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Solid-State Deuterium Nuclear Magnetic Resonance of Crystallinity in Poly(vinyl chloride)

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ABSTRACT: The solid-state deuterium NMR spectrum of free radical polymerized (50 °C) PVC-d_3 has been obtained at 46 MHz as a function of temperature. The spectrum at room temperature displays the full static quadrupolar powder pattern. At 140 °C, about 50 °C above T_g, the spectrum consists of a motionally narrowed line from the amorphous PVC phase centering a weak quadrupolar powder pattern with almost full splitting. The powder-pattern portion of this latter spectrum is attributed to the crystallinity present in the sample at that temperature. The syndiotacticity (0.57) and crystallinity of the PVC-d_3 are higher than values reported for typical commercial PVCs. The amount of crystallinity was estimated by line shape simulation of the crystalline pattern to be 18.7% at 140 °C. By combining this result with DSC data on the same sample, we calculate the heat of melting of 100% crystalline PVC to be 74 kJ/kg. In contrast to the 50 °C polymerized PVC-d_3, no narrow component or amorphous phase is observed at 140 °C for a deuterated PVC prepared in urea–canal complex at −78 °C, a result which is consistent with the DSC curve that shows no T_g up to 220 °C.

Introduction

Recently solid-state deuterium NMR has become established as an important technique for studying phase structure and chain mobility in polymers available in deuterated form.[1-5] Both semicrystalline and totally amorphous polymers have been studied. The technique has a number of advantages once the deuterated polymer is available. For semicrystalline polymers, solid-state deuterium NMR has the advantage that signals due to the amorphous and crystalline regions can be obtained separately, because the ^{2}H NMR spectrum is quite sensitive to chain mobility.

Poly(vinyl chloride) (PVC) prepared by typical, commercial free-radical polymerization has a low degree of crystallinity.[6] More highly stereoregular, and hence more highly crystalline, PVC can be prepared by other methods.[6,7] The amount of crystallinity in PVC has been determined by a number of standard methods, including X-ray diffraction, infrared spectroscopy, density, and thermal analysis.[8] For commercial PVC, the amount of crystallinity is typically thought to be about 5–20%.[6] However, there is some disagreement on this point, probably because of the different methods used or polymers studied.

Here we report the solid-state deuterium NMR spectrum at 46 MHz of free radical polymerized PVC-d_3 as a function of temperature. These results yield an estimate of the degree of crystallinity of the PVC. When combined with results from differential scanning calorimetry (DSC), an estimate is made of the heat of melting of 100% crystalline PVC.

Experimental Section

Preparation of PVC-d_3. The synthesis of the monomer has been described earlier.[9] The polymer was made by charging 10 g of monomer and 25 g of water with 0.4 g of Methocel and 0.25 g of caproyl peroxide. After reaction for 10 h at 50 °C, 10 g (100%) of PVC-d_3 was recovered and washed three times with water before drying at 80 °C.

Preparation of Urea–Clathrate PVC-d_3. Urea (USP, 10 g), 2.5 g of vinyl-d_3 chloride, and 0.1 mL of distilled methanol were aged at −55 °C for 4 days and then exposed to cobalt-60 radiation at −78 °C for 16 h. The product was washed three times with methanol and dried at 50 °C, yielding 1.8 g (72%).

DSC and TGA Measurements. A Perkin-Elmer Model DSC-2B differential scanning calorimeter was used at 40 K/min heating and cooling rates as described elsewhere.[10] TGA measurements were run under nitrogen with a Cahn System 113 at a heating rate of 30 K/min.

