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Helical Jump Motions in Isotactic Poly(4-methyl-1-pentene) Crystallites Revealed by 1D MAS Exchange NMR Spectroscopy

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Much attention has been paid to the understanding of chain dynamics in the crystalline phase of semicrystalline polymers because it plays an important role in the macroscopic properties, such as mechanical creep, drawability, and crystallization. Solid-state NMR, in particular the application of advanced 2D exchange NMR spectroscopy, provides exact information about the motional process in the crystallites.[1−8] Such experiments utilize the orientation-dependent ^{13}C chemical shift anisotropy (CSA),[1−3] ^{13}C−^{13}C dipole−dipole,[4] or ^{2}H quadrupolar interaction:[5] molecular reorientations are directly related to changes in the resonance frequencies which can be observed by the 2D exchange methods. So far, it has been demonstrated that polyethylene (PE),[4] poly(oxymethylene) (POM),[1,2] poly(ethylene oxide) (PEO),[3] isotactic poly(propylene) (*i*-PP),[2,5] and form III of *i*-poly(1-butene) (*i*-PB)[6,7] show surprising helical jump motions around their chain axes. Most of these investigations, however, require ^{13}C or ^{2}H isotope labeling to overcome low sensitivity and provide spectral resolution. Also, the 2D exchange methods consume long times and are thus not feasible for the extraction of time kinetic parameters. In addition, if polymer has many functional groups, determination of motional process for all the functional groups requires skill for isotope labeling. The applications of these methods, therefore, were limited only to the crystalline polymers having simple chemical structures. In recent years, several 1D exchange NMR methods have been developed to satisfy the above demands.[9−15]Among them, center-band-only detection exchange (CODEX) NMR[14,15] is particularly suitable for investigation of molecular motions of polymers with complicated chemical structures (i.e., many different resonances in the NMR spectrum) and carbons with relatively small CSA (i.e., aliphatic groups).

Isotactic poly(4-methyl-1-pentene) (*i*-P4M1P) exhibits a disordered 7_2 helical conformation in the ordinal crystallite, form I,[16] and shows unusual density property compared to the other semicrystalline polymers: the crystalline density (0.828 g/cm^3) is slightly lower than the amorphous one (0.838 g/cm^3) at 20 °C.[17] This unique character should influence thermal properties and molecular motions of *i*-P4M1P. So far, many methods, such as mechanical,[17−20] dilatometry,[17] X-ray diffraction,[18,20,21] elastic modulus,[21] and ^{1}H wide line NMR,[22] have been applied to characterize thermal properties and molecular motions of *i*-P4M1P. The glass transition temperature, T_g, is commonly accepted to be 20−50 °C.[17−19,22] On the other hand, there are contrary results on molecular motions in form I crystallites. Mechanical investigations showed there appears a very broad and weak peak around 120−150 °C and implied an occurrence of overall chain dynamics.[17−19] It was also, however, reported that the mechanical peak around 120−150 °C becomes unnoticeable with increasing crystallinity[17] and does not appear for *i*-P4M1P fibers with crystallinity of 75%.[20] X-ray diffraction and elastic modulus measurements showed that both thermal expansion coefficient and elastic modulus are exceedingly small and large, respectively, compared to the other semicrystalline polymers.[21] However, the lack of temperature dependence of these values up to 150 °C denied overall chain dynamics in form I crystallites. ^{1}H wide line NMR on a highly crystalline sample showed that the ^{1}H second moment continuously decreases with increasing of temperature from 20 to 180 °C and suggested the presence of side-chain motions in the crystallites.[22] The different interpretations may arise from unusual density and the chemically complicated structure of *i*-P4M1P.

In this communication, we present results for both the side- and main-chain dynamics with correlation times, τ_c, in the millisecond range, obtained by the CODEX NMR method and demonstrate for the first time that the polymer chains in form I crystallites perform helical jump motions, not accompanied by additional side-chain motions.

i-P4M1P with an average molecular weight (M_w) of 180 000 was purchased from Poly Science Co. Ltd. Initially, form III was obtained by crystallization into semidilute toluene solution (0.25 wt %).[23] Form I was obtained from form III via a crystal−crystal transformation.[24] DSC measurement was conducted using a Seiko SSC/6000 (DSC6200) in a N_2 atmosphere with a heating rate of 20 °C/min. The crystallinity, 69%, was obtained from the ratio $\Delta H/\Delta H_c$, where ΔH is heat of fusion for the sample investigated here and $\Delta H_c = 61.7$ J/g is that for fully crystalline material.[20,25]

