here we choose the asymmetric polymerization of achiral monomers.[5] The asymmetric alternating copolymerization of carbon monoxide with mesogen-substituted α-olefins[6−9] provides SCLCPs having a chiral poly(1,4-ketone) as the backbone. We will discuss the relation between the stereoregularity of the backbone and the liquid crystalline behavior of the polymers. Very recently, two examples of liquid crystalline poly(1,4-ketone)s appeared in the literature. Sudhölter and Rieger reported a polyketone with a regio- and stereoirregular backbone;[10] Osakada reported poly(allene-*alt*-CO).[11]

Aliphatic 1-alkene **1** with a mesogenic substituent was prepared as described previously[12] and subjected to an asymmetric alternating copolymerization with carbon monoxide using $[Pd(CH_3)(CH_3CN)(L1)]\cdot\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}$ (L1 = (*R*,*S*)-BINAPHOS) as shown in Scheme 1.[7] The highly head-to-tail and isotactic polyketone **2** was thus obtained. Atactic head-to-tail polyketone **3**[8] and regio- and stereoirregular polyketone **4**[13] were also prepared using 1,2-bis(dicyclohexylphosphino)ethane (L2) and 1,3-bis(diphenylphosphino)propane (L3), respectively. The stereoregularity of polymers **2**, **3**, and **4** was confirmed by ^{13}C NMR (Figure 1). In a carbonyl carbon region, there is a sharp resonance at 214.6 ppm, representing the highly isotactic structure of **2** (Figure 1a). From our previous studies on propene/CO and styrene/CO copolymerizations,[6,7] we assume that the absolute configuration of the chirotopic carbon is *S*. In contrast, the resonance at 213.8 ppm is broadened due to the atactic nature of **3** in Figure 1b. The carbonyl peaks of random polyketone **4** are too broad to discuss the structure (Figure 1c).[13] Instead, the resonances of the other two backbone carbons at 41−47 ppm indicate that orientation of the substituents on the backbone is rather irregular.

Scheme 1



The thermal properties and liquid crystalline behavior of polyketones **2**, **3**, and **4** were investigated by polarized optical microscopy (POM) and differential scanning calorimetry (DSC) analysis (Figure 2). All transitions are reversible and do not change on repeated cooling and heating cycles. Upon heating, polymer **2** shows a glass transition at 53 °C, crystallization at 88 °C (ΔH = 1.30 kcal/mol), and a melting transition at 149 °C. Atactic polyketone **3** also crystallized at 84 °C with a much smaller enthalpy value ($\Delta H = 0.40$ kcal/mol). On cooling, isotactic **2** changed its phase from isotropic liquid to chiral nematic at 106 °C ($\Delta H = 0.18$ kcal/mol) and then smectic around 85 °C. The transition was observed under the microscope. The chiral nematic texture is shown as Figure 3. Atactic **3** exhibited a nematic phase at 115 °C ($\Delta H = 0.29$ kcal/mol) and then a smectic phase below 102 °C. In contrast to the regioregular **2** and **3**, enantiotropic nematic phases were observed for regioirregular polyketone **4** in the temperature ranges of 39−111 °C (heating) and 106−33 °C

[†] Kyoto University.

[‡] Japan Science and Technology Corporation (JST).

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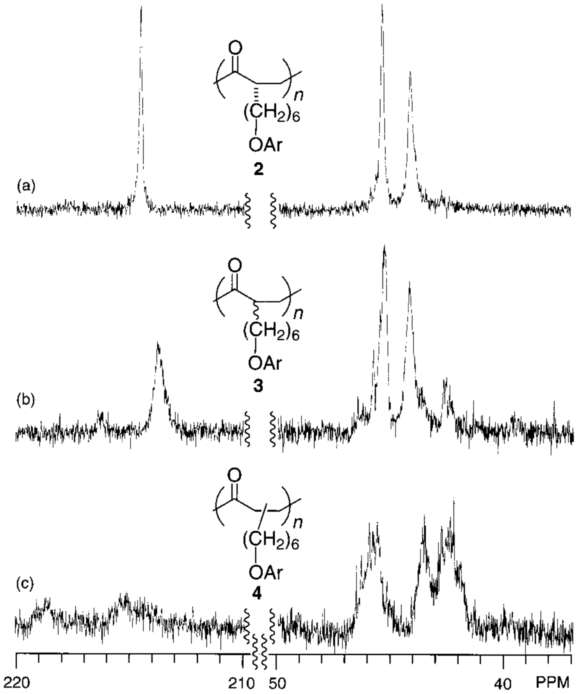

Figure 1. ^{13}C NMR spectra of the carbonyl carbons (left column) and the other two backbone carbons (right column) of (a) **2**, (b) **3**, and (c) **4**. (a) The sharp resonance at 214.6 ppm represents the highly isotactic structure of **2**. (b) The resonance at 213.8 ppm is broadened due to the atactic nature of **3**. (c) The carbonyl peaks are too broad to discuss the structure. The complex resonances at 41−47 ppm indicate that structure of **4** is irregular.

