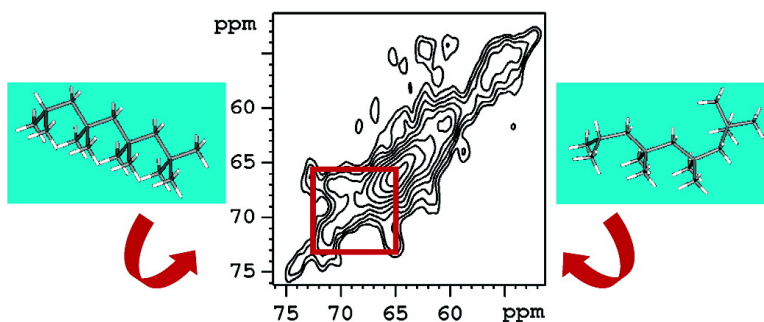


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The Glass Transition Time Scale and Configurational Entropy in Polymers: An Experimental Molecular View

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Molecular processes involving slow conformational exchange are assumed to give rise to glass-to-liquid transitions in synthetic high polymers. The time scale and length scale of both individual segmental dynamics and correlated-chain, or cooperatively rearranging, motions are currently receiving widespread attention in the literature.^{1–3} A variety of experimental methods, ranging from bulk calorimetry and mechanical methods to neutron scattering and positron annihilation spectroscopies, comprise the current arsenal devoted to this fundamental problem in materials science.⁴ Spiess and co-workers have demonstrated that solid-state exchange NMR is particularly useful for interrogating polymer chain dynamics above the calorimetric glass transition temperature T_g .^{5–10} In each case, dynamics were observed on time scales of less than 1 s, for temperatures at least 8 K above the calorimetric T_g . In this communication, we examine the time scale for conformer interchange at the calorimetric T_g for polyisobutylene (PIB) using two-dimensional (2D) ^{13}C exchange NMR and demonstrate that the time scale of the T_g process is on the order of several seconds.

Figure 1 illustrates the vastly different information content obtained from the traditional differential scanning calorimetry (DSC) T_g experiment versus that from 2D ^{13}C exchange NMR. The DSC trace for PIB shown in Figure 1 was collected using a 2 K/min scan rate, resulting in a broad transition spanning a 5 K range (203–208 K). Other than suggesting a heterogeneous distribution of heat capacities, the DSC result provides little information concerning the molecular dynamics, or their time scales, involved in the transition. Parts a–c and d–f of Figure 1 show the 2D MAS ^{13}C exchange results for the main-chain CH_2 group in PIB at temperatures corresponding to the onset (203 K) and completion (208 K) of the DSC T_g , respectively. (Temperatures in the 4-mm MAS probe were calibrated using the PbNO_3 chemical shift thermometry method,¹² and are accurate to within ± 1 K; 2000 L/min cooling gas flow rates were used to minimize temperature gradients in the sample.) PIB is particularly advantageous for this type of experiment, since its ^{13}C spin–lattice relaxation time constant $T_1 = 3.0$ s at 205 K, thereby preserving signal for longer mixing times, and the chain displays all three possible conformer environments. Three different chemical exchange times are shown at each temperature, and the 1D CP/MAS spectrum for this CH_2 resonance is shown above each contour plot. The broad peak reflects the distribution of CH_2 groups for chain segments in trans–trans (tt), trans–gauche (tg), or gauche–gauche (gg) conformations along the polymer backbone. In agreement with previous reports, little or no exchange is observed for a 1-s mix time (or less) at 203 or 208 K, as indicated by the lack of any off-diagonal intensity.^{7,8} However, for longer mixing times, exchange events are observed between the individual tt, tg, and gg peaks, as shown by the increased off-diagonal intensity at the 2 and 4-s mixing times. Examination of the ratio of an individual peak width perpendicular to the diagonal, vs parallel to the diagonal, shows that conformer exchange is essentially complete after 4 s at 208 K (see Figure 1f). While the amount of

