Side-Chain Conformation and Dynamics for the Form II Polymorph of *Isotactic* Poly(1-butene) Investigated by High-Resolution Solid-State ^{13}C NMR Spectroscopy

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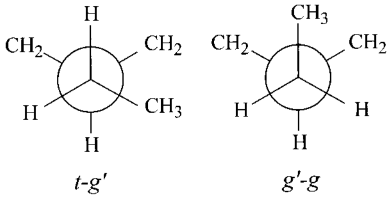
Introduction

Isotactic poly(1-butene) (*i*-PB) is a semicrystalline polymer and has an ethyl group as the side chain. This polymer shows four polymorphs,[1] I, I′, II, and III, depending on the preparing conditions. The main chains of the four polymorphs adopt the common helical, ...(tg')(tg')... or $(tg')_n$, conformations with slightly different dihedral angles.[2−5] There are two possible side-chain conformations as shown in Scheme 1. X-ray diffraction analysis,[2−5] however, assumed that the side chains in all the forms adopt only the $t-g'$ conformation. *i*-PB crystallizes from the melt as form II (tetragonal with an 11_3 helix)[4] below 373 K.[6] Lowering the temperature below 333 K, form II spontaneously transforms into a stable form, form I (twinned hexagonal with a 3_1 helix),[2] via a crystal-to-crystal process over several weeks.[7] Form III (orthorhombic with a 4_1 helix)[5] crystallizes from a toluene solution, and spontaneously transforms into form I′ (untwined hexagonal with a 3_1 helix)[3] also via a crystal-to-crystal process just below its melting temperature ($T_m = 367$ K) within several hours.[8] These transformations are directly related to the conformational stability of the initial and final forms.

Some solid-state NMR methods were applied to investigate the chain dynamics and conformation of *i*-PB.[9−13] From ^{1}H broad-line and relaxation measurements, Maring et al.[9] showed that the polymer chains in the final forms, forms I and I′, are rigid well above the glass transition temperature ($T_g \sim 250$ K), while those in the initial forms, forms II and III, are mobile. In our previous paper,[10] we described detailed main- and side-chain dynamics for form III over a wide temperature range. The polymer chain in form III performs 90° helical jump motion above 240 K, and the side chain remains in the $t-g'$ conformation at 240 K. Above 338 K, the main chain shows conformational and motional change. For the side chain, the population of the $g'-g$ conformation increases and a fast transition between the $t-g'$ and $g'-g$ conformations occurs. Beckham et al.[11] elucidated using ^{13}C 2D exchange NMR that the main chain in form II adopts locally distributed conformations and shows conformational transitions among them above T_g. These investigations indicate that the two transformations from forms II and III into I and I′, respectively, require conformational disordering of the initial forms. Although some ^{13}C NMR studies[12,13] were performed, the side-chain conformation in form II has not been well understood so far. This may be attributed to similarities in motional frequencies[9] and conformations[12,13] between form II and the amorphous phase. In our previous report,[10] we showed that the side chain in the amorphous sample obtained by the melt−quench method adopts the $t-g'$ and $g'-g$ conformations at 199 K.

Scheme 1



t-g′ *g′-g*

In this paper, we measure cross-polarization (CP) and magic-angle sample spinning (MAS) NMR spectra of the form II-rich sample with a high crystallinity of 79% and the amorphous sample in the low-temperature region of 165−283 K. We investigate the side-chain conformation and dynamics in form II as well as in the amorphous sample and demonstrate an interesting result that side-chain conformation in form II is disordered and side-chain mobility is higher than that in the amorphous phase. We also pay attention to the main-chain conformations in the same temperature range.

Experiments

i-PB with a weight-average molecular weight of 185 000 was purchased from Poly Science Co. Ltd. The isotacticity is higher than 90%. The amorphous sample was obtained by a rapid quench with liquid N_2 after melting the virgin sample in an oil bath at 413 K. The form II-rich sample was prepared by transformation of the form III-rich sample at 370 K.[8,10] The form III-rich sample was obtained by precipitation from a toluene solution (2 wt %) at room temperature.[10]

