Conformational Exchange near the Glass Transition: Two-Dimensional ^{13}C NMR Study of Atactic Polypropylene

The chain dynamics in polymer melts are considered usually to involve conformational (trans–gauche) transitions.[1] As pointed out, for example by Helfand,[2] such motions need not be strictly local processes, as described by kink[3] or three-bond motions[4] involving rotations by well-defined angles about spatially fixed C–C axes. Conformational transitions can also arise via relaxation processes involving larger chain units, leading to translational and angular displacements of different amplitudes for the corresponding monomer units. Experimental evidence for the latter view was recently provided by a number of ^2H NMR studies of hydrocarbon chain dynamics.[5-8] Notably, however, no manifestation of slow trans–gauche transitions at temperatures close to the caloric glass transition temperature T_g was found in reorientational angle distributions determined by two-dimensional (2D) NMR for atactic polypropylene (aPP) or polystyrene.[6-8] The data could be fitted adequately on the basis of an isotropic rotational diffusion model incorporating small angular steps with mean correlation times following the WLF equation[9] over 10 orders of magnitude.[6-8]

The "absence" of trans–gauche transitions was puzzling, since its barrier (~15 kJ/mol) is much smaller than the apparent activation energy (>600 kJ/mol) for the α process at T_g. A more direct approach for detecting trans–gauche transitions makes use of the changes they produce in the local electronic structure. These can be monitored by high-resolution NMR, where the isotropic chemical shift is known to be a sensitive probe of polymer stereochemistry.[10-13] For example, ^1H and ^{13}C NMR spectra of polypropylene in solution reveal stereochemical configurations, while high-resolution solid-state ^{13}C MAS NMR experiments distinguish between different molecular conformations[14,15] and packing,[16,17] e.g., the different helical conformations of isotactic (iPP) and syndiotactic (sPP) polypropylene. The static 2D exchange NMR experiment applied to deuterated atactic (aPP) and isotactic polypropylene[6] demonstrates the dependence of the type of rotational motion on chain conformation and packing. Diffusive motion on a time scale of milliseconds to seconds was observed above the glass transition for aPP, while in iPP helical jumps occur about its 3_1 helix axis. In the present paper, we report 2D ^{13}C NMR exchange spectra of aPP, recorded under conditions of magic-angle spinning, that permit the study of ultraslow polymer dynamics with high spectral resolution. For the first time, ultraslow exchange between different conformations involving the methylene group in the vicinity of T_g is demonstrated.

The aPP sample (M_w = 100 000, M_w/M_n = 2.4[18]) was obtained by metallocene-catalyzed polymerization of propylene for 12 h at 293 K.[19] The content of isotactic (mm), heterotactic (mr), and syndiotactic (rr) triads was 0.39, 0.40, and 0.21, respectively, corresponding to average block lengths n_{iso} = 3.0 and n_{syn} = 2.1. The glass transition temperature T_g was determined to be 239 ± 1 K from DSC measurements (cooling rate 2 K/min). Solid-state ^{13}C NMR spectra were acquired on a Bruker MSL-300 spectrometer (^{13}C frequency 75.47 MHz). A Bruker MAS probe was used with a proton 90° pulse length of 3.9 μs. Temperature stability and calibration were essential because of the highly temperature-dependent nature of polymer motions in the vicinity of T_g. The temperature was calibrated to ±1 K using line splittings in high-resolution ^1H NMR spectra of methanol isolated in a 2-mm-diameter sphere as an internal standard. No hysteresis effects were observed after different heating and cooling cycles. All chemical shifts are given relative to TMS with an uncertainty of ±0.3 ppm.

In Figure 1, ^{13}C CP/MAS NMR spectra of aPP are shown at two different temperatures. At 250 K (Figure 1a), distinct splittings of the methylene (CH_2; 48.6 and 44.6 ppm) and methyl (CH_3) signals (22.0 and 18.4 ppm) are observed, whereas the methine (CH) signal at 27.2 ppm does *not* appear as a doublet. Further lowering of the temperature to T_g does not alter the spectrum. With increasing temperatures, however, the splittings decrease and, at about 259 K, the peaks coalesce. Spectra recorded at 262 K (Figure 1b) exhibit signals only at 46.6 ppm (CH_2), 27.4 ppm (CH), and 21.5 ppm (CH_3). A comparison with chemically shifted peak positions in solid-state ^{13}C NMR spectra of iPP and sPP[15] indicates that the splittings of 4 ppm for the methylene carbons in aPP (Figure 1a) are of an intramolecular, conformational origin. Packing effects in different forms of iPP with different thermal histories[16] result in splittings in the range of only 0.5–1 ppm. The downfield peak of the CH_2 doublet of aPP (48.6 ppm) corresponds to those CH_2 carbons in sPP characterized by two trans carbons in the γ position, whereas the upfield CH_2 signal of aPP at 44.6 ppm matches the CH_2 peak of iPP (44.5 ppm) with a tg environment. The shoulder observed at 40 ppm in Figure 1a (see also Figure 2b) is near the location expected for the gg conformation, though the signal is weak and henceforth will be neglected. These splittings show that at lower temperatures such conformational sequences persist for relatively long times. At ambient temperature, however, conformational transitions interchanging tt and tg sequences lead to motional averaging.