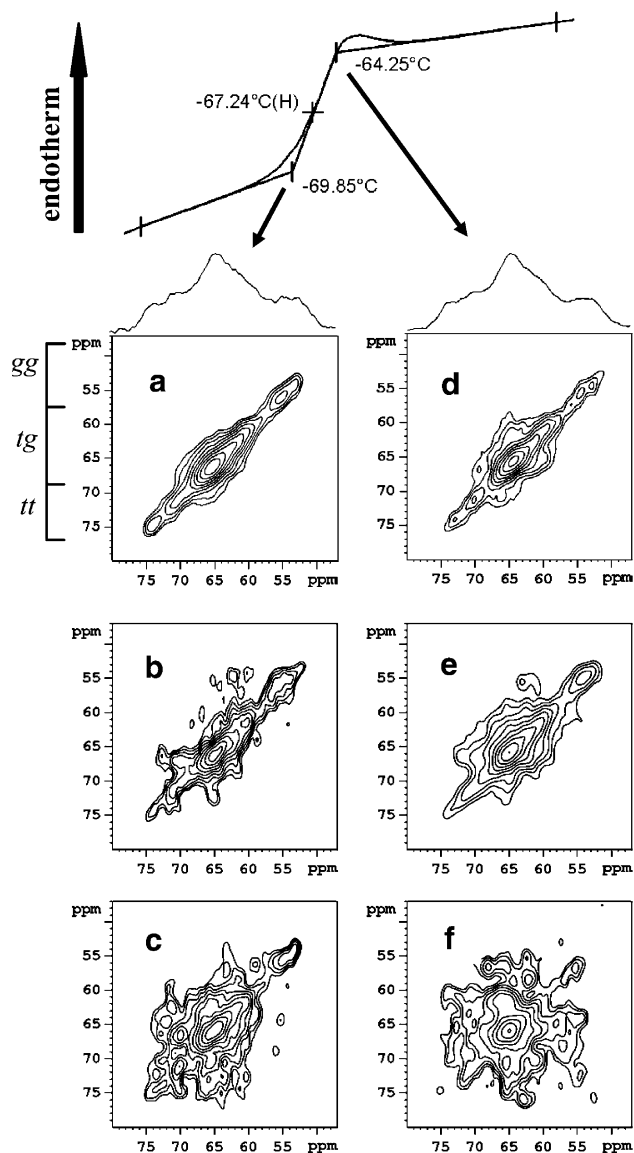


Figure 1. Comparison of DSC T_g trace obtained with a 2 K/min scan rate (top) with 2D ^{13}C exchange spectra at (a) 203 K and 1 s mix time; (b) same as (a) at 2 s mix; (c) same as (a) at 4 s mix; (d) 208 K at 1 s mix time; (e) same as (d) at 2 s mix; (f) same as (d) at 4 s mix. Spinning speeds were 4 kHz.

conformational exchange is clearly reduced in 1a–c vs 1d–f, chain segment dynamics are observed at both temperatures for the 2 and 4-s mixing times.

The 2-s exchange time in Figure 1b indicates a surprising result, in that the first process at the glass transition onset appears to involve exchange between a small subset of tt and tg conformers (65–75 ppm region). While each diagonal peak in Figure 1b is

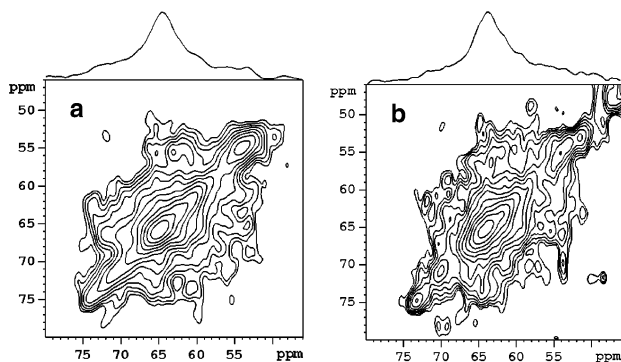


Figure 2. 2D exchange spectrum at 208 K of (a) methylene carbons in pure PIB with a 2 s mixing time; (b) methylene carbons of PIB in a 50:50 blend with PEB using a 100 ms mixing time. Slices through the 65-ppm trans-gauche peak are shown on the top axis, and within the signal-to-noise limits, exhibit the same features.

