adjustable parameters: (d_0, N_0) = (374 Å, 400). Large variations in N_0 and d_0 can be permitted as long as $N_0 d_0^{-2}$ is held constant. Equally adequate fits are obtained for the remainder of the Tanabe et al.[1] data. We omit them here to conserve space. We have drawn curves for two different values of T_m, the equilibrium melting point of polyethylene, since the exact value is a matter of controversy.[9]

One important difference between eq 7 and 8 needs to be mentioned. Equation 8 has no real solutions when $N_0\beta\Delta g < 1$. This fact led to speculation about a melting point depression.[2] Since eq 7 has a root for any $\Delta g \geq 0$, melting point depression is not expected to occur.

Any completely rigorous mathematical treatment of the premelting phenomenon would require exact mathematical expressions for each of the two thermodynamic forces discussed above. Unfortunately, approximations only are available for either. Equation 17 of ref 2 represents the crystallization force, but it is only valid for small ΔT. Likewise, classical rubber elasticity theory is already an approximation when applied to bulk networks. We undoubtedly introduce additional approximations when we apply it to the thin amorphous domains of semicrystalline polymers. One should not expect complete accuracy from the present model.

The parameters N_0 and d_0 supposedly characterize the initial isotropic state of the amorphous domains. However, this state is probably never achieved. It is entirely possible that the amorphous domains are already anisotropic at the moment of crystallization. At the very best, N_0 and d_0 characterize the isotropic state to which the system would extrapolate if it could be heated above the melting point.

The concept of premelting has never been completely accepted, presumably because spontaneous, reversible, partial melting many degrees below the melting point appears thermodynamically unsound. Many polymer scientists have adopted an alternative explanation for the observed crystallinity changes. It is argued that thinner crystals nucleate and grow within the amorphous domains at lower temperatures. These thinner crystals would melt at or near the temperature at which they formed and so would disappear upon reheating. However, no new nucleation can occur if, as we are asserting, the two phases are in metastable equilibrium at all temperatures, just as nucleation from the bulk melt cannot occur at the equilibrium melting temperature. Since this metastable equilibrium is the only way of reconciling the existence of transport between the phases with their coexistence at arbitrary temperature, we conclude that the concept of premelting is a sound one.

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Communications to the Editor

^{15}N T_1 Measurements of Semicrystalline Nylon 6

High-resolution solid-state NMR is becoming an important tool for characterizing polymer systems. Cross polarization and magic angle spinning (CP/MAS) along with high-power decoupling allow acquisition of high-resolution spectra of natural abundance ^{13}C nuclei with good sensitivity. Relaxation studies have identified noncrystalline regions poorly characterized by X-ray.[1] Recently, we have demonstrated that solid-state CP/MAS NMR of natural abundance ^{15}N is readily obtainable on solid polyamides.[2,3] In addition, ^{15}N CP/MAS peaks were shown to correlate with the two predominant crystal forms found in most solid polyamides, i.e., the α and γ crystal forms. Resonances were observed for other regions that could not be assigned to either crystal form. Further study by NMR and molecular modeling calculations showed nitrogen chemical shifts to be extremely sensitive to conformation about the amide group providing a tool for observing ordered region conformations in solid polyamides.[4]

Our interest in examining the previously unobserved noncrystalline and amorphous regions in polyamides by ^{15}N CP/MAS prompted us to prepare an isotopically enriched polyamide sample. We chose to prepare an ^{15}N-enriched sample of nylon 6 because it is an important commercial polyamide that has been thoroughly characterized in the solid state by many techniques (DSC, IR, X-ray) including solid-state ^{13}C NMR.[5,6] Nylon 6 was prepared by anionic polymerization of ϵ-caprolactam.

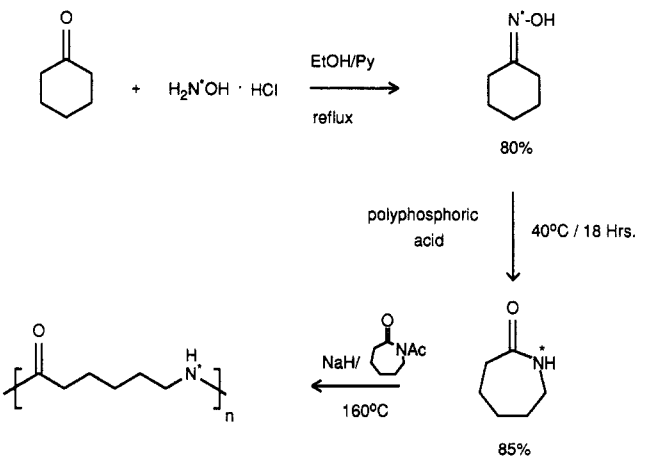

Figure 1. Reaction scheme for preparation of ^{15}N-enriched nylon 6.

