be likened to directional or regiosequence isomers. In addition, each of these will be subject to the various stereoconfigurational possibilities described above so that the central fluorine in the CCC triad will reside in more than just three magnetically nonequivalent environments. Closer inspection of spectrum c in Figure 12 reveals some fine structure and at least five lines, but these are strongly overlapping so that the pattern is not amenable to any ready interpretation beyond the demonstration that *trans*-PBD:CFCl is highly stereoirregular.

Conclusions

Polybutadienes trap fluorochlorochlorocarbene generated according to the Seyferth method very efficiently, and exhaustive reaction of the double bonds may be realized. The glass-transition temperatures of the adducts increase linearly with conversion, and extrapolation of the values for the trans polymer gives a T_g of −85 °C for the starting material. Monomer and stereosequence are not subject to a neighboring-unit effect during the reaction, although it appears there is a bias in the distribution of syn and anti isomers for the cis polymer. The more hindered syn isomer is preferred when :CFCl adds to a cis double bond.

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Spin–Lattice Relaxation of Dipolar Energy of Polypropylenes

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ABSTRACT: The temperature dependence of the spin–lattice relaxation rate [T_{1D}^{-1}] of the dipolar energy of the protons of polypropylene is reported. Measurements for three samples demonstrate that it is sensitive to motions involved in both the α and β relaxations of polypropylene.

Introduction

Segmental motions of polymers produce efficient relaxation of nuclear spins.[1] Careful measurements of line widths,[2] spin–lattice relaxation times of the Zeeman energy in the laboratory frame, T_1,[3] and in the rotating frame, $T_{1\rho}$,[4] time constants for the decay of spin order,[5] and relaxation under dipole–dipole suppression experiments[6,7] complement other spectroscopic techniques such as light scattering and dielectric dispersion measurements and mechanical relaxation measurements in analyzing the dynamic properties of polymeric materials.[8]

For a spin system subject to anisotropic interactions, magnetic dipole–dipole couplings among spins provide an energy reservoir. Fluctuations of internuclear vectors efficiently return this dipolar reservoir to thermal equilibrium, a process easily monitored with NMR pulse techniques.[9] The exponential time constant, T_{1D}, for this relaxation process measures molecular reorientational dynamics of the system.[9]

For many polymers in bulk, anisotropic motions produce an effective proton dipolar reservoir.[10,11] The heterogeneity of semicrystalline polymers can result in a fractionation of this reservoir. This subdivision of the dipolar reservoir is observed as nonexponential relaxation of the dipolar energy, for example for the protons of the polyethylene. Nonexponential relaxation has also been observed for other magnetic parameters, particularly for the spin-locked magnetization.[12]

Polypropylene is the quintessential polymer for investigation with NMR spectroscopy.[12] This semicrystalline polymer exhibits several thermal transitions that involve quenching of molecular motions. The side-chain methyl group experiences motions that may be different from those of the backbone chain and which may play a major part in relaxing the overall spin system when spin diffusion is effective.[2,4,8,12] Various forms of polypropylene, ranging from the atactic highly amorphous material to the highly crystalline isotactic material, have different mechanical properties.[13] The mechanical relaxation properties can be correlated with the morphology, such as the amount of amorphous material. We report measurements of the relaxation rate of the dipolar energy of the protons of polypropylene as a function of temperature and amorphous content.

Experimental Section

The samples of polypropylene were given to us by Dr. Walter Freeman of Hercules, Inc. They were used as received. NMR

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Table I
Properties of Polypropylene Samples

sample	% crystalline[a]	MW	transitions in the range 170–425 K
highly crystalline isotactic	>81	100 000[b]	365
20% amorphous	20	150 000[c]	265 289
highly amorphous	<2	20 000[c]	262

[a] Determined by comparison of infrared bands for amorphous and crystalline materials. [b] Number-average molecular weight. [c] Viscosity-average molecular weight, determined on decalin solutions.

relaxation times were measured with a spectrometer built in this laboratory, operating at a frequency of 56.405 MHz for the proton resonance. The 90° pulse width is 1.4 μs; the dead time of the video amplifier is of the order of 4 μs. The pulse sequence of Jeener and Broekaert[9a] was used to determine the spin–lattice relaxation rate, T_{1D}^{-1}, of the dipolar order. The time between the initial 90° pulse and the 45° pulse was adjusted to produce the maximal Jeener echo, typically 10 μs, and the time between this first 45° pulse and the 45° read pulse was varied to determine the decay of the dipolar order. All decays were exponential within experimental error. The data were taken in no special order, and samples were never heated above 423 K.

We determined thermal transitions of these samples with a Perkin Elmer DSC-2 differential scanning calorimeter. Crystallinity was determined by infrared spectroscopy.

