lyzed the polarization inversion mechanism of PVDF form I under high electric field based on a soliton model, i.e., the motion of a defect composed of a complicated sequence of trans and gauche bonds. Intercorrelation of Figures 6 and 7 suggests the possibility of the application of such a hypothesis to the analysis of the polarization inversion mechanism and its temperature dependence for the copolymer samples.

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Solid-State ^{19}F NMR Investigations of Annealed Poly(tetrafluoroethylene)

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ABSTRACT: Solid-state ^{19}F NMR spectroscopy is used to follow the disorientation of crystallites in poly(tetrafluoroethylene) during annealing at 300 °C. The rapid shrinkage is accompanied by disorientation of crystallites. Over prolonged periods, NMR indicates that a totally random orientation is not achieved. The NMR technique is exceptionally sensitive to the nonrandom orientational distribution.

Introduction

During the processing of polymeric materials, annealing at temperatures near the melting point is often performed in order to relieve internal stresses induced during fabrication. Such processing results in a material whose properties, such as impact strength, dimensional stability, and heat resistance, are frequently superior to those of the unannealed material.[1] When a drawn semicrystalline polymer is annealed, shrinkage of the sample is accompanied by a rapid relaxation of strained tie molecules that connect crystalline lamellae.[1] This relaxation process causes rapid disorientation of the crystallites.[1] The nature of the changes that occur during annealing of semicrystalline polymers is, therefore, complex and requires analytical techniques sensitive to subtle structural and motional changes. Techniques such as mechanical testing, electron microscopy, and X-ray diffraction have been used to monitor structural changes accompanying annealing, and these applications have been reviewed elsewhere.[1-3] Each technique suffers from certain limitations. Some methods yield only limited orientation information; others are sensitive to ordering in only the crystalline or amorphous fraction of the material. Solid-state nuclear magnetic resonance (NMR) spectroscopy is sensitive to molecular motion (through the study of relaxation times) and structure (through the analysis of orientation-dependent interactions).[4,5] The chemical-shift interaction has been shown to be valuable for studying orientation in drawn[6-13] and annealed[14] semicrystalline polymers. This approach can be used to derive a complete orientation distribution function, and the NMR spectrum does contain information about both phases. The analysis is limited, however, to spectra in which unobscured resonances may be observed. We report here a quantitative NMR spectroscopic study of the annealing of poly(tetrafluoroethylene) (PTFE) at 300 °C. Our results confirm that the observed sudden shrinkage of the polymer that occurs during annealing is accompanied by rapid disorientation of the crystallites. Even after extended periods of time at this temperature, the NMR analysis reveals that the crystallites do not relax back to the totally random distribution that the material had before drawing.

Theory

A static anisotropic distribution of crystallite orientations in a sample of a drawn polymer produces an NMR spectrum characteristic of the distribution of crystallite axes relative to the magnetic-field direction, $\vec{B}_0$. Analysis of the changes in the spectral line shape produced by varying the angular position of the draw axis relative to

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$\vec{B}_0$ allows one to infer properties of the orientation distribution function, $N(\theta)$, of the crystallite axes. Full details of this procedure have been given previously.[11-13]

The distribution function $N(\theta)$ for a uniaxially oriented sample may be conveniently expressed in terms of the even-ordered Legendre polynomials in $\cos\theta$:[15]

$$N(\theta) = \sum a_l P_l(\cos\theta) \qquad (1)$$

This summation is subject to the condition that

$$\int_0^{\pi/2} N(\theta)\sin\theta\,\mathrm{d}\theta = 1 \qquad (2)$$

so that the normalization coefficients a_l are given by[15]

$$a_l = \frac{2l+1}{4\pi}\langle P_l(\cos\theta)\rangle \qquad (3)$$

where $\langle P_l(\cos\theta)\rangle$ represents the average of $P_l(\cos\theta)$ over the interval $\theta = 0$ to $\pi/2$. Thus, a measurement of the averages $\langle P_l(\cos\theta)\rangle$ can be used to develop an approximation to $N(\theta)$ by truncating the sum in eq 1 after a finite number of terms. for low-to-moderate elongations ($\langle P_2(\cos\theta)\rangle \leq 0.70$), one needs relatively few (three or four) terms in this expression to obtain a good approximation to the true $N(\theta)$.[16]

For an unoriented polymer sample, $N(\theta)$ is constant and $\langle P_l(\cos\theta)\rangle = 0$ for all $l > 0$. For a perfectly ordered sample, all $\langle P_l(\cos\theta)\rangle = 1$. The values $\langle P_l(\cos\theta)\rangle$ may, therefore, be used individually to characterize the degree of orientation in the polymer. It has been shown[11-13] that these averages may be extracted from an analysis of the angular variation of the moments of the chemical-shift dispersion of the NMR line shape. The limitation of this procedure is primarily the accuracy with which one may measure the moments of the NMR spectrum.