broad, reflective of the inhomogeneous distribution of longer-range conformer sequences, relatively narrow off-diagonal ridges are observed at 2 s. In contrast, the same exchange time in 1e shows a larger and more diffuse off-diagonal intensity between tt and tg segments, and also within the tg peak region (60–67 ppm). The fact that the exchange patterns exhibit increased off-diagonal intensity as the temperature is increased rules out dipolar-mediated spin-diffusion as the operative spin-exchange pathway. (This was further confirmed by the comparison of 2D experiments at T_g with and without ^1H spin decoupling during the mixing time, in which identical exchange patterns were observed.) We believe that the NMR data provided here, in contrast to scan-rate specific calorimetric endotherms, give the basis for a functional definition of the glass transition as that temperature *and time* range over which isolated chain segments access all possible conformer states, versus a subpopulation of lowest-energy conformers.

The site-specific dynamics revealed by the 2D exchange experiment indicate changes in local glass transition temperature/time scale upon formation of a miscible polymer blend. Parts a and b of Figure 2 show results obtained at 208 K for a pure PIB sample and a 50:50 wt % blend of PIB and polyethylene-co-butene (PEB), respectively. The PEB contained 49 mol % 1-butene units randomly incorporated into the chain. The 2D exchange patterns appear almost identical in terms of their off-diagonal intensity distribution, as confirmed by taking a slice through the tg peak at 63 ppm in each. This slice is shown as the top trace on each contour plot. However, while the PIB exchange pattern required a 2-s mixing time to achieve the off-diagonal signal in 2a, the PIB/PEB blend pattern in 2b was obtained after only 100 ms. A major question in the study of polyolefin blend miscibility is the identification of the thermodynamic driving force for mixing, and in this case, PIB/PEB blends have been shown to be miscible for the PEB composition used here.^{13,14} The results of Figure 2 suggest that the rate of conformational dynamics of the PIB chains in the blend with PEB are enhanced or, stated differently, that the PIB “local T_g ” is depressed in the blend.

The reduced exchange time (a kinetic quantity) of the PIB chains in the PIB/PEB blend may be related to the increased configurational entropy S_c (a thermodynamic quantity) using Adams–Gibbs theory,^{15,16} one form of which is shown below:

$$\tau_{\text{ex}} = \tau_0 \exp(c/TS_c)$$

Here, τ_{ex} is the exchange time for the redistribution of a single conformer’s magnetization among all possible conformers, as measured by the 2D slices shown in Figure 2. This exchange time is analogous to a structural relaxation time, and represents the extent of conformational relaxation along the chain. Using the data from Figure 2, in which $\tau_{\text{ex}} = 2$ s and 100 ms for pure PIB and PIB in the PIB/PEB blend, respectively, we can solve for the configurational entropy ratio $S_{\text{blend}}:S_{\text{pure}}$. In this way, the constants τ_0 and c , and the temperature T , cancel from the equation. The resulting $S_{\text{blend}}:S_{\text{pure}} \geq 3.33$, indicating that the PIB chains in the blend with PEB have a much larger configurational entropy and, therefore, more accessible conformations per unit time, than pure PIB. Similar results were obtained by comparing equivalent 2D slices for PIB and PIB/PEB at 4 and 1.5 s mix times, respectively, at the same temperature as Figure 2. While these data are not shown for brevity, a similar $S_{\text{blend}}:S_{\text{pure}} \geq 3.4$ result was obtained. These results suggest that entropy drives miscibility in this particular polyolefin blend, and the ability to place quantitative limits on key thermodynamic parameters should prove critical to a complete understanding of the heretofore anomalous results in the area of polyolefin miscibility. Further, Adams–Gibbs theory requires that this increased entropy in the blend corresponds to smaller-sized cooperatively rearranging regions at a given temperature, i.e., a shorter T_g length scale.^{1–3} Local motions become dominant in this regime, and the 2D exchange is clearly sensitive to these subtle changes. An alternative experimental strategy is to match the necessary equivalent 2D exchange patterns vs T , thereby obtaining thermally activated configurational entropy changes in any amorphous polymer for which conformationally inequivalent signals are present. We plan to pursue additional experiments as a route to understanding the glass transition length scale and polymer miscibility.

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