The NMR experiments were performed with a Bruker ASX200 spectrometer operating at 200.1 MHz for ^{1}H and 50.3 MHz for ^{13}C. Typical NMR experimental conditions were as follows: 90° pulse length, 4.4 μs; contact time, 1 ms; recycle delay, 4 s; ^{1}H decoupling field strength, 57 kHz; MAS frequency rate, 2 kHz. Chemical shifts were externally referenced to the methine carbon of adamantane at 29.5 ppm. The temperature was calibrated using methanol[14] and ethylene glycol.[15]

Results and Discussion

Parts a and b of Figure 1 show the ^{13}C CPMAS and direct polarization (DP) MAS NMR spectra, respectively, for the form II-rich sample at 370 K. The CP method enhances only the carbon signals for form II.[10] The observed carbon signals at 11.8, 28.1, 34.5, and 38.8 ppm are assigned to the methyl, side-chain methylene (s-

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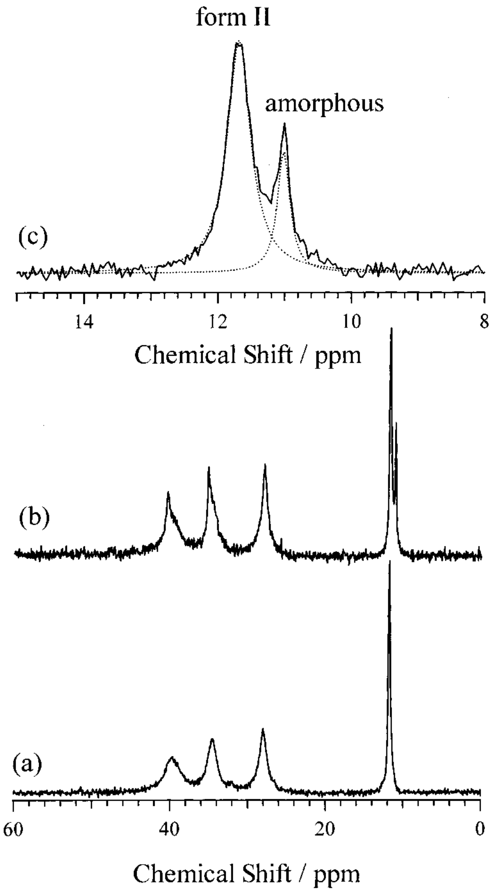

Figure 1. ^{13}C CPMAS and DPMAS NMR spectra for the form II-rich sample at 370 K: (a) ^{13}C CPMAS spectrum; (b) ^{13}C DPMAS spectrum with the repetition time of 8 s (this repetition time is long enough for the magnetization of the methyl carbon to relax fully to the thermal equilibrium); (c) ^{13}C DPMAS spectrum for the methyl region of the form II-rich sample. The dotted line is the best-fitted one to the observed line shape using a sum of two Lorenztian line shapes. The intensity ratio for form II to the amorphous phase is 79/21.

methylene), methine, and main-chain methylene (m-methylene) carbons, respectively. The DP method polarizes the carbon signals for both form II and the amorphous phase, so that the main-chain and s-methylene signals with narrower line widths for the amorphous phase are overlapped with the carbon signals for form II (Figure 1b), though the methyl signal for the amorphous phase appears separately at 11.0 ppm. The methyl signals obtained by the DP method are fitted with a sum of two Lorenztian line shapes assuming a two-phase structure as shown in Figure 1c. The crystallinity of the present form II-rich sample is evaluated to be 79% at 370 K. This value is much higher than those (ca. 40%) of the samples employed in the previous investigations,[11−13] leading to facile investigation of temperature-dependent conformations for form II.

Figures 2 and 3 show the ^{13}C CPMAS NMR spectra at 165−283 K for the amorphous and form II-rich samples, respectively. At 283 K, all of the signals except for the methyl ones (Figures 2d and 3d) are broad, suggesting the existence of dynamic and structural heterogeneities not only in the amorphous sample but also in form II. With decreasing temperature to 251 K ($\sim T_g$), the conformational transitions of the main chain become slow with frequencies less than several hertz in the form II and amorphous phases.[11] The line widths of the main-chain signals at this temperature (Figures 2c and 3c) are thus ascribed primarily to the conformational distribution of the main chains.

