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High-Resolution Solid-State ^{13}C NMR Study of Isotactic Polypropylenes Isothermally Crystallized from the Melt

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Received May 3, 1989; Revised Manuscript Received December 28, 1989

ABSTRACT: The phase structure of isotactic polypropylenes isothermally crystallized from the melt has been examined at different temperatures by solid-state high-resolution ^{13}C NMR spectroscopy using VT/MAS (variable temperature/magic angle spinning). On the basis of ^{13}C spin-lattice relaxation and computer line-shape analyses, it has been found that polypropylene samples are composed of not only crystalline and amorphous components but also another noncrystalline component with 3_1-helical conformation. Similar NMR analyses at different temperatures have revealed that a reversible structural change between the 3_1-helical and random conformations occurs in the noncrystalline region at 60-110 °C.

Introduction

Solid-state high-resolution ^{13}C NMR spectroscopy is a powerful technique for characterizing the crystalline and noncrystalline regions of semicrystalline polymers.[1-13] Recently we found on the basis of the measurements of ^{13}C spin-lattice and spin-spin relaxation times and computer line-shape analyses for the total dipolar decoupling/magic angle spinning (DD/MAS) spectra that polyethylene samples crystallized from the melt were composed of not only crystalline and amorphous phases but also crystalline-amorphous interphase.[1] The thickness of the interphase was estimated to be about 30 Å, which corresponds well to the theoretical value calculated using a lattice model by Flory et al.[14]

Isotactic polypropylene, which is also a highly crystalline polymer, has already been studied by several groups using solid-state high-resolution ^{13}C NMR spectroscopy. Bunn et al.[11] measured CP/MAS spectra of annealed and quenched α-form (monoclinic) and β-form (hexagonal) samples at room temperature. The doublets with 1:2 intensity were observed for CH_2 and CH_3 resonance lines of the annealed α-form sample. They supposed that these doublets were derived from the presence of two different packing sites in crystals on the basis of the arrangement of the molecular chain in a unit cell of α-form. They also suggested that disappearance of these doublets for quenched α-form and β-form samples was due to the decrease in crystalline perfection and the absence of the different sites, respectively.

Lyerla et al.[12] measured ^{13}C spin-lattice relaxation times (T_{1C}) over a wide temperature range from room temperature down to 105 K. They concluded that T_{1C}'s of not only CH_3 but also CH_2 and CH resonances depended on CH_3 rotational motion, and the broadening of the CH_3 resonance around below -100 °C was also due to modulation of CH_3 rotational motion at the frequency of proton nutation in the presence of the decoupling field. Recently Tonelli et al.[13] also reported solid-state high-resolution ^{13}C NMR spectra of isotactic polypropylenes. They used samples that were carefully characterized by X-ray crystallography and reconfirmed the results obtained by Bunn et al.

In this paper, we report new results on the solid-state structure and molecular motion for isothermally bulk-crystallized isotactic polypropylenes. We have particularly paid attention to the crystalline-noncrystalline structure (phase structure) of this polymer and its dependence on temperature. For this purpose we have used some isotactic polypropylenes isothermally crystallized from the melt and measured solid-state high-resolution ^{13}C NMR spectra and different spin relaxation parameters at various temperatures using the VT/MAS system.

Experimental Section

Isotactic polypropylene (Showa Denko K. K. MA510) was purified by Soxhlet extraction with toluene to remove low molecular weight compounds and the atactic polypropylene. The molecular weight and isotacticity of the purified sample were $M_w = 2.30 \times 10^5$ from GPC and (mm) = 98.0% from the analysis for the methyl region of the ^{13}C NMR spectrum in solution, respectively.