Solid-state NMR measurements were conducted on a Varian INOVA 400. The ^{13}C carrier frequency is 100.5 MHz, and a standard Varian 7 mm VT_CPMAS probe was used in the experiments. The 90° pulse of ^{1}H and ^{13}C are 3.5−3.8 and 4.1−4.5 μs, respectively. The cross-polarization time and delay time were set to 1 ms and 2 s, respectively. The magic angle spinning (MAS) frequency was set to 3 and 5.5 kHz. The sample temperature was carefully adjusted using a standard procedure.[26] The CODEX NMR spectra were obtained by accumulations of 1024 transients. The mixing-time dependence of the CODEX experiments totally required a machine time of about 20 h.

CODEX NMR relies on the signal decay due to dephasing of the magnetization, owing to changes in orientation-dependent CSA. The latter is due to molecular reorientation of CSA tensor of the carbon under investigation during mixing time t_m.[14,15] For a $Nt_r/2$ period, the magnetization evolves under the orientation-dependent CSA interaction, which is recoupled by two

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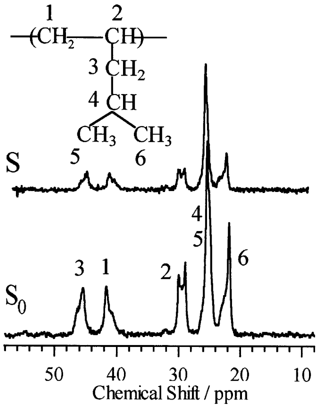

Figure 1. ^{13}C CODEX NMR spectra for form I crystallites of *i*-P4M1P, with $t_m = 107$ ms, and MAS frequency of 3 kHz and a recoupling value of $Nt_r = 2$ ms at 71 °C.

successive 180° pulses per MAS rotation period t_r, where N is integer. Then, the magnetization is stored along z direction and does not dephase during t_m, which must be set to an integer multiple of t_r. If no molecular motion occurs during t_m, the magnetization evolves after a readout pulse and another $Nt_r/2$ period and is refocused at the beginning of the detection period. In this case, there is no decay in the signal intensity. If, however, molecular motion does occur during t_m, the orientation-dependent frequency before and after t_m is different, and thus, the magnetization is not completely refocused. The resulting dephasing is observed as the signal-intensity decay. To remove the T_1 and T_2 effects during Nt_r, a reference spectrum S_0 is obtained.[14,15] Plotting the ratio (S/S_0), motional correlation times and information about the motional geometry are obtained. A more detailed description in the CODEX experiment can be found in refs 14 and 15.

Figure 1 shows the CODEX NMR spectra for form I crystallites at 71 °C. The signal assignment is represented in Figure 1 according to the assignment of Rosa et al.[27] It is noted that two CH_3 signals show different chemical shifts due to the γ gauche effect, though one CH_3 signal overlaps with the side-chain CH signal, indicating that side-chain motion around the side-chain CH_2−CH bond is relatively slow compared to the frequency difference. The exchange spectrum, S, in Figure 1 shows an apparent decay of all the signals compared to those of S_0, indicating that overall chain dynamics significantly occurs in form I crystallites within $t_m = 107$ ms. Previous X-ray diffraction results indicate that there is no significant change up to 180 °C except for a small wavenumber side shift due to thermal expansion.[21] The possible overall motions, therefore, are suggested to be helical jumps around the chain axes in the crystallites.

The dependence of the ratio (S/S_0) on the value Nt_r under a fixed t_m depends on the CSA parameters and the topology of the dynamic process, i.e., the reorientational angle. The experimentally determined Nt_r dependence, thus, can extract the exact motional mode from reorientational angle simulation. Previous investigations showed that Nt_r dependence of (S/S_0) is very sensitive to reorientational angle.[14,15] Figure 2 shows the Nt_r dependence of (S/S_0) of the main-chain CH_2 carbon, which shows a steep decay in the initial period, indicating that *i*-P4M1P performs molecular motions with a large angle displacement in form I crystallites. To run calculations of the Nt_r dependence, information about both the principal axes values and their orientations in a frame of reference is needed. The values for the main-chain CH_2 carbon were obtained by 2D separation of undistorted CSA powder pattern in MAS NMR method[28] and are given in the caption of Figure 2. In several polymers consisting of aliphatic carbons, the CSA tensor directions for the main-chain CH_2 carbon in the $-CCH_2C-$ moiety have been investigated.[29−31] Because of the local symmetry, the results show almost similar tensor directions as σ_{33} is perpendicular to the H−C−H plane, σ_{22} is H−C−H angle bisector, and σ_{11} is orthogonal to both directions.[30,31] Adopting these orientations for the principal axes of the main-chain CH_2 carbon for form I crystallites, the simulated solid line in Figure 2 represents disordered 7_2 helical jump motion around the chain axis, based on the disordered 7_2 helical structure.[16] There is a good agreement between the experimental and simulated ones. For *i*-PP crystallites, however, the σ_{22} direction for the main-chain CH_2 carbon deviates by 30° from the H−C−H angle bisector.[29] The dotted and broken lines in Figure 2 show +30° and −30° deviations of the σ_{22} axis, respectively, from the common σ_{22} direction. It is found that such deviations do not largely influence the simulated (S/S_0) curves, which are compatible with the experimental data within the margins of error. These simulations indicate that the Nt_r dependence basically depends on the jump angle while slight deviations of the CSA directions do not influence the curve seriously.

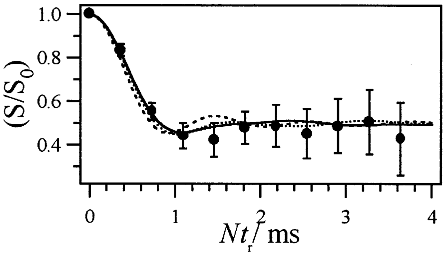

Figure 2. Nt_r dependence of the ratio (S/S_0) of the main-chain CH_2 carbon with $t_m = 107$ ms under MAS frequency of 5.5 kHz at 60 °C. The solid line shows the simulated average curve for the helical jumps in the disordered 7_2 helical conformations. Each jump angle was calculated on the basis of disordered 7_2 helical conformations obtained by X-ray diffraction.[16] The principal axes values (σ_{11}, σ_{22}, σ_{33}) for the CSA tensor are (63, 40, 22 ppm), respectively, with an error with ±3 ppm. The dotted and broken lines show simulated ones for the helical jump motion assuming σ_{22} direction to be deviated by +30° and −30°, respectively, from the H−C−H bisector.

In the mixing-time experiment, not only molecular motion but also spin diffusion contributes to the spin exchange with increasing a mixing time, especially under MAS conditions.[32,33] In nonspinning experiments, spin diffusion is weak due to the different CSA orientations of the interacting spins and the consequently different resonance frequencies. In MAS, however, the resonance frequencies become time dependent and occasionally match each other during the course of a MAS rotation period, leading in turn to a much enhanced spin diffusion rate. To eliminate the spin-diffusion effect, we conducted a spin-diffusion correction as follows: $(S/S_0)^* = (S/S_0)/(S_{SD}/S_{0SD})$, where (S_{SD}/S_{0SD}) shows the signal decay due to spin diffusion and was obtained at −15 °C where no molecular dynamic process is expected in the dynamic window of the method. In this study, the ratios (S_{SD}/S_{0SD}) for all the signals range between 0.91 and 0.93 at $t_m = 800$ ms.

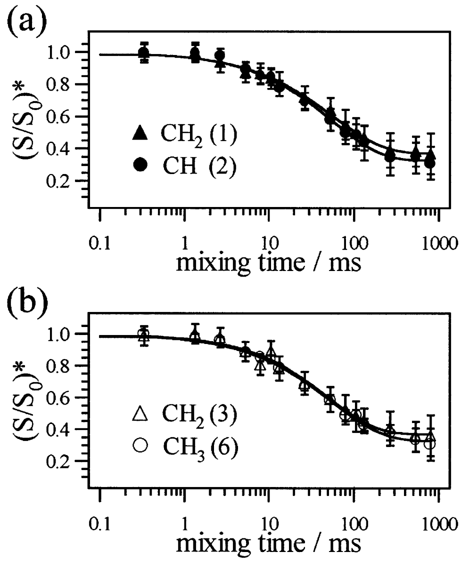

Figure 3. Mixing time dependence of $(S/S_0)^*$ of (a) the main-chain and (b) the side-chain carbons with recoupling value of $Nt_r = 2$ ms and under MAS frequency of 3 kHz at 71 °C. The solid lines are best fitting ones to the experimental data, using $1 - a(1 - \exp(-\tau_c/t_m)^{\beta_{kww}})$. The description of the fitting parameters is written in the text.

Table 1. Best-Fitted Parameters to Mixing Time Dependence of the Ratios $(S/S_0)^*$ for the Resolved Main- and Side-Chain ^{13}C Signals for Form I Crystallites of *i*-P4M1P at 71 °C

		a	τ_c/ms	β_{kww}
CH$_2$	(1)[a]	0.63 ± 0.02	57 ± 5	0.73 ± 0.04
CH	(2)	0.67 ± 0.02	56 ± 5	0.76 ± 0.05
CH$_2$	(3)	0.63 ± 0.02	50 ± 7	0.78 ± 0.07
CH$_3$	(6)	0.67 ± 0.02	55 ± 5	0.73 ± 0.04

[a] Numbering denotes each functional group of *i*-P4M1P shown in Figure 1. Errors are σ.

Parts a and b of Figure 3 show the mixing time dependence of the ratios $(S/S_0)^*$ for the resolved main-chain and side-chain ^{13}C signals, respectively. The ratios for all the signals decay with increasing t_m. The asymptotic value for infinite mixing time, $(S/S_0)_f^*$, is equal to the inverse of the number of nonequivalent sites, p, that an atom can occupy during the molecular reorientation. In the case of a noncrystalline environment, the number of nonequivalent sites approaches infinity, which means $(S/S_0)_f^* = 0$.[14] On the other hand, crystalline segments have finite sites due to structural restriction and symmetry in the lattice.[14] When each segment would be able to jump to either one of the other six nonequivalent sites in the 7_2 helix by helical jump motions, $(S/S_0)_f^*$ would be $^1/_7 = 0.14$. The obtained results in Figure 3 are fitted to the equation $1 - a(1 - \exp(-\tau_c/t_m)^{\beta_{kww}})$, where $0 < a < 1$ and $a = (p - 1)/p$; τ_c and β_{kww} are center of the correlation time and stretched exponential coefficient. The solid lines shown in Figure 3 are best fitted to the experimental data, and the obtained fitting parameters are listed in Table 1. All the parameters for the main-chain signals show good agreements with those for the side-chain ones. This means that helical jump motions happen, and no additional side-chain motion occurs in form I crystallites. This result is supported by the fact that two CH$_3$ signals show the different isotropic chemical shift values as shown in Figure 1.[27] The continuous decrease of ^{1}H second moment in the region 20−180 °C,[22] therefore, should be attributed to non-side-chain motion but also to helical jump motions in form I crystallites. Furthermore, the obtained parameters show more detailed dynamic information. From $a = 0.63{-}0.67$, the number of available sites is close to 3, showing that jumps over two sites happen within $t_m = 800$ ms. The value of $\beta_{kww} = 0.73{-}0.78$ means a distribution of correlation times with the width between 0.56 and 0.59 decades. The obtained correlation times of 50−57 ms at temperature 71 °C close to T_g indicate that helical jump motions in the crystallites also contribute to the mechanical peak with a typical frequency of 1 Hz at around 20−50 °C,[17−20] which is widely accepted to be T_g in the present case. Such large-amplitude motions in the crystallites at temperatures close to T_g were previously reported in PEO[3] and form III of *i*-PB.[7] It is, however, still an open question as to whether chain dynamics in crystallites continues below T_g or not. We will approach this general problem by investigating chain dynamics of *i*-P4M1P crystallites in the varied temperatures. The result will be published elsewhere.

In conclusion, it was found by application of CODEX NMR that the polymer chains in form I crystallites of *i*-P4M1P perform helical jump motions in the same manner as PE,[4] *i*-PP,[2,5] form III of *i*-PB,[6,7] POM,[1,2] and PEO[3] crystallites. It was also found that helical jump motions are not accompanied by additional side-chain motions. The presence of helical jump motions at temperatures close to T_g can reasonably explain thermal properties, such as mechanical behavior,[20] small elastic modulus, and large thermal expansion coefficiency,[21] and previous ^{1}H NMR results[22] for form I crystallites. 1D-MAS exchange NMR methods opened the possibility for detailed dynamic investigation of polymers even with complicated chemical structures.

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