Any calculation involving integrals over the complete NMR line shape is, necessarily, an average over all species contributing to the spectrum. For a semicrystalline polymer, this implies that they reflect any anisotropy present in both the crystalline and amorphous regions. However, from the spectra observed, it appears that there is little order in the amorphous phase of the deformed PTFE[11,13] and that it is reasonable to assume that all angle-dependent effects are due to orientation in the crystalline regions alone.

Experimental Section

The samples of PTFE used had previously been drawn to extension ratios, λ ($=L/L_0$), of 1.40, 1.75, and 2.10. These are the same PTFE samples used for earlier orientation studies of drawn PTFE.[11-13] Portions of each sample of measured initial length L were annealed in air with free ends at 300 °C for periods of time ranging from 1 to 100 min. This temperature is well below PTFE's crystalline melting point of 347 °C,[17] yet is high enough to impart considerable motion to the polymer molecules.[10] After annealing for a specified period, the samples were cooled to room temperature at rates of 140–170 °C/h. The final length, L', was measured at room temperature, as were the degree of crystallinity and the orientation parameters.

The orientation parameters were determined from the NMR chemical-shift spectrum.[11-13] The MREV-8 pulse cycle[4,5] was used to circumvent the effects of ^{19}F–^{19}F dipolar interactions, permitting the observation of the ^{19}F chemical-shift spectrum. Details of the instrumentation are given elsewhere.[18] The degree of crystallinity measured by the infrared technique[19] was 58 ± 5% before and after annealing.

Results

As expected, all of the samples undergo considerable shrinkage at 300 °C. In fact, this shrinkage process occurred so rapidly at this high temperature that there is little correlation between the shrinkage ($1 - L'/L$) and the length of time the sample was in the 300 °C bath.

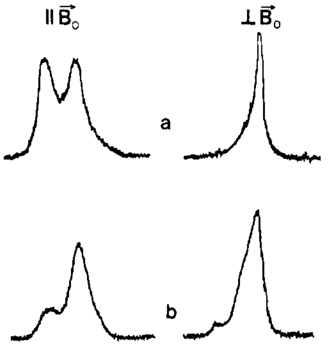

Figure 1. Comparison of (a) unannealed and (b) annealed PTFE ($\lambda_0 = 2.10$) for two orientations of the draw axis relative to the magnetic field.

Table I
Results of Moment Analyses of Annealed PTFE[a]

λ'	$\langle P_2\rangle$	$\langle P_4\rangle$
	$\lambda_0 = 1.40$	
1.40	0.23	−0.06
1.27	0.10	0.02
1.24	0.07	0.02
1.14	0.02	0.03
	$\lambda_0 = 1.75$	
1.75	0.33	0.11
1.53	0.12	0.02
1.34	0.05	0.02
1.24	0.05	0.02
1.17	0.02	0.03
	$\lambda_0 = 2.10$	
2.10	0.42	0.14
1.50	0.15	0.01
1.39	0.15	0.01
1.30	0.11	0.01
1.27	0.12	0.02
1.17	0.02	0.02

[a] All $\langle P_l\rangle$ values ±0.03.

It is clear from the NMR spectra shown in Figure 1 that considerable relaxation has taken place. These spectra were taken at two orientations (parallel to and perpendicular to $\vec{B}_0$) for one sample whose draw ratio before annealing, λ_0, was 2.10. Spectra of both the original and the relaxed material are given for comparison. The fact that the two line shapes for the annealed samples are quite similar, whereas those for the unannealed sample are different, indicates that the distribution of crystallite orientations is more nearly random after the annealing process. There is some residual orientation, however, as evidenced by the fact that the line shape for the annealed polymer does change as a function of angular position relative to $\vec{B}_0$.

By measuring spectra of the annealed material at several angles β, the moments of the distribution can be calculated.[11-13] The results of these measurements are shown in Table I. It is evident that the values of $\langle P_2(\cos\theta)\rangle$ depend strongly on the shrinkage, whereas the values of $\langle P_4(\cos\theta)\rangle$ are, within experimental error, constant. A plot of $\langle P_2(\cos\theta)\rangle$, also known as the Hermanns orientation function, vs. shrinkage is shown in Figure 2. The relationship is linear, in agreement with results for other polymers.[2]

As revealed in the spectra of Figure 1, the randomization process that occurs during annealing is incomplete. This can be observed directly after the distribution functions $N(\theta)$ are actually determined based on the results in Table I. These functions for the annealed samples whose original

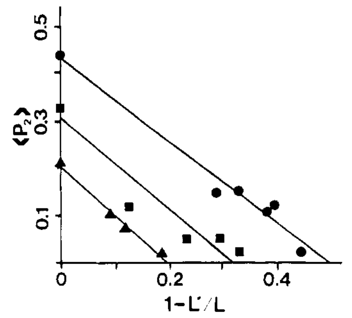

Figure 2. $\langle P_2(\cos\theta)\rangle$ vs. shrinkage $(1 - L'/L)$: (●) λ_0 = 2.10; (■) λ_0 = 1.75; (▲) λ_0 = 1.40.