Results and Discussion

The relaxation rate, T_{1D}^{-1}, of the dipolar energy reservoir reflects reorientational fluctuations.[9,12] In the "strong-collision" theory,[9b] it is determined by the correlation time for orientational jumps that change the dipolar energy, by

$$T_{1D}^{-1} = k/\theta \tag{1}$$

where θ is the correlation time for the reorientational process and k is a measure of the nature of the jump process. Generally k is of the order of unity or slightly larger.[9b] Thus, T_{1D}^{-1} is an approximate measure of the rate of the reorientational process.

Figure 1 displays the spin–lattice relaxation rate, T_{1D}^{-1}, of the proton dipolar energy of the three polypropylene samples as a function of temperature. Both the highly amorphous (1a) and 20% amorphous (1b) materials exhibit thermal transitions near 265 K, attributed to the β relaxation.[13] As can be seen in Figure 1, the change in T_{1D}^{-1} reflects a change in mobility at or near this temperature. Over the same range of temperatures, the T_2^* for both samples increases, also signaling a dramatic change in mobility. (Data not shown.) At temperatures much above 280 K, T_2^* for the highly amorphous material, in fact, becomes so long and T_{1D} so short that it is not possible to produce a state of dipolar order in a time short compared to the relaxation time, T_{1D}, a requirement of the pulse method for measuring T_{1D}.[9] Nonequilibrium states of excess dipolar energy for these two polypropylene samples only persist for times less than 1 ms at temperatures above 280 K. T_{1D}^{-1} of polyethylene protons diverges at its α transition in a similar manner.[10,11]

For the 20% amorphous sample, however, T_{1D}^{-1} exhibits anomalous behavior at temperatures near 280 K (Figure 1b). It begins to increase with increasing temperature but then decreases over a very small temperature range, above which it appears to undergo a second divergence. This behavior is distinctive and reproducible. A similar anomalous change in $T_{1\rho}$ of a semicrystalline polypropylene has been reported by McBrierty et al.[1b]

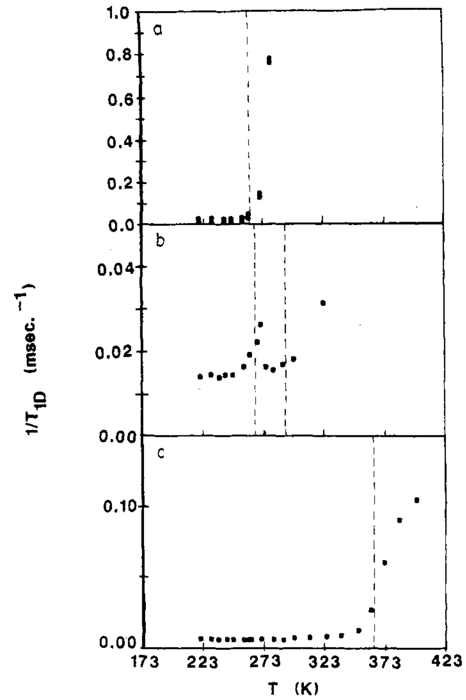

Figure 1. Spin–lattice relaxation rate, T_{1D}^{-1}, of the proton dipolar energy as a function of temperature for polypropylenes of varying morphology: (a) highly amorphous; (b) 20% amorphous; (c) highly crystalline isotactic. The dotted lines indicate the observed thermal transitions, as measured by differential scanning calorimetry.

This anomalous behavior may arise because the sample has two (or more) isolated spin reservoirs that experience the onset of reorientation at slightly different temperatures. If this were the case, the Jeener echo at temperatures above the anomaly and that below should have different intensities, corresponding to the relative numbers of spins participating in the dipolar order. Using a sample of adamantane as a standard, we found that the numbers of spins that participate in the dipolar order above and below the temperature of the anomaly are, within the error of the measurement (±10%), equal. Thus, two separate reservoirs are not being observed. This anomaly must arise because a second reorientational motion is activated for the sample having 20% amorphous material and it affects all the spins contributing to the dipolar echo.

Highly crystalline isotactic polypropylene shows no change in T_{1D}^{-1} in the region near 265 K. Instead, T_{1D}^{-1} is virtually temperature-independent up to temperatures near 365 K, where a similar divergence is seen. At the highest temperature at which we were able to make measurements (≈400 K), this highly crystalline polypropylene has a sufficiently long T_{1D} (and a sufficiently short T_2^*) that Jeener echoes could be generated. Thus, for isotactic polypropylene at these temperatures, magnetic dipolar order exists, and the motions activated above the transition at 365 K must not be isotropic for times on the order of T_2^* at these temperatures.