(cooling).[10] From the observations mentioned above, the following features have been elucidated. (1) The asymmetric center of the backbone induces chirality in the liquid crystalline phase of **2**.[3,4] (2) The liquid crystalline behaviors of **2** and **3** are monotropic, while that of **4** is enantiotropic. This difference suggests that the stereoregularity induced crystallinity in **2** and **3**. (3) The crystalline phase of **2** is much more stable than that of **3** as can be seen in the enthalpy values.

Although the head-to-tail and isotactic 1,4-polyketones form polyspiroketals, occasionally,[8] the contribution of the spiroketal structure to the thermal behavior of **2** is less probable, at least after the first heating. When **2** was analyzed by IR, the C=O absorption increased slightly after the first heating, remained constant, and never disappeared during subsequent cooling−heating scans regardless of the phases.[14]

In conclusion, we reported the synthesis and thermal properties of liquid crystalline side-chain polyketones with different backbone stereoregularities. Significant influences of the backbone structure have been manifested: that is, higher stereoregularity increased stability of the crystalline phase, and moreover, the liquid crystalline phase of isotactic **2** was endowed with chirality due to the chirotopic center in the backbone.[15]

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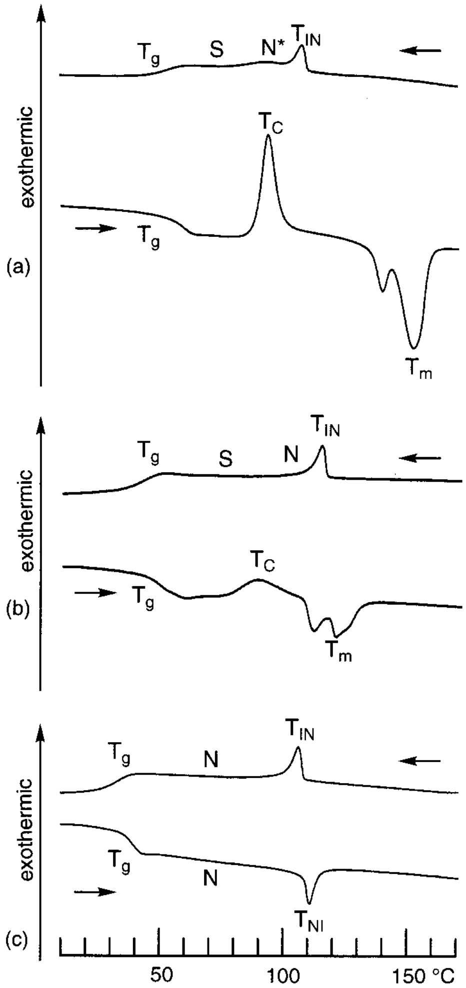

Figure 2. DSC analyses of the first cooling and the second heating of polymers (a) **2**, (b) **3**, and (c) **4**. The scanning rate was 20 °C/min. The phases were determined by polarized optical microscopy observations.

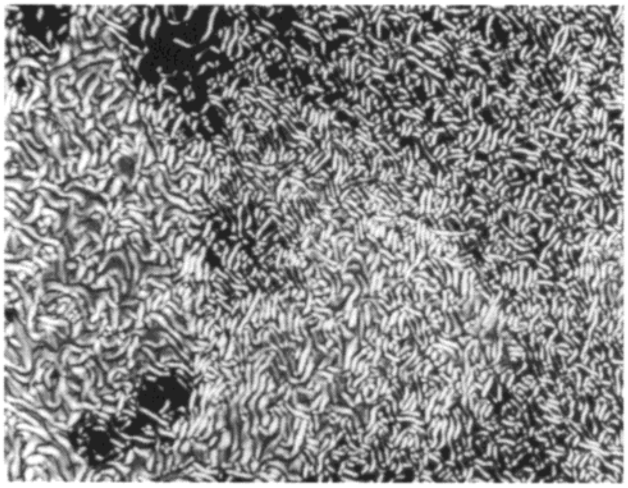

Figure 3. Fingerprint texture of polymer **2** (×400) at 100 °C on cooling.

Supporting Information Available: The experimental procedure for the preparation of polymers **2**, **3**, and **4** and the temperature variable IR of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Currently, it is not clear why polyketone **2** forms the chiral nematic phase. This may originate either from the slightly twisted stacking of nematic sheets in which mostly linear main chains are included[16] or from a helical conformation of the main chain.[17]

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