Isotopic enrichment of the monomer was accomplished using commercially available ^{15}N-labeled hydroxylamine hydrochloride. Details of the polymer synthesis will be reported in a future paper. Here we report preliminary ^{15}N NMR characterization of nylon 6 including the first report of ^{15}N T_1 values for a solid polyamide.

Sample Preparation. Poly(ϵ-caprolactam) (20% ^{15}N enrichment) was prepared using the scheme outlined in Figure 1. The crude product was extracted with methanol to remove unreacted monomer. The extracted samples

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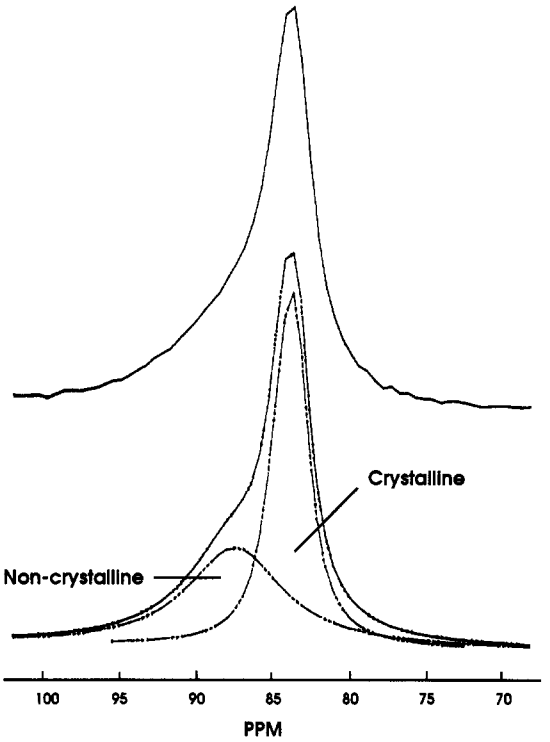

Figure 2. ^{15}N CP/MAS spectrum of nylon 6. The bottom traces show the TENSOR calculated fit along with the individual (crystalline and noncrystalline) components.

were melt-pressed into films and then prepared with two different thermal treatments: quenched from the melt in ice ("quenched") and annealed at 150 °C for 2 h ("annealed"). A portion of the crude polymer was retained to examine the in situ reaction product ("in situ").

^{15}N NMR. Spectra were obtained on a Bruker MSL-200 NMR spectrometer operating at a field strength of 4.7 T and equipped with a Bruker MAS probe. The ^{15}N resonance frequency was 20.287 MHz, and that of the ^{1}H was 200.13 MHz. Samples were melt-pressed into films and then placed in fused zirconia rotors fitted with Kel-F caps and spun at 3.0–3.2 kHz with dry air. Crystalline glycine was placed in the rotor with the samples as an internal chemical shift reference (0 ppm). CP/MAS spectra were obtained with a standard cross-polarization pulse sequence using a 3.5-μs ^{1}H 90° pulse and a mixing pulse of 2 ms. High-power decoupling was used during a 50-ms acquisition time with a nutating field of 62–68 KHz. ^{15}N spin–lattice relaxation times (T_{1N}) were obtained using the CP 90-τ-90 pulse sequence of Torchia.[7] Spectra without cross polarization were obtained using a 90° ^{15}N pulse with broad-band decoupling during acquisition. Peak deconvolution of the overlapping crystalline and amorphous resonances in the CP/MAS spectrum was accomplished using TENSOR, a Bruker-supplied Pascal program for simulating overlapping NMR resonances as combinations of Lorentzian or Gaussian lineshapes.

CP/MAS and T_{1N} of Crystalline and Amorphous Nylon 6. The CP/MAS spectrum of nylon 6 is shown in Figure 2, upper trace. The spectrum shown is similar to natural abundance ^{15}N spectra previously reported.[2,3] The main strong peak clearly overlaps a broader resonance at lower field. The overlapping peaks were fit with a composite line shape (Figure 2) and the individual components deconvoluted as shown. From the deconvoluted components, the upfield resonance is located at 84.2 ppm with a line width at half-height of 2.4 ppm. This peak was previously correlated with the α crystal form of nylon 6.[2,3] The broader downfield resonance is centered at 87.2 ppm and possesses a line width at half-height of 6.3 ppm. This resonance had not been observed in our previous work with polyamides at the ^{15}N natural abundance level. We believe this to be the signal from the noncrystalline or "amorphous" fraction of the nylon sample since its chemical shift appears midway between the α and γ resonances typically observed for nylon 6 and other nylons.[3] (The γ form gives a sharp resonance at 88.5 ppm).[2]