Dynamic mechanical studies indicate that the α relaxation involves crystalline portions of the material and is observed as a transition in the range from 300 to 365 K, the temperature at which it occurs depending on the crystalline content of the material.[13] The transition corresponding to the β relaxation is observed near 265 K and is associated with amorphous regions of the polymer. Two other relaxations, δ and γ, are associated with reorientation and rotation of the methyl side chains.[13] At room temperature, the frequencies of these relaxations are so high that they do not significantly affect T_1, nor would they be expected to affect T_{1D} at these temperatures.

From Figure 1a, it is clear that the motions involved in the β relaxation affect the proton dipolar order of highly amorphous polypropylene. The observed behavior of T_{1D}^{-1} for the isotactic material shows that the motions involved in the α relaxation at 365 K also influence the proton dipolar reservoir. Therefore, both relaxations must involve substantial changes in the orientation of the proton–proton vectors.

The anomalous behavior of T_{1D}^{-1} of the material with a 20% amorphous content shows that this sample is subject to both the α and β relaxations, as is observed by dynamic mechanical measurements.[13] We believe the failure to observe a change in the size of the dipolar reservoir for this sample indicates that all of the observable spins are affected by these motions. It is known that the α and β relaxations of such partially amorphous polypropylenes are coupled, with the α relaxation being facilitated by the presence of the β relaxation.[13] Such a coupling of the two relaxations is not inconsistent with the observed results for the T_{1D}^{-1} in the 20% amorphous polypropylene, since our results indicate that all the spins are affected by both relaxations.

The effect of a transition on T_{1D}^{-1} is a rapid increase of the relaxation rate with increasing temperature, signaling the sudden onset of motion that reorients the internuclear vectors. At least over the limited range ($223 \text{ K} < T < 265 \text{ K}$) we have examined, the values of T_{1D}^{-1} seem to be temperature-independent below the lowest transition temperature. One can rationalize the data for the amorphous and isotactic samples by assuming that two processes affect dipolar order in each of these samples, one of which is roughly temperature-independent and one of which becomes effective at or just above the transition temperature. If one assumes that the rates are additive, then

$$1/\theta = 1/\theta_0 + 1/\theta_T \tag{2}$$

where θ_0 is the correlation time for the temperature-independent contribution and θ_T is the correlation time for the temperature-dependent part activated at the transition. Although the motional state must surely be more complex, this model is sufficient to give the gross behavior of each of these two polypropylene samples. At temperatures below the transition, the temperature-dependent contribution, $1/\theta_T$ is assumed to be negligible and relaxation is dominated by the first term of eq 2. When the second term becomes comparable to the first, it has a substantial effect on relaxation of the dipolar energy. The 20% amorphous material represents a case for which two temperature-dependent mechanisms are present. Similar effects due to multiple relaxation mechanisms have been seen in a completely different context for relaxation of the dipolar energy of lithium by translational diffusion and interaction with conduction electrons.[9b]

The system of protons in polypropylene is complex in its dynamics.[12] Spin–lattice relaxation in the rotating frame is at least triexponential. Spin diffusion that provides efficient communication of all protons with fast-relaxing species seems to contribute a pathway for relaxation, and the various subreservoirs of spin-locked magnetization are not isolated from each other. This is also demonstrated in the relaxation of the carbon magnetization of polypropylene in the rotating frame,[4] for which it is found that methyl motions dominate relaxation of the methylene and methine carbons, as well as the methyl carbons. It therefore seems reasonable to assume that spin diffusion to fast-relaxing regions may also be an effective mechanism for loss of magnetic dipolar order. Such a mechanism may be responsible for the temperature-independent contribution to the relaxation. Some further evidence for this proposal is the fact that the temperature-independent contributions to T_{1D}^{-1} for these three samples are proportional to the second moments of the proton lines, as would be expected if spin diffusion were dominant.

One can compare our results for polypropylene with the recent reports of T_{1D}^{-1} measurements for polyethylene protons.[10,11] We do not observe nonexponential decay of dipolar order in polypropylene, in contrast to the case of polyethylene. Apparently, polypropylene acts as a single dipolar reservoir, whereas polyethylene has at least two separate dipolar reservoirs. We believe that spin diffusion must be sufficiently strong that, in a very short time, any inhomogeneities in the dipolar energy of polypropylene are smoothed out. The effects on T_{1D}^{-1} of thermal transitions in polypropylene are analogous to those of polyethylene. The effects of both the α and β relaxations on T_{1D}^{-1} of the protons of polypropylene containing 20% amorphous material are observed separately. These observations indicate that T_{1D} is a sensitive barometer of the changes in reorientational dynamics of polypropylene but that the effects of spin diffusion may interfere with the interpretation of the changes in terms of local motions, as it does for other magnetic resonance parameters.

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