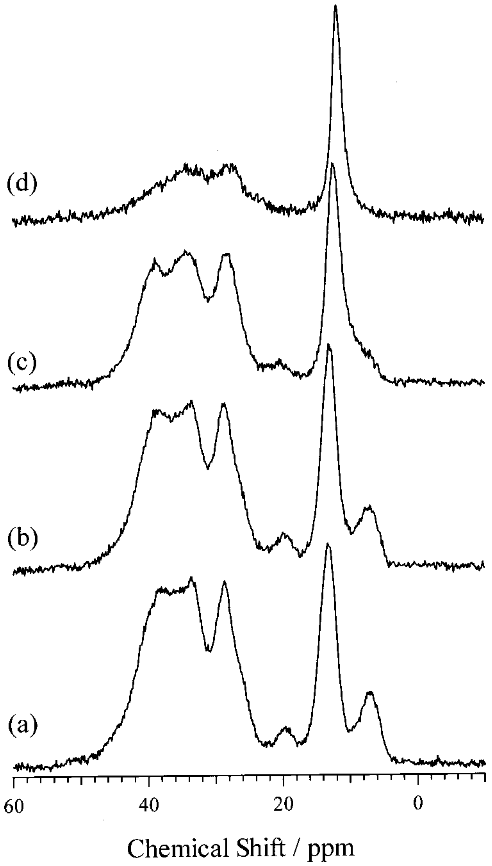

Figure 2. ^{13}C CPMAS NMR spectrum for the amorphous sample of *i*-PB at various temperatures: (a) 165, (b) 210, (c) 251, and (d) 283 K.

Hereafter, we pay attention to the spectral changes of the form II-rich and amorphous samples below T_g. We consider the chain conformation in the amorphous phase in the form II-rich sample is equivalent with that in the amorphous sample. The methyl carbons in the amorphous sample show the two resolved signals below 210 K (Figure 2, parts a and b). On the basis of the so-called γ-gauche effect,[16] the resolved signals at 13.3 and 7.3 ppm are assigned to the methyl carbons in the $t{-}g'$ and $g'{-}g$ side-chain conformations,[10,12] respectively. Similarly, the methyl carbons in the form II-rich sample show the resolved signals at 165 K (Figure 3a), even though their separation is not so clear compared to that in the amorphous sample below 210 K. Parts a and c of Figure 4 show the temperature-dependent line shapes of the methyl signals in the amorphous sample and form II, respectively. Subtraction of the methyl signals for the amorphous sample from those for the form II-rich sample using the crystallinity of 79% yields the two resolved signals at 7.8 and 13.3 ppm for the methyl carbons in form II at 165 K (Figure 4c). It is, therefore, concluded that the side chain in form II also adopts the $t{-}g'$ and $g'{-}g$ conformations. This contrasts remarkably with the side-chain conformation for the other forms of *i*-PB at low temperatures.[10,12,13]

With increasing temperature, the resolved signals are merged into a single resonance in both form II and the amorphous sample, even though the temperature-dependent line-shape change for the former is moderate compared to that for the latter. The line-shape changes are brought about by the transition between the $t{-}g'$

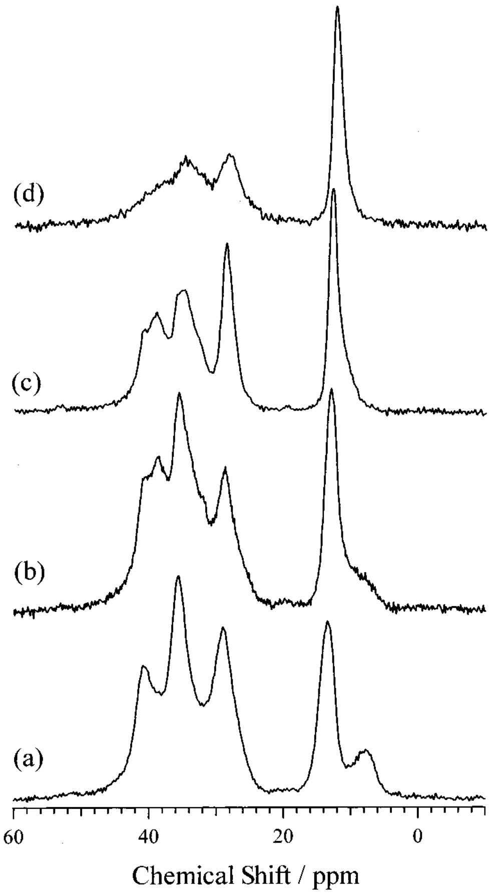

Figure 3. ^{13}C CPMAS NMR spectrum for the form II-rich sample of *i*-PB at various temperatures: (a) 165, (b) 210, (c) 251, and (d) 283 K.