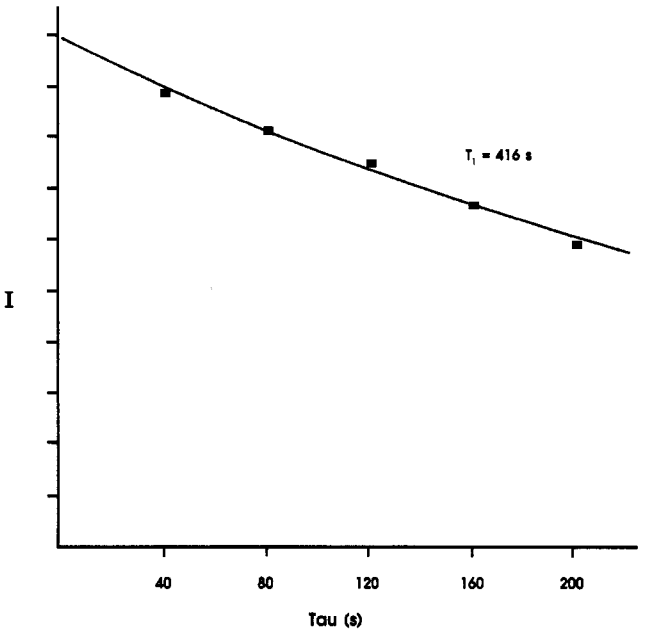

Figure 3. ^{15}N spin–lattice relaxation of nylon 6. Plot of intensity of ^{15}N resonance at 84.2 ppm versus τ along with single-exponential fit used to determine T_1.

To conclusively identify the downfield resonance as that of the amorphous region and not that of the γ crystal form, relaxation experiments were conducted to evaluate the mobility of each region by monitoring spin–lattice relaxation times (T_{1N}). When the method of Torchia was used, relaxation times T_{1N} were obtained at 300 K for resonances at 84.2 ppm (α crystal resonance) and 87.2 ppm (approximate position of the amorphous resonance) for these samples. Peak intensities were plotted vs τ and the data fitted to an exponential decay function: $I = I_0 e^{-\tau/T}$ where I_0 is the intensity at $\tau = 0$ and T is the spin–lattice relaxation time (T_{1N}). Figure 3 shows a plot of magnetization decay for the crystalline component of the annealed sample. The crystalline component at 84.2 ppm had a T_{1N} of 416 s. Figure 4 shows the two-component decay of the downfield amorphous fraction of the same sample with a T_{1N} of 29.6 s and an additional component with T_{1N} of 1.9 s. The two shorter T_1's indicate that this resonance is not from the rigid γ crystal form but rather from an amorphous fraction with much greater mobility than the crystalline portion of the sample. In addition, the detection of *two* T_{1N}'s may indicate two types of noncrystalline regions: a bulk amorphous fraction with liquidlike mobility and a noncrystalline "interphase" region with restricted motion. Similar phase morphology is observed in polyethylene where the crystalline and the noncrystalline interphase regions are clearly delineated by their T_{1C} relaxation times.[1] To our knowledge, this is the first report of NMR observation of an interphase region in a semicrystalline polyamide as well as the first relaxation measurements of crystalline and amorphous regions by ^{15}N CP/MAS.

We took advantage of the difference in spin–lattice relaxation times T_{1N} between the two phases to directly

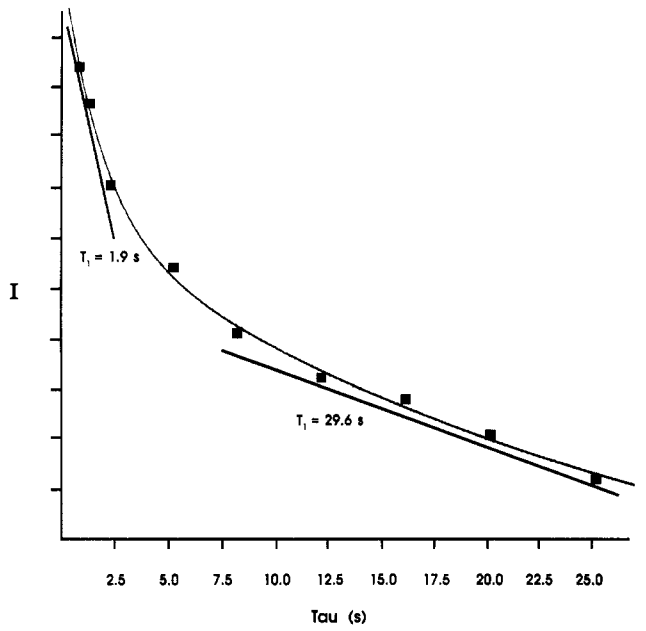

Figure 4. ^{15}N spin–lattice relaxation of nylon 6. Plot of intensity of ^{15}N resonance at 87.2 ppm versus τ. The biexponential fit is plotted along with individual T_1 components showing two-component decay.