To check whether these trans–gauche transitions correspond to chain dynamics of the α-process near T_g (WLF), the time scale of the conformational exchange must be established as a function of temperature. In the ultraslow regime with correlation times $\tau_c \geq 1$ ms, where deviations from Arrhenius behavior are most pronounced, this can be investigated by 2D exchange NMR:[20] a mixing time t_m is inserted between an evolution time t_1, where a given ^{13}C spin evolves with frequency ω_1, and a detection time t_2, where the same spin evolves with frequency ω_2.[20,21] If the frequency is the same before and after the mixing time ($\omega_1 = \omega_2$), the signal is confined to the diagonal, with a line shape corresponding to that of the 1D spectrum. Different frequencies ($\omega_1 \neq \omega_2$) after the mixing time lead to off-diagonal cross peaks in 2D exchange spectra. A frequency change during t_m ($\geq \tau_c$) may arise from molecular reorientation[6,22,23] or chemical exchange.[21]

As an example, Figure 2 shows two 2D ^{13}C CP/MAS NMR spectra which were recorded at the same temperature (250 K), but with different mixing times t_m. The cross peaks seen in the CH_2 and CH_3 regions of Figure 2a indicate that the conformations of certain carbon segments are altered when t_m = 500 ms. During a mixing time of only 5 ms, however, few segments actually change their conformation. Therefore, the off-diagonal intensity in Figure 2b is weak, and the line shape of the essentially diagonal spectrum corresponds to the 1D spectrum shown in Figure 1a. Several 2D ^{13}C MAS NMR spectra have been recorded at temperatures of 238–260 K over a range of mixing times.[24] Simulations of exchange intensities are in progress to extract correlation times from these data. Preliminary analysis indicates that the average τ_c (10^{-3} s $\leq \tau_c \leq$ 1 s) of the conformational exchange in aPP

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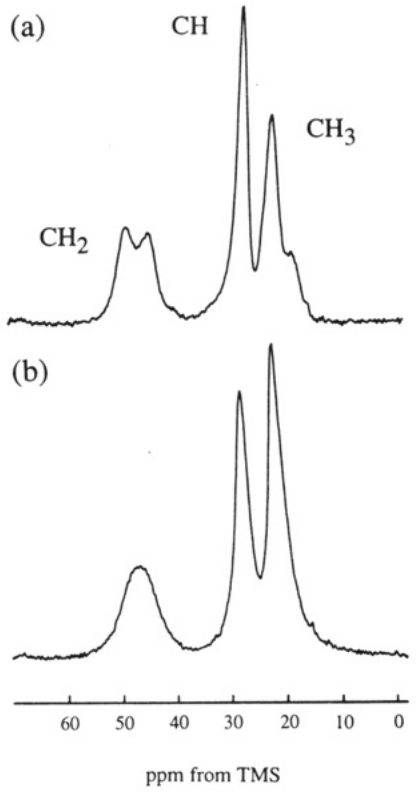

Figure 1. ^{13}C CP/MAS NMR spectra of atactic polypropylene at temperatures below and above coalescence of the CH_2 signals: (a) T = 250 K and $\omega_R/2\pi$ = 3500 Hz (120 scans, 800-μs contact time, 1.5-s recycle delay), and (b) T = 262 K (same parameters as (a) but with 600 scans).

exhibits a temperature dependence similar to diffusive rotational α processes observed in static 2D ^{13}C exchange NMR experiments.[24] This proves that the conformational transitions are indeed tightly coupled to the chain motions of the α process. Below T_g, however, conformational exchange, as well as rotational diffusion, is frozen on the time scale of these NMR measurements, i.e., 1 s. The full analysis of the data currently underway must take into account a heterogeneous distribution of correlation times, recently shown to be responsible for the nonexponential loss of correlation above T_g.[25]