and $g'-g$ side-chain conformations. Polymer dynamics is oftentimes characterized by adopting a distribution of motional rates.[17] The observed line-shape change, however, is not resolved enough to adopt such a distribution, and then, is simply simulated by adopting a two-sites exchange model with a conformational transition rate, k. It is noted that this assumption may bring about the underestimation of the activation energies. The line shape in the amorphous sample is independent of temperature below 179 K (data are not shown), whereas that in form II continues to vary until 165 K. The chemical shifts of the methyl signals in form II at 165 K are similar to those of the amorphous sample at 210 K. We, therefore, assume that the natural line widths and the chemical shifts for form II have the same values as those of the amorphous sample. The simulated spectra for the amorphous sample and form II are shown in Figure 4, parts b and d, respectively. From the temperature dependent k values shown in the simulated spectra the activation energies for the conformational transitions are evaluated to be 21 ± 2 and 10 ± 3 kJ/mol for the amorphous sample and form II, respectively. The large difference in the obtained activation energies clearly indicate that the side-chain mobility is higher in form II than that in the amorphous sample.

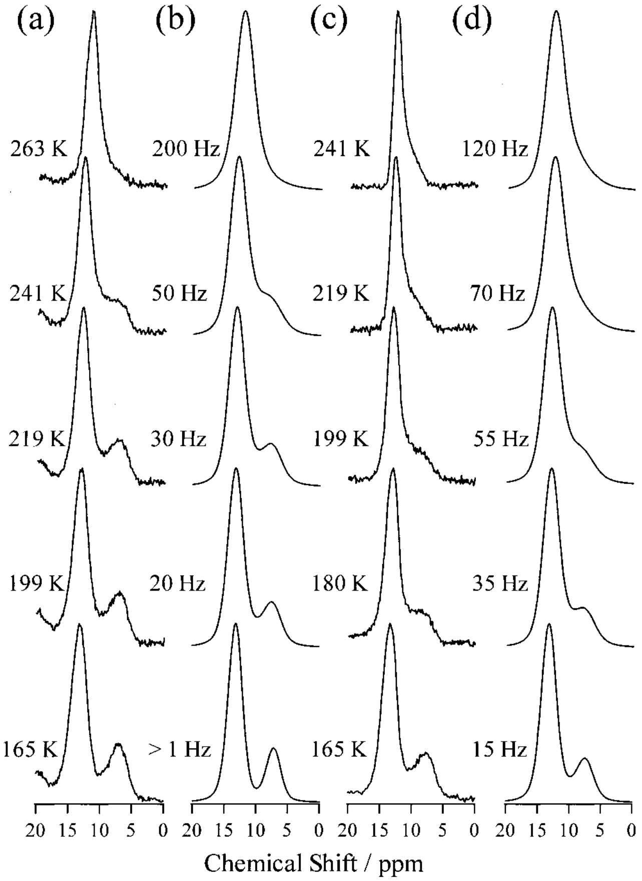

Figure 4. ^{13}C CPMAS NMR spectra for the methyl carbons of the amorphous and form II phases: (a) observed and (b) simulated spectra for the amorphous phase; (c) observed and (d) simulated spectra for the form-II phase. The observed methyl signals for the form-II phase were obtained by subtracting the corresponding signals for the amorphous phase from the methyl signals for the form II-rich sample using the crystallinity of 79%. The simulated spectra were obtained with a conformational transition rate, k, as a parameter, a Gaussian distribution of Lorenztian peaks with a broadening of 40 Hz, and the chemical-shift separation of 6.0 ppm. The ratios for the $t-g'/g-g'$ side-chain conformations are fixed to be 76/24 and 78/22 for the amorphous and form-II phases, respectively.