Table I

sample	% xtal	param	amorphous phase (87.2 ppm), s		crystalline phase (84.2 ppm), s
in situ	23	T_{1N}	*a*	26	111
melt quenched	29	T_{1N}	2.7	19	230
annealed (160 °C)	45	T_{1N}	1.9	29.1	416

[a] The short T_1 component was not observed for this sample.

observe the amorphous fraction. An MAS spectrum of the ^{15}N-labeled nylon 6 was obtained without cross-polarization. By using a recycle delay of 5–10 s, the ^{15}N magnetization in the crystalline regions is quickly saturated. The nuclei in the amorphous region with shorter T_{1N} can then be observed directly. When this method was used, the spectrum of the amorphous region was obtained (Figure 5, lower trace). This spectrum is nearly identical with the deconvoluted peak from the CP/MAS spectrum shown in Figure 4; i.e., the resonance is broad and downfield of the α crystal peak but upfield from the observed position of the γ crystal peak. Spectral subtraction gives the center trace in Figure 5. Now the resonance for the α crystal form is clearly seen as a symmetrical Lorentzian line with contributions from the noncrystalline region removed.

^{15}N T_1 measurements are also reported in Table I for the in situ prepared sample as well as methanol-extracted samples that were quenched from the melt. The amorphous regions in all samples have shorter relaxation times than the crystalline regions, a fact consistent with ^{13}C relaxation studies of these materials.[5] In addition, the in situ prepared samples have shorter T_{1N} values than any of the methanol-extracted samples. Since the T_{1N} values are associated with motions of the polymers, a shorter T_{1N} value for the in situ sample indicates more rapid motion, due either to plasticization by residual caprolactam in the sample or differences in the crystalline regions. We are continuing our relaxation studies to confirm the proposed phase morphology and correlate the effects of plasticizers and thermal history on ^{15}N relaxation times.

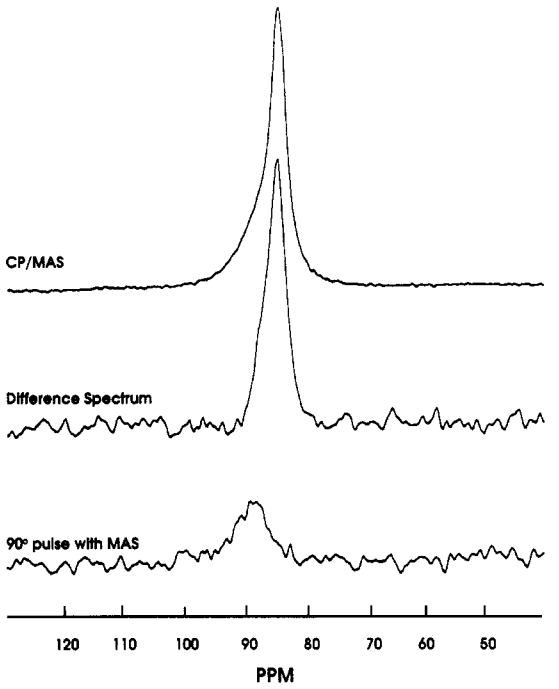

Figure 5. ^{15}N MAS spectra of nylon 6 at 300 K. Upper trace: Spectrum with cross-polarization; main peak for α crystal form is seen along with overlapping resonance downfield. Lower trace: ^{15}N spectrum obtained using a 90° ^{15}N pulse (no CP) showing only the noncrystalline region with shorter T_{1N}. Center trace: Spectral subtraction of upper and lower traces showing the symmetrical resonance line for the α crystal form of nylon 6.

Acknowledgment. We gratefully acknowledge a Department of Defense instrumentation grant with which we purchased our Bruker MSL-200 spectrometer. This research was supported in part by a grant from the Office of Naval Research. We also thank Dr. William L. Jarrett for helpful discussions concerning the NMR pulse experiments reported here.

Registry No. Nylon 6, 25038-54-4.

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Received May 1, 1989;
Revised Manuscript Received June 20, 1989

Oligo(trichlorosilyl)styrenes: Highly Functionalized Silicone Precursors[1]

Silicon-based materials have a special place in polymer chemistry, being used as cross-linking agents, as components in copolymers (e.g., poly(styrene)–poly(dimethylsiloxane) block copolymers), and in their own right as

