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Chiral and Steric Recognition in Optically Active, Isotactic, Alternating α-Olefin−Carbon Monoxide Copolymers. Effect on Physical Properties and Chemical Reactivity

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Chiral and steric recognitions play critical roles in selective binding and resultant high stereo- and enantioselectivity in chemical reactions mediated by bioactive macromolecules such as enzymes and nucleic acids. While selective interactions between small, chiral, organic compounds have been studied extensively,[1] there are very few documented examples (mostly polyesters) of chiral recognition between macromolecules possessing main-chain chirality.[2] Herein, we report the presence of both strong chiral and steric recognitions between optically active, highly isotactic, alternating α-olefin−carbon monoxide copolymers with 1,4-keto groups in the backbone[3] (Figure 1) and their effect on both the physical properties and chemical reactivity of the polymers. Thus, an alternating α-olefin−carbon monoxide copolymer with a given chiral sense for the tertiary carbons in the main chain can distinguish (a) between the two possible chiral senses for the tertiary carbons in the main chain of a second α-olefin−carbon monoxide copolymer even when the latter has a different pendant alkyl group and (b) between the length of the pendant alkyl group in two different copolymers whose tertiary carbons have the same chiral sense.

Using a regio- and isospecific and enantioselective catalyst system, we have recently achieved the synthesis of chiral, isotactic, alternating α-olefin−carbon monoxide poly(1,4-ketone)s with one kind of configuration (*R* or *S*) for the tertiary carbons in the backbone.[4] The molecular weights and molecular weight distributions of the copolymers are shown in Table 1. The degree of stereoregularity (percentage of isotactic *RRR*/*SSS* triad) in the propylene−carbon monoxide (P−CO), 1-butene−carbon monoxide (B−CO), and allylbenzene−carbon monoxide (A−CO) copolymers was found to exceed 95%, and in the case of isotactic P−CO copolymer, the enantiomeric excess in either the *R* or *S* copolymer was determined to be >90%.[4]

Enantiomerically pure (+ or −), chiral, isotactic P−CO copolymer showed a melting point of 171 °C. Most remarkably, the precipitation of a 1:1 (weight ratio) mixture of (+)-P−CO/(−)-P−CO copolymers from $CHCl_3/(CF_3)_2CHOH-CH_3OH$ solution led to the formation of a crystalline, (±)-P−CO stereocomplex (or enantioplex[5]) with a much higher melting temperature (T_m = 239 °C). The same effect was also observed for the other isotactic α-olefin−carbon monoxide copolymers, and the results are summarized in Table 1. In addition to the large differences in melting points, the solubilities (e.g., in CH_2Cl_2) of the (±)-P−CO and (±)-B−CO stereocomplexes were dramatically lower than those of the corresponding enantiomerically pure polymers. Dipolar attraction between neighboring carbonyl groups (i.e., C=O- -C=O)[6] appears not to be the cause for the large difference in physical properties since virtually identical IR (KBr) C=O stretching frequencies (1706 cm^{-1}) were observed for both chiral and (±)-B−CO copolymers.

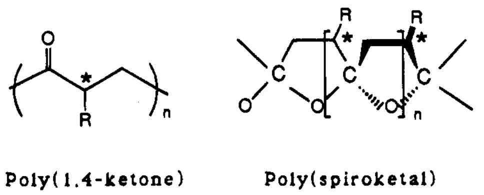

Figure 1. Repeating units present in alternating α-olefin−carbon monoxide copolymers.

Table 1. Molecular Weights[a] and Melting Points[b] of Isotactic, Alternating α-Olefin−Carbon Monoxide Poly(1,4-ketone)s

copolymer	M_p (M_w/M_n)	mp (T_m), °C
propylene−CO	3.6 × 10^4 (2.4)	
chiral (+) or (−)		171
(±) complex[c]		239
1-butene−CO	3.8 × 10^4 (2.8)	
chiral (+) or (−)		137
(±) complex[c]		265
allylbenzene−CO	7.1 × 10^3 (2.0)	
chiral (+) or (−)		62
(±) complex[c]		169

[a] Molecular weights and molecular weight distributions were measured by GPC relative to polystyrene standards. [b] Melting points were determined by DSC. [c] The (±) complexes of isotactic α-olefin−carbon monoxide copolymer samples were prepared by dissolving a 1:1 mixture of the (+) and (−) copolymers in a 3:1 (v/v) $CHCl_3/(CF_3)_2CHOH$ mixture and precipitating into CH_3OH.