NMR Measurements. Deuterium NMR spectra were acquired at 46 MHz on a Bruker CXP-300 spectrometer. Typical conditions were as follows: 90° radio frequency pulse width, 3.4 μs; pulse repetition time, 10 s; spectral width, 5 MHz; 2048 data points zero filled to 8192; accumulations, 300–740. A line broadening of 500–1000 Hz was used. The quad-echo pulse sequence with or without alternation was used for spectral acquisition with a delay time of 30 μs. Spin–lattice relaxation times (T_1) were measured using a presaturation sequence followed by a relaxation delay, with detection via the standard quad-echo sequence. The proton NMR spectrum of PVC-d_3 in THF-d_8 was obtained at 200.1 MHz and 50 °C on a Bruker WH-200 FTNMR spectrometer.

Results and Discussion

Figure 1 shows the solid-state deuterium NMR spectrum of free radical polymerized PVC-d_3 as a function of temperature. The spectrum at 24 °C (Figure 1A) was obtained using the phase-alternated quad-echo sequence, $90(+x,-x)-t-90(y)-t-\text{acq.}(x,y)$, and is the characteristic static quadrupolar powder pattern for the ^{2}H nucleus in a C–D bond. The splitting is 123.3 kHz. The pattern is somewhat distorted, mainly in the wings. Deuterium NMR spectra of solids are subject to distortions because the effective irradiation power of the excitation pulse is not distributed uniformly over the spectrum.[11] This combined with relatively low signal-to-noise ratio in the wings gives the relatively flat appearance in Figure 1A–C, which is often typical of solid-state ^{2}H spectra.[4] Another possibility is difficulty in spectral phasing. The origin of the artifacts at about 200 kHz from the center of the spectrum in Figure

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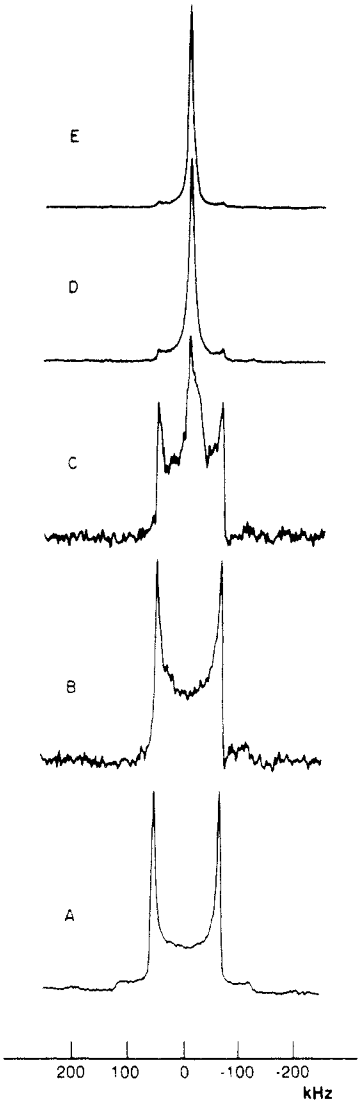

Figure 1. ^{2}H solid-state NMR spectra of PVC-d_3 at 46 MHz as a function of temperature. (A) Ambient temperature, spectrum taken using the quad-echo sequence with phase alternation; (B) 100 °C; (C) 120 °C; (D) 140 °C; (E) 150 °C. Spectra B–E were taken using the quad-echo sequence without phase alternation and are the result of 300 accumulations.

1A is not known. Because the temperature of observation is below T_g, the powder pattern observed at 24 °C arises from both the crystalline and glassy amorphous regions.

The full static pattern is still present at 100 °C (Figure 1B), about 10 °C above the thermal (DSC) T_g. This spectrum and the remaining high-temperature spectra were taken using the quad-echo sequence without phase alternation. The latter spectra were acquired with fewer transients; hence, the wings of the pattern were not observed clearly. At 120 °C (Figure 1C), a spectral component appears in the center which is partially motionally narrowed. At higher temperatures (140 °C and above, Figure 1D,E) this component is in the extreme narrowing limit and highly motionally narrowed. We assign the center peak to the amorphous fraction of PVC. The behavior of this motionally narrowed component is similar to that of atactic polystyrene-d_3 (deuterated on the backbone), which is totally amorphous and