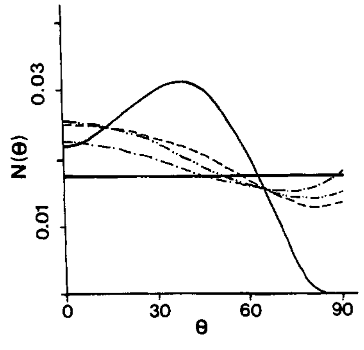

Figure 3. $N(\theta)$ for annealed PTFE (λ_0 = 1.40): (---) λ' = 1.14; (-··) λ' = 1.24; (-·-) λ' = 1.27; (—) λ' = 1.40 (unannealed). The solid horizontal line indicates the value for a random distribution.

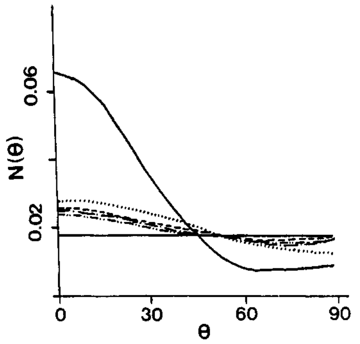

Figure 4. $N(\theta)$ for annealed PTFE (λ_0 = 1.75): (-·-) λ' = 1.17; (-··) λ' = 1.24; (---) λ' = 1.34; (···) λ' = 1.53; (—) λ' = 1.75 (unannealed). The solid horizontal line indicates the value for a random distribution.

draw ratios were 1.40, 1.75, and 2.10 are shown in Figures 3–5, respectively. These figures also display orientations functions for the unoriented and drawn cases for comparison. It is obvious that the crystallites have suddenly relaxed to a distribution that is very nearly random but that still retains some anisotropy. The small deviations from the isotropic distribution cannot be simply attributed to errors in the calculated moments of $N(\theta)$ since all spectra clearly exhibit some residual orientation, just as Figure 1 does. The curves in Figures 3–5 sometimes increase near θ = 90°, but this effect is due to truncation of the series in eq 1. Even though the crystallites do not regain their original random orientations, the relaxation processes do seem to be leading toward that state. This can be seen by plotting $N(\theta)$ for θ = 0° and θ = 90° vs. λ', the residual draw ratio (L'/L_0), as in Figure 6. The value of $N(\theta)$ at these angles can be extrapolated to very near (within ±0.003) $N(\theta)$ = 0.018, the constant value characteristic of a random distribution, at λ' = 1.0, which corresponds to the original length of the polymer before drawing. In other words, it appears that, if the polymer had been able to relax to its original unoriented length, its crystallites would have regained a random distribution of orientations.

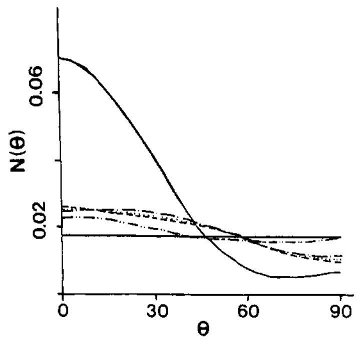

Figure 5. $N(\theta)$ for annealed PTFE (λ_0 = 2.40): (-·-) λ' = 1.17; (-··) λ' = 1.27; (···) λ' = 1.30; (---) λ' = 1.39; (—) λ' = 2.10 (unannealed). The solid horizontal line indicates the value for a random distribution.

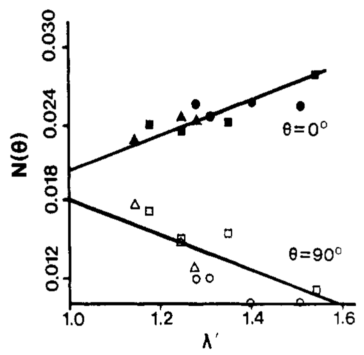

Figure 6. $N(\theta)$ at two angles vs. λ' for PTFE for all samples. Open symbols, θ = 0°; filled symbols, θ = 90°.

Conclusions

The relationship between the shrinkage and randomization processes that occur when drawn PTFE is annealed at 300 °C has been investigated by analyzing the moments of the solid-state NMR spectra of the material. The relationship between various measures such as residual extension ratio and $\langle P_2(\cos\theta)\rangle$ of these two processes is at least approximately linear in all cases. Shrinkage occurs very rapidly at 300 °C, and this is accompanied by a sudden disorientation of the crystallites of the polymer. Neither the shrinkage nor the randomization process is complete, however, and the residual extension is related to the residual orientation.