The chemical shifts and the line shapes of the main-chain signals for the amorphous sample are almost independent of temperature below T_g (Figure 2, parts a and b). This means that the main-chain conformations are frozen below T_g in the amorphous phase. For the form II-rich sample, intensities at the high-field sides of the methine and m-methylene signals are reduced with decreasing temperature, resulting in apparently sharp and symmetric line shapes at 165 K (Figure 3a). On the basis of the γ-gauche effect, both the side- and the main-chain conformations are responsible for the line-shape change of the m-methylene signal. The content of the $g'-g$ side-chain conformation is so small (at most 22%) that one can neglect its contribution on the overall line shape of the m-methylene signals. This is supported by the fact that the line shape of the m-methylene signal in the amorphous sample is almost independent of temperature despite the existence of the $g'-g$ side-chain conformation. The methine signal is, on the other hand, solely affected by the main-chain conformation. The observed line-shape change for the main-chain region in the form II-rich sample should be attributed to the conformational change of the main chain in form II, and the observed narrowing of the line widths for the main-chain signals with lowering temperature should be attributed to ordering of the distributed conformations for the main chains. In the same temperature region, the side-chain mobility is reduced with lowering temperature. Theoretical conformational analysis[18] on *i*-PB indicated that the side-chain conformation and mobility are strictly correlated with the main-chain conformations. It is, therefore, suggested that the main-chain disorder in form II is related to reduction of the side-chain mobility. Such a structural correlation between the side and the main chains was not observed in the amorphous sample, because the main-chain conformation in the amorphous phase is frozen below T_g.

Conclusions

We have elucidated for the first time that the side-chain conformation in form II is disordered as well as in the amorphous sample, and the side-chain mobility in form II is higher than that in the amorphous sample. Furthermore, the distributed main-chain conformations in form II are partially ordered with reduction of the side-chain mobility. It is suggested that the side-chain dynamics influences the main-chain conformations in form II. This is consistent with our previous conclusions for form III of *i*-PB.[10]

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References and Notes

(1) Holland, F. V.; Miller, L. R. *J. Appl. Phys.* **1964**, *35*, 3241.

(2) Natta, G.; Corradini, P.; Bassi, I. W. *Nuovo Cimento Suppl.* **1960**, *15*, 52−67.

(3) Miller, L. R.; Holland, F. V. *Polym. Lett.* **1964**, *2*, 519−521.

(4) Petraccone, V.; Pirozzi, B.; Corrasini, P. *Eur. Polym. J.* **1976**, *12*, 323−327.

(5) Cojazzi, G.; Malta, V.; Celotti, G.; Zannetti, R. *Macromol. Chem.* **1976**, *177*, 915−926.

(6) Fu, Q.; Heck, B.; Strobl, G.; Thomann, Y. *Macromolecules* **2001**, *34*, 2502−2511.

(7) Geacintov, C.; Schotlan. S. R.; Miles, B. R. *J. Polym. Sci., Part C* **1964**, *6*, 197−207.

(8) Goldbach, G.; Peitscher, G. *Polym, Lett.* **1968**, *6*, 783−788.

(9) Maring, D.; Meurer, B.; Weill, G. *J. Polym. Sci., Part B: Polym. Phys.* **1995**, *33*, 1235−1247.

(10) Miyoshi, T.; Hayashi, S.; Kaito, A.; Imashiro, F. *Macromolecules* **2002**, *35*, 2624−2632.

(11) Beckham, W. H.; Schmidt-Rohr, K.; Spiess, W. H. *ACS Symp. Ser.* **1995**, 242−253.

(12) Belfiore, L. A.; Schilling, F. C.; Tonelli, A. E.; Lovinger, A. J.; Bovey, F. A. *Macromolecules* **1984**, *17*, 2561−2565.

(13) Maring. D.; Wilhelm, M.; Spiess, W. H.; Meurer, B.; Weill, G. *J. Polym. Sci., Part B: Polym. Phys.* **2000**, *38*, 2611−2624.

(14) VanGeet, L. A. *Anal. Chem.* **1970**, *42*, 679−680.

(15) Raiford, S. D.; Fisk, L. C.; Becker, D. E. *Anal. Chem.* **1970**, *51*, 2050−2051.

(16) Zemke, K.; Schmidt-Rohr, K.; Spiess. W. H. *Acta Polym.* **1994**, *45*, 148−159.

(17) Kaji, H.; Tai, T.; Horii, F. *Macromolecules* **2001**, *34*, 6318−6324.

(18) Ajo, D.; Granozzi, G.; Zannetti, R. *Makromol. Chem.* **1977**, *178*, 2471−2481.

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