By resolving distinct ^{13}C resonances from different trans–gauche sequences at the CH_2 segments in aPP, we demonstrate that residual conformational order is present in this amorphous polymer. Slow chain dynamics above T_g, leading to exchange between different conformations, have been detected by high-resolution 1D and 2D NMR. These conformational transitions occur on the same time scale as rotational motions detected by 2D NMR on static samples, but do not involve the well-defined rotational angles expected[6] for kink or three-bond motions in a static environment predicted by lattice models. The trans–gauche transitions are detected here because they lead to a change in the *isotropic* chemical shift, which can be detected *independent* of molecular orientation. Thus, the combination of 2D NMR techniques exploiting isotropic *and* anisotropic nuclear spin interactions shows directly that trans–gauche conformational transitions are accompanied by substantial angular displacements of the units involved. This strongly supports models which ascribe conformational changes to relaxation of longer chain units[2] and explains the tight coupling to the cooperative motions of the α process manifested in macroscopic material properties.

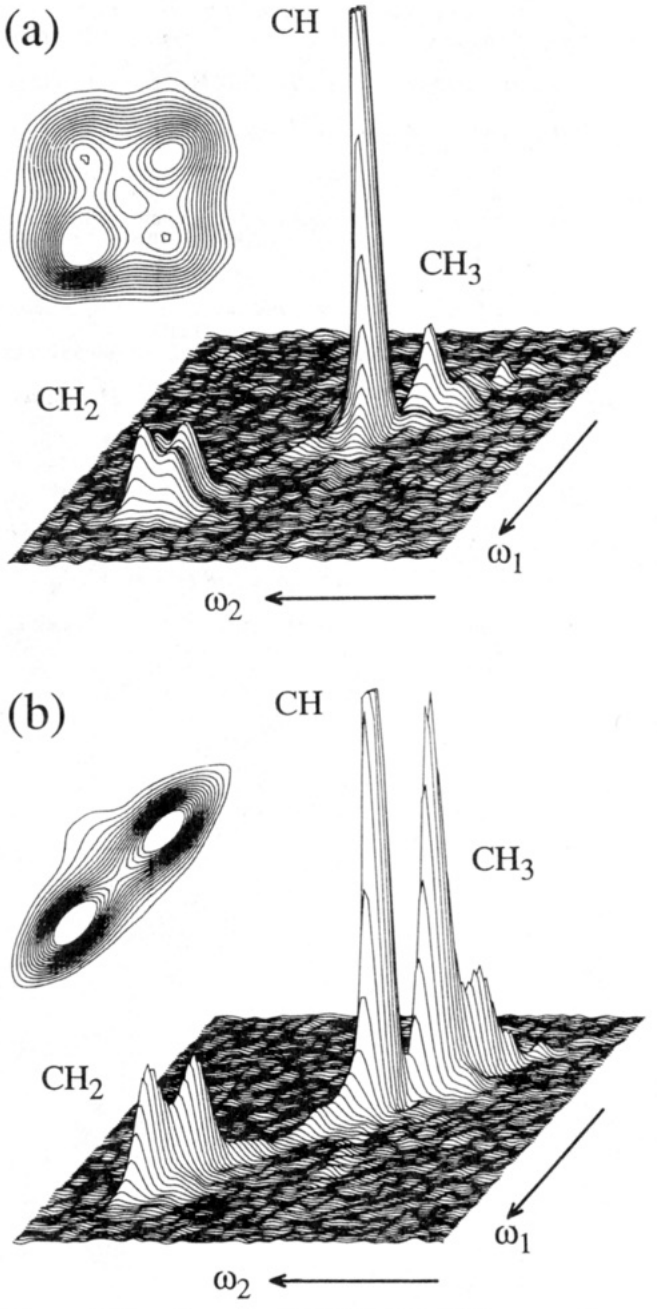

Figure 2. Two-dimensional ^{13}C CP/MAS NMR spectra of atactic polypropylene at 250 K (same parameters as Figure 1a) acquired with mixing times of (a) 500 ms and (b) 5 ms. The CH signals have been truncated to display the methylene (CH_2) peaks more clearly. A contour plot of the CH_2 chemical shift region is shown as an inset for each spectrum. The spectra were each acquired over a period of 4 h. The intensity of the methyl resonance in (a) is reduced by T_1 relaxation.[20]

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