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Registry No. PTFE, 9002-84-0.

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Microstructure of Poly(vinyl alcohol) by 100-MHz Carbon-13 NMR[†]

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ABSTRACT: The microstructure of atactic and highly isotactic poly(vinyl alcohol) samples has been studied by 100-MHz carbon-13 NMR spectroscopy. Resolution-enhanced spectra show sensitivity to heptad and hexad tactic sequences. The highly isotactic sample obeys first-order Markov statistics while the atactic sample is Bernoullian. Spectra taken in Me_2SO-d_6 and in D_2O as solvents show marked differences, which may be due to conformation changes. Weak features, arising from reversed monomer sequences and other structural irregularities, have been identified in the spectrum of the atactic sample. A spin-echo NMR experiment with gated decoupling was used in the assignment of these weak features.

Introduction

Poly(vinyl alcohol) has been studied extensively by both proton and carbon-13 NMR, the objectives being the determination of tacticity and the detection and identification of structural irregularities such as end groups, branches, and reversed monomer sequences.

In the proton spectra, spin-spin splittings complicate the methine and methylene proton resonances and make tacticity determinations difficult. However, a number of workers showed that, when dimethyl-d_6 sulfoxide is used as a solvent, exchange of the hydroxyl protons is suppressed and three distinct hydroxyl proton resonances can be observed, corresponding to monomer units at the centers of isotactic, heterotactic, and syndiotactic triad sequences.[1-3]

Carbon-13 NMR spectra of poly(vinyl alcohol) samples taken at 25.14 MHz in D_2O solution were reported by Inoue et al.[4] Similar spectra, taken at 22.63 MHz in D_2O and dimethyl-d_6 sulfoxide solutions, were reported by Wu and Ovenall.[3] Both groups found that the methine carbon atom resonances were sensitive to triad tacticity, while structure visible in the methylene carbon atom resonances was interpreted in terms of partially overlapping tetrads. In later work at 22.63 and 67.9 MHz by Wu and Sheer,[5] additional fine structure was observed in the methine carbon atom resonances of poly(vinyl alcohol) samples dissolved in dimethyl-d_6 sulfoxide, and this was interpreted in terms of pentads.

The possibility of detecting 1,2-glycol units in poly(vinyl alcohol) by carbon-13 NMR was investigated by Inoue et al.[4] These can arise from occasional monomer inversion during the polymerization of vinyl acetate to give poly(vinyl acetate), from which the poly(vinyl alcohol) is prepared by hydrolysis. A model polymer prepared by the hydrolysis of poly(vinyl carbonate) and containing 17 1,2-glycol units per 100 monomer units was examined by these authors. A distinctive methylene carbon atom resonance attributed to 1,2-glycol units was observed, but the sensitivity was too low for the detection of 1,2-glycol units in normal poly(vinyl alcohol) samples, which would typically be an order of magnitude lower in concentration.

Adelman and Ferguson,[6] using 220-MHz proton NMR, studied structural irregularities in poly(vinyl alcohol) but were unable to detect 1,2-glycol units directly.

Recently, Amiya and Uetsuki have reported an investigation into the microstructure of poly(vinyl alcohol-*co*-crotonic acid) by proton and carbon-13 NMR.[7] Weak peaks in the 50.15-MHz carbon-13 NMR spectrum of a poly(vinyl alcohol) sample were assigned to carbon atoms in 1,2-glycol structures.

In the present work, carbon-13 NMR spectra of isotactic and atactic poly(vinyl alcohol) samples have been obtained with a spectrometer operating at 100.6 MHz. The high resolution and sensitivity of this instrument have been utilized in obtaining detailed information on tacticity and irregular structures.

Experimental Section

The highly isotactic sample had been studied previously.[3,5] The atactic sample was a commercial product, prepared by hydrolysis of a free radical initiated poly(vinyl acetate).

Carbon-13 NMR spectra were obtained at 100.6 MHz, using a Bruker WM-400 high-resolution NMR spectrometer. The samples were examined as solutions in dimethyl-d_6 sulfoxide (Me_2SO-d_6) and in D_2O in 10-mm NMR tubes. Sample temperatures were regulated at 50 °C, using the standard Bruker variable-temperature unit. Broad-band proton decoupling resulted in some dielectric heating of the solutions. To ensure that this did not vary from one sample to another, all samples were made up to a standard height of 3 cm (approximately 2 mL) and vortex plugs were used. Sample temperatures were measured by using similar NMR tubes containing 10% (w/v) solutions of the atactic polymer, into which a thermocouple was inserted through the hole in the vortex plug. These were allowed to come to equilibrium under the particular data collection sequence being used, i.e., with gated or continuous broad-band proton decoupling. The temperature inside the NMR tube was then adjusted to 50 °C by

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[†] Contribution No. 3169.

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