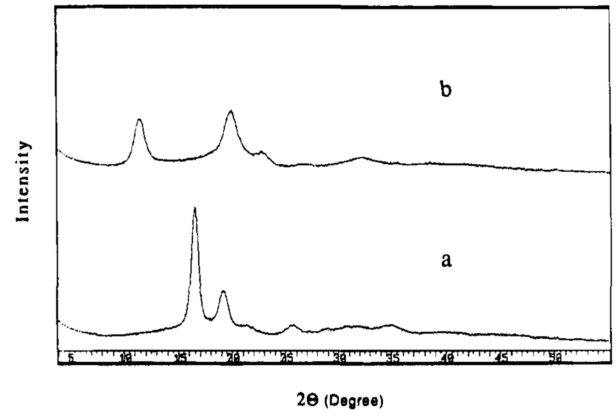

Figure 2. X-ray (Cu Kα) powder diffractions of (a) enantiomerically pure, isotactic, (−)-propylene−carbon monoxide copolymer and (b) (±) stereocomplex of isotactic, propylene−carbon monoxide copolymer.

The dramatic increase in the melting points and decrease in the solubilities for the (±) stereocomplexes appear to be due to the increase in the compactness of the polymer crystalline phases. This hypothesis is supported by the results of the X-ray powder diffraction (XRD) measurements of the copolymer samples. For example, the XRD spectra of the enantiomerically pure (−)-P−CO and (±)-P−CO copolymer samples were found to be quite distinct (Figure 2). The former exhibited two principal diffraction peaks at 16.5° (*d*-spacing = 5.37 Å) and 19.1° (*d*-spacing = 4.64 Å), while the corresponding peaks in

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(1) Review: Jacques, J.; Collet, A.; Wilen, S. H. *Enantiomers, Racemates, and Resolutions;* Wiley: New York, 1981; Part 1.

(2) Leading references: (a) Tsuji, H.; Ikada, Y. *Macromolecules* **1993,** *26,* 6918. (b) Ikada, Y.; Jamshidi, K.; Tsuji, H.; Hyon, S.-H. *Macromolecules* **1987,** *20,* 906. (c) Ritcey, A. M.; Prud'homme, R. E. *Macromolecules* **1992,** *25,* 972. (d) Lavallée, C.; Prud'homme, R. E. *Macromolecules* **1989,** *22,* 2438. (e) Green, M. M.; Garetz, B. A.; Munoz, B.; Chang, H.-P. *J. Am. Chem. Soc.* **1995,** *117,* 4181. (f) Moore, J. S.; Stupp, S. I. *J. Am. Chem. Soc.* **1992,** *114,* 3429.

(3) Reviews on alternating olefin−carbon monoxide copolymers: (a) Sen, A. *Acc. Chem. Res.* **1993,** *26,* 303. (b) Sen, A. *Adv. Polym. Sci.* **1986,** *73/74,* 125.

(4) Jiang, Z.; Sen, A. *J. Am. Chem. Soc.* **1995,** *117,* 4455.

(5) We wish to suggest the word *enantioplex* for complexes between two *chiral* polymer chains. This situation is different from complexes formed between two tactic but *achiral* polymer chains as in polyolefins. For examples of the latter, see: Tan, Y. Y.; Challa, G. *Encycl. Polym. Sci. Eng.* **1989,** *16,* 554. Papisov, I. M.; Litmanovich, A. A. *Adv. Polym. Sci.* **1988,** *90,* 139.

(6) Lai, T.-W.; Sen, A. *Organometallics* **1984,** *3,* 866.

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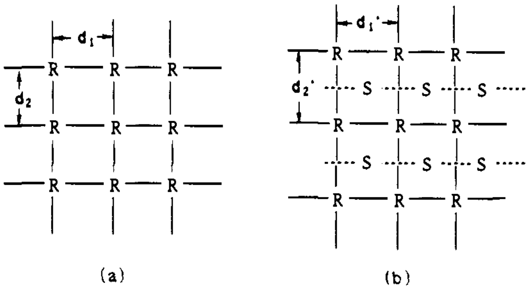
Table 2. Melting Points[a] of Chiral, Isotactic, Alternating α-Olefin–Carbon Monoxide Poly(1,4-ketone) Blends

polyketone blend	1 (+)-P–CO[b,c] 1 (+)-B–CO	1 (+)-P–CO[b,c] 1 (−)-B–CO	1 (+)-P–CO[b,c] 1 (−)-P–CO 1 (+)-B–CO	1 (+)-B–CO[b,c] 1 (−)-B–CO 1 (+)-P–CO
mp (T_m), °C	137 175	230	239	265

[a] Melting points were measured by DSC. [b] The ratios were molar ratios of the repeating units: P–CO, propylene–CO; B–CO, 1-butene–CO. [c] (+) or (−): sign of the molar optical rotation in $CHCl_3$.