After melting at 230 °C the sample was isothermally crystallized at 100 °C for 1 h or at 140 °C for 6 days (hereafter abbreviated to PP100 and PP140, respectively). It was confirmed by X-ray analysis that the crystal structure was α-form (monoclinic) for both samples. The degree of crystallinity was determined from density measurements and DSC. Here, the values 0.936 and 0.850 g/cm^3 were assumed for the crystalline and amorphous densities and 2.10 kcal/mol for the heat of fusion of crystals.[15]

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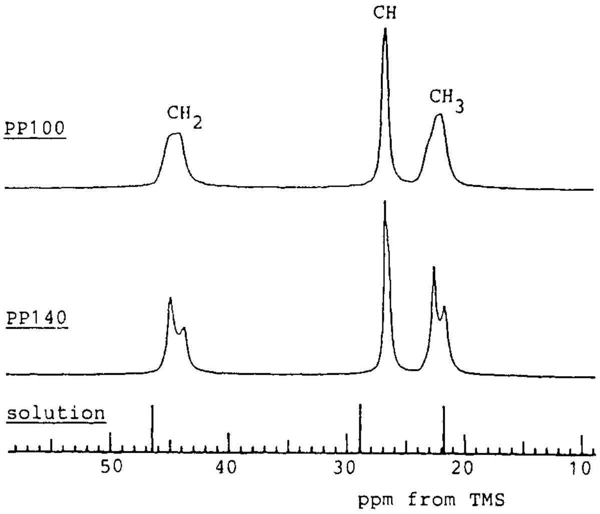

Figure 1. 50-MHz CP/MAS ^{13}C NMR spectra of PP100 and PP140 at room temperature and scalar-decoupled ^{13}C NMR spectrum of isotactic polypropylene in solution.

Solid-state high-resolution ^{13}C NMR measurements were carried out on a JEOL JNM-FX200 spectrometer operating at a field strength of 4.7 T. The radio frequency of 50.1 MHz (field strength B_1 of 6.52 mT ($\gamma B_1/2\pi$ = 69.4 kHz)) was used for the detection of ^{13}C resonance. The ^{1}H Hartmann–Hahn matched and DD field were 1.63 mT (69.4 kHz) and 1.28 mT (54.3 kHz), respectively. MAS was carried out at a rate of 3.2–3.4 kHz at room temperature or 4.1–4.3 kHz above room temperature using the VT/MAS system. Calibration of the temperature above room temperature was performed by measuring the narrowing of the resonance line at a melting point for some organic compounds with well-defined melting points. The chemical shift relative to tetramethylsilane was determined at room temperature by using the crystalline peak at 89.11 ppm[16] of polyoxymethylene as an internal reference.

Results and Discussion

Figure 1 shows 50-MHz CP/MAS ^{13}C NMR spectra of PP100 and PP140 at room temperature together with a stick-type ^{13}C NMR spectrum of the isotactic sequence in solution. CH_2 and CH resonances of the crystallized samples exhibit upfield shifts from those in solution, reflecting the difference in conformation in the solid and solution states. Moreover, CH_2 and CH_3 doublets are clearly observed for PP140, which are related to the contribution from the crystalline region as reported by Bunn et al.[11]

Figure 2 shows CP/MAS ^{13}C NMR spectra of PP140 obtained at different temperatures using the VT/MAS system. In this experiment attention must be paid to the possible change in structure for the sample during the measurement. Actually, 147 °C, which is the highest temperature for the measurement, is higher than the crystallizing temperature, 140 °C. However, melting began at 150 °C in the DSC thermograph, and CP/MAS ^{13}C NMR spectra at 43 °C were the same before and after the measurement at 147 °C. This indicates that an annealing effect is negligible during the VT/MAS measurements.

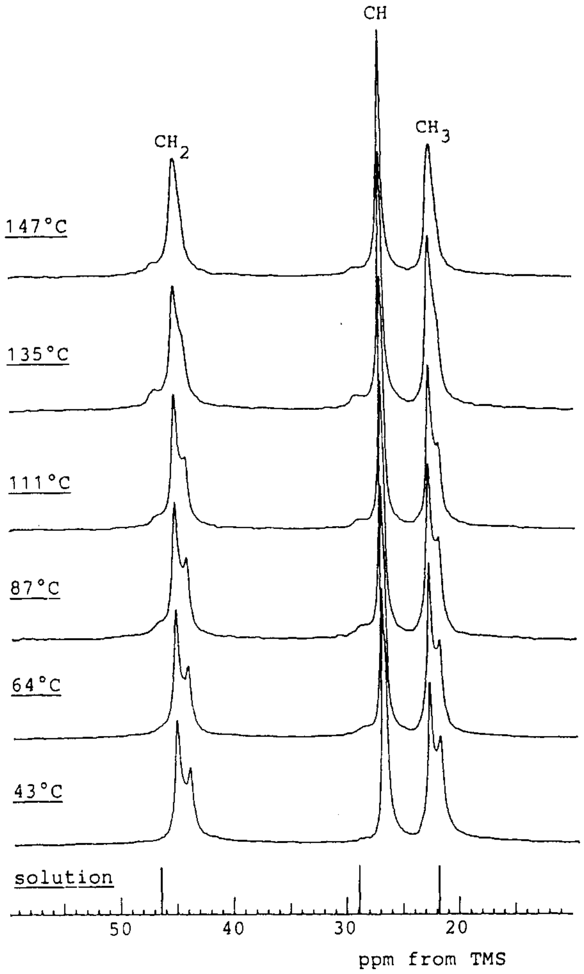

Figure 2. CP/MAS ^{13}C NMR spectra of PP140 above room temperature.

From Figure 2 some important results can be derived. CH_2 and CH_3 doublets, which are clearly observed at room temperature, tend to change to singlets with increasing temperature, as a result of the downfield shift for the upfield lines. If the doublets truly stem from the presence of the different packing sites in a unit cell as proposed by Bunn et al.,[11] such a difference may disappear at higher temperatures. In order to ascertain this point, we have measured X-ray diffraction patterns for a polypropylene sheet, which exhibits almost the same NMR spectra as PP140. This sheet was made as follows: melted at 230 °C for 6 min, crystallized at 30 °C for 5 min, and then annealed at 160 °C for 1.5 h. X-ray diffraction patterns of the sample obtained at different temperatures are shown in Figure 3. This measurement was performed using a Mettler FP82 hot stage, FP80 central processor as a sample holder, a temperature controller, and a Rigaku X-ray diffraction system equipped with PSPC (position-sensitive proportional counter). It is obvious that no significant change is recognized except for slight shifts of diffraction angles due to thermal expansion of the crystals. A possible explanation of these NMR and X-ray results may be made by the packing effect, which causes the CH_2 and CH_3 doublets for PP140 as proposed by Bunn et al.,[11] and molecular motion in the crystalline region, which becomes more active at higher temperatures and averages each crystalline carbon resonance over the two sites. This molecular motion is most likely a 3-fold jump rotation about the 3_1-helical chain axis; such a motion would produce little change in the X-ray diffraction patterns at higher temperatures as is observed. Probably this molecular motion is related to the crystal relaxation, which is the so-called α-relaxation. In order to examine this motional model, the simulation of the ^{13}C chemical shifts and the relative intensities of the CH_2 doublets are in progress as a function of the jump frequency of the two sites or multiple sites.

At higher temperatures in Figure 2, relatively broad lines become visible downfield for the CH_2 and CH resonances. This can be seen more clearly in DD/MAS ^{13}C NMR spectra at the same temperature range shown in

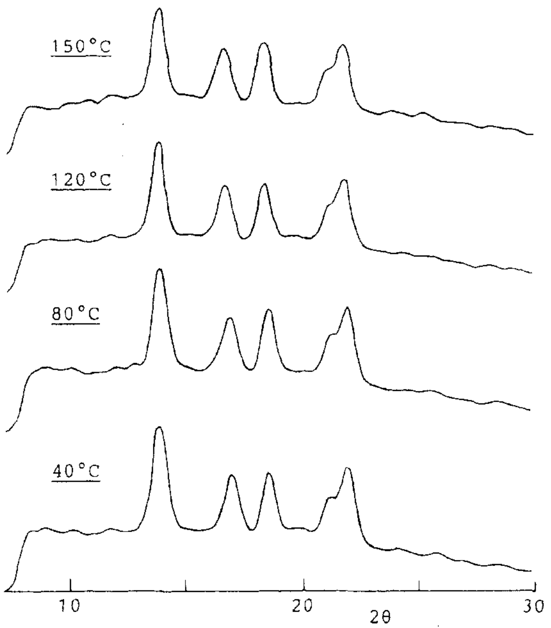

Figure 3. Wide-angle X-ray diffraction patterns above room temperature.

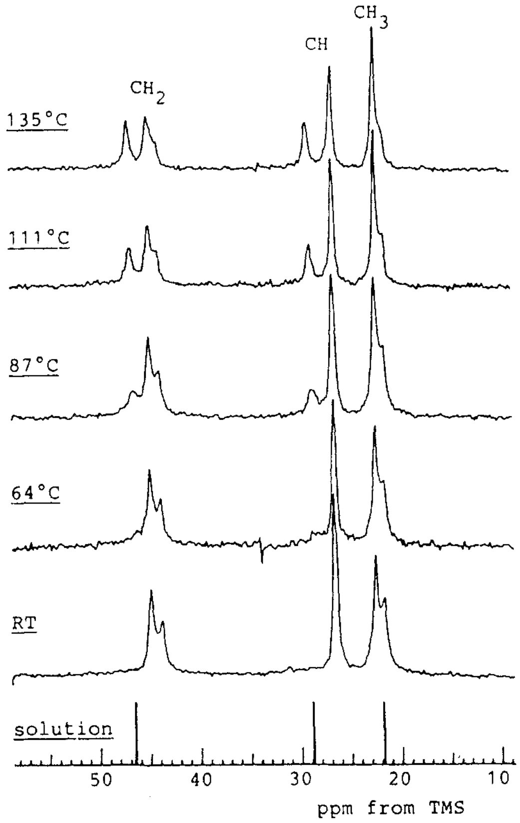

Figure 4. DD/MAS ^{13}C NMR spectra of PP140 above room temperature.

Figure 4. Since their chemical shifts are very close to those of the isotactic sequence in solution as seen in Figure 4, these resonance lines can be assigned to the amorphous component. Further evidence of this assignment is obtained by spin relaxation and line-shape analyses as described below.

In an attempt to investigate the phase structure of PP140 in detail, ^{13}C spin-lattice relaxation times (T_{1C}) have been measured using Torchia's pulse sequence[17] and a modified saturation recovery method. The results obtained at 87 °C are listed in Table I. CH_2 and CH resonances contain three components with different T_{1C}'s, reflecting different molecular mobilities in the crystalline and noncrystalline regions. The longest and shortest T_{1C} components can be assigned to crystalline and amorphous components, respectively, while the origin of the component with medium T_{1C} values will be described below. On the other hand, only two T_{1C} values are observed for the CH_3 line, probably due to the fact that two of the three values are indistinguishable. The longer T_{1C} of the CH_3 line, which is assigned to the crystalline component by the doublet line shape, is much shorter than those of the crystalline component of the CH_2 and CH lines. This is due to CH_3 rotation present even in the crystals as reported by Lyerla et al.[12]

Table I
^{13}C Spin-Lattice Relaxation Times (T_{1C}) of PP140 at 87 °C

	CH_2		CH		CH_3
	46.43 ppm	44.82 ppm	28.76 ppm	26.60 ppm	22.39 ppm
		69.1		47.1	1.31
T_{1C}/s		7.1		4.9	0.47
	0.20		0.32		

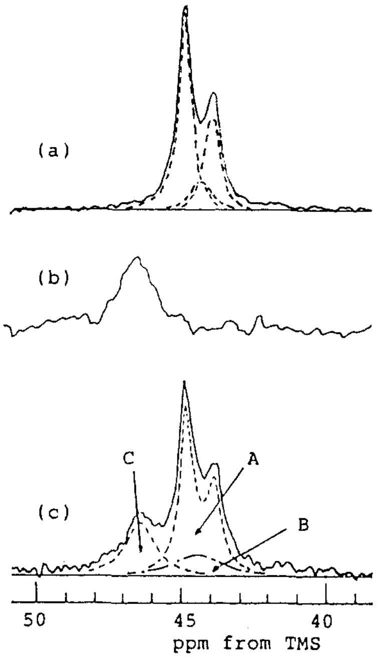

Figure 5. ^{13}C NMR spectra of PP140 at 87 °C: (a) crystalline spectrum obtained using Torchia's pulse sequence with the delay time of 40 s; (b) amorphous spectrum obtained using the saturation recovery method with the delay time of 2.0 s; (c) DD/MAS spectrum.

Next we have determined the line shape of each component using the difference of the T_{1C} values. Figure 5a shows the CH_2 resonance of the crystalline component, which has been recorded by Torchia's pulse sequence. The delay time to suppress the shorter T_{1C} components is 40 s. The result of a computer line-shape analysis is also shown in Figure 5a, where a Lorentzian function is assumed for each contribution.[18] According to this analysis, the crystalline spectrum is composed of a doublet with 1:2 relative intensity and an additional singlet centered at 44.24 ppm. The latter component may be ascribed to somewhat the disordered crystalline component, but the molecular mobility must be still highly restricted because the T_{1C} value of this component does not significantly differ from that of the other crystalline component. Alternatively, this component may be an artifact produced by assuming Lorentzians for the resonance lines. Accordingly, in the line-shape analysis described below, the composite curve of the three Lorentzians is used as

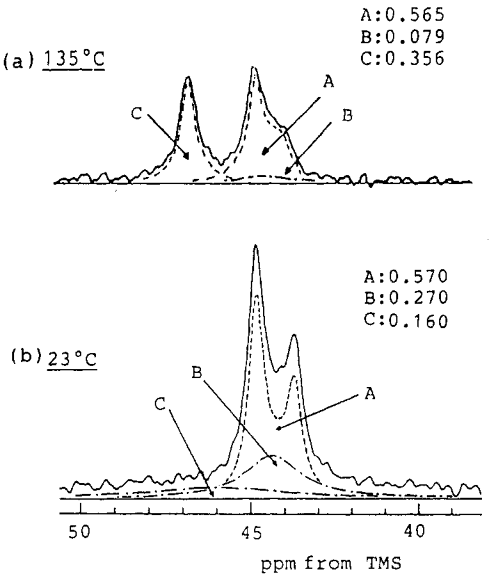

Figure 6. DD/MAS ^{13}C NMR spectra of PP140: (a) at 135 °C; (b) at room temperature.

a line shape for the crystalline component.

The spectrum of the shortest T_{1C} component, shown in Figure 5b, has been obtained by the saturation recovery method, in which the time for the recovery of magnetization is set at 2.0 s to suppress the longer T_{1C} components. This spectrum, which corresponds to the amorphous component mentioned above, can be represented by a Lorentzian function centered at 46.63 ppm with a line width of 60 Hz. Although 25% of the component with T_{1C} = 7.1 s may also appear at 44.82 ppm, this component does not significantly affect the Lorentzian line shape of the amorphous component at 46.63 ppm. Figure 5c shows the DD/MAS ^{13}C NMR spectrum, which has been obtained by a 45° single pulse with the delay time of 240 s and thus reproduces the contributions from all structural components, and the result of the line-shape analysis by a computer. In this computer analysis, the chemical shifts of the crystalline and amorphous components were assumed to be constant. Interestingly, it is found that the DD/MAS spectrum is composed of not only the crystalline and amorphous contributions, which are described by curves A and C, respectively, but also another Lorentzian component described by curve B. This component can be assigned to the component with T_{1C} = 7.1 s because this contribution is well recognized for the partially relaxed spectra obtained for the shortest relaxation times by the saturation recovery method.

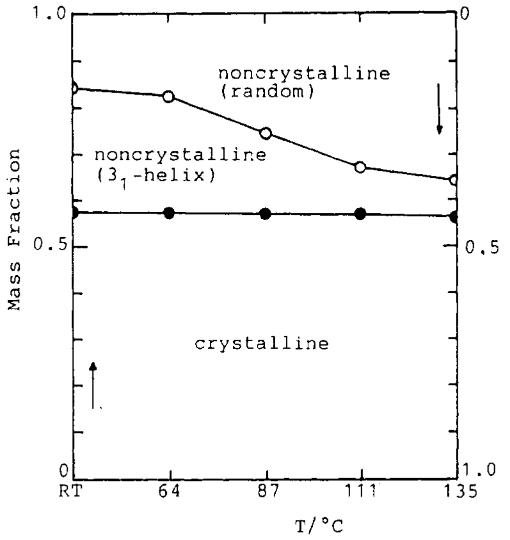

Figure 7. Temperature dependence of the phase structure of PP140.

Table II
Degrees of Crystallinity of PP100 and PP140 from Density, DSC, and NMR Measurements

sample	density	DSC	NMR
PP100	0.718	0.454	0.480
PP140	0.828	0.540	0.570

Similar line-shape analyses for DD/MAS spectra measured at various temperatures shown in Figure 4 were performed, and the results at room temperature and 135 °C are shown in parts b and a, respectively, of Figure 6. In both parts, A and C correspond to crystalline and amorphous components, respectively, similar to Figure 5c. The line widths of components A and B are almost the same at this temperature range, whereas that of component C becomes narrow from 240 Hz at room temperature to 30 Hz at 135 °C. Since the glass transition temperature (T_g) of isotactic polypropylene is close to room temperature (~10 °C from mechanical measurements), narrowing of the resonance for the amorphous component can be explained by the onset of the segmental motion of the order of 10^2–10^4 Hz. Moreover, Figure 6b suggests that one may fail to notice the amorphous component of polypropylene below T_g because of the wide line width of the amorphous component. It is very important to analyze the spectrum obtained below T_g by considering the results above T_g.

The mass fractions of the three components are plotted against the temperature in Figure 7. Since in this temperature range the mass fraction of A stays nearly constant and any melting is not recognized in the DSC thermograph, component A is assigned to the crystalline component and then component B is assigned to the noncrystalline component. Since the chemical shift of B is close to the average of chemical shifts for the doublet of the crystalline component, component B may be ascribed to segments dominated by the 3_1-helical chain conformation as in the crystalline region. This component would most likely be located in the transition region between the crystalline and amorphous regions. However, such a helical chain may be transformed to a random chain at higher temperatures as is seen from the change in mass fraction between components B and C. In addition, the results at room temperature before and after the measurements at a temperature above 100 °C were almost the same. This structural change is thus found to be reversible, because no difference is detected in the mass fraction of each component at room temperature before and after the measurements at higher temperatures. These findings are very interesting because such conformational changes may be associated with the physical properties such as the elastic modulus for isotactic polypropylene.

For PP100 a similar analysis has been made, and then it is found that the mass fractions of components A–C were 0.480, 0.300, and 0.220 at room temperature, respectively. The mass fraction of A corresponds to the degree of crystallinity. For comparison we have determined the degrees of crystallinity of PP140 and PP100 by density measurements and DSC and listed them in Table II together with the mass fraction of component A obtained by the NMR analysis. It should be noted here that for both PP140 and PP100 the degrees of crystallinity by density measurements are much higher than those by DSC and NMR. In the case of density measurements

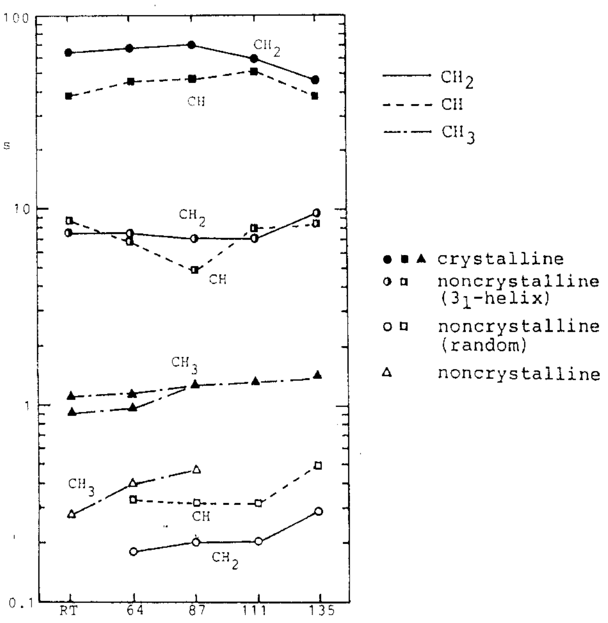

Figure 8. ^{13}C spin-lattice relaxation times (T_{1C}) of PP140 above room temperature.

the degree of crystallinity is calculated assuming that the sample consists of the crystalline and amorphous components. Therefore, the degree of crystallinity must be overestimated because our samples consist of not only crystalline and amorphous components but also another noncrystalline component with the density possibly higher than that of the amorphous component.

As noted above, Lyerla et al.[12] found that T_{1C}'s of CH$_2$ and CH resonances showed their minima around −100 °C, while the T_{1C} values of the CH$_3$ carbons monotonically change at −105 to +60 °C. However, they did not discriminate between the crystalline and noncrystalline contributions. We have measured T_{1C}'s of the crystalline and noncrystalline components from room temperature to 135 °C, taking into account the phase structure. In Figure 8 the T_{1C} values are plotted against the temperature. T_{1C}'s of the amorphous component for the CH$_2$ and CH resonances are shorter than those for the CH$_3$ resonance. This means that the molecular motion of the main chain is greatly enhanced and the T_{1C} relaxation is mainly induced by the time fluctuation of the ^{13}C–^{1}H dipolar interaction in the CH and CH$_2$ groups. On the contrary, the T_{1C} values of the crystalline component for the CH and CH$_2$ carbons are much higher than the corresponding values for the CH$_3$ groups. This suggests that the T_{1C} relaxation for the CH and CH$_2$ carbons in the crystalline region may be greatly affected by the CH$_3$ rotation. In addition, the situation seems to be the same for the noncrystalline component with 3$_1$-helical conformation. As for the CH$_3$ carbons their T_{1C} values gradually increase with increasing temperature for both crystalline and noncrystalline components. Therefore, the correlation times for all methyl rotations exist in the so-called extreme narrowing condition. If the single-correlation-time model is assumed for all methyl relaxations over this temperature range, then the questionalbe conclusion follows, namely, that methyl rotation is enhanced in the crystalline region relative to the noncrystalline region. The single-correlation-time model is probably not appropriate for both crystalline and noncrystalline regions. In the noncrystalline region the overall random reorientation of the rotation axis of the methyl group will be superposed on the methyl rotation. In contrast, such a motion contributing to megahertz spectral density is highly hindered in the crystalline region. However, some limited motion may be superposed on the methyl rotation of the crystalline component, for example, the fluctuation of the C–C rotation axis on the order of picoseconds.[20,21] In order to analyze molecular motions in detail we will measure T_{1C}'s for each component over a wider temperature range.

Acknowledgment. We express our thanks to Dr. D. L. VanderHart of NIST for his useful discussion. We are also grateful to Professor D. C. Bassett and Dr. R. H. Olley of the University of Reading for suggesting the crystallization conditions of polypropylene samples.

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