$$d_1 \sim d_1', d_2 < d_2'$$

Figure 3. Suggested crystal lattices for (a) enantiomerically pure, isotactic, α-olefin–carbon monoxide copolymers and (b) (±) stereocomplexes of isotactic, α-olefin–carbon monoxide copolymers.

the latter were at 11.4° (*d*-spacing = 7.76 Å) and 19.4° (*d*-spacing = 4.57 Å). The difference in the crystal structure between the two can be explained[7] by assuming the incorporation of a layer of (*R*)-P–CO copolymer chains in between two adjacent layers of (*S*)-P–CO copolymer chains and vice versa in the (±) or *R*/*S* stereocomplex crystal lattice (Figure 3). This will be expected to significantly affect only one of the d-spacings as was observed. Such an arrangement in the (±) or *R*/*S* crystallite results in an overall increase in the degree of packing, in comparison to crystallites of either enantiomerically pure copolymer, and an increase in melting point and decrease in solubility can be anticipated. The melting point increase was observed not only in a 1:1 (weight ratio) mixture of (+) and (−), isotactic α-olefin–carbon monoxide copolymers, but also in a nonequivalent mixture. For instance, DSC measurements showed that (+)-B–CO copolymer mixed with either 50% or 20% (−)-B–CO copolymer had the same, single melting point (265 °C); a separate melting point for the pure (+)-B–CO copolymer was not observed. Clearly, during the crystallization, (±)-B–CO stereocomplex crystals were formed preferentially even in nonequimolar blends and, moreover, stereocomplexation strongly inhibited the homocrystallization of the (+)-B–CO copolymer.

Chiral recognition and the resultant selective stereocomplexation between two different, isotactic α-olefin-carbon monoxide copolymers were also investigated, and the results are summarized in Table 2. The data clearly show that the stereocomplexation between a (+)/(−) pair of two different, isotactic α-olefin–carbon monoxide copolymers occurred preferentially over the homocrystallization of the individual enantiomerically pure copolymers, and the stereocomplexation between the (+)/(−) pair of the same copolymer took place preferentially over the complexation between a (+)/(−) pair from two different copolymers. *Thus, the chiral α-olefin–carbon monoxide copolymers can discriminate on the basis of both chirality and sterics.* For example, while a 1:1 (molar ratio of repeating units) mixture of the (+)-P–CO and (+)-B–CO copolymers exhibited two melting points at 137 and 171 °C corresponding to the homocrystallites of (+)-B–CO and (+)-P–CO copolymers, respectively, a 1:1 (molar ratio of repeating units) mixture of the (+)-P–CO and (−)-B–CO copolymers showed only a single melting temperature at 230 °C, indicating the formation of a new stereocomplex. On the other hand, a 1:1:1 (molar ratio of repeating units) mixture of (+)-P-CO/(−)-P–CO/(+)-B–CO copolymers and a 1:1:1 mixture of (+)-B–CO/(−)-B–CO/(+)-P–CO copolymers exhibited single melting points at 239 and 265 °C, respectively, due to the formation of corresponding (±)-P–CO and (±)-B–CO crystallites. At the same time, the homocrystallization of (+)-B–CO copolymer in the former and (+)-P–CO copolymer in the latter and stereocomplexation between (−)-P–CO and (+)-B–CO copolymers and between (−)-B–CO and (+)-P–CO copolymers were strongly inhibited.

Finally, the chiral recognition between the enantiomerically pure, isotactic α-olefin–carbon monoxide copolymers also had an influence on the chemical reactivity. For example, we had earlier observed that, over a period of 7 days, the chiral, isotactic, A–CO copolymer isomerized in $CDCl_3$ solution (concentration: 4 mg/mL) at ambient temperature to a polymer with predominantly spiroketal repeating units (see Figure 1).[4] This transformation was monitored by both NMR spectroscopy and optical rotation measurements. However, under identical reaction conditions, no isomerization was observed for a 1:1 mixture of the (+)- and (−)-A–CO copolymers over a period of 30 days. This change in reactivity was presumably due to the formation of a stereocomplex in solution which inhibited the 1,4-ketone/spiroketal isomerization reaction.

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[7] (a) Matsubayashi, H.; Chatani, Y.; Tadokoro, H.; Dumas, P.; Spassky, N.; Sigwalt, P. *Macromolecules* **1977**, *10*, 996. (b) Sakakihara, H.; Takahashi, Y.; Tadokoro, H.; Oguni, N.; Tani, H. *Macromolecules* **1973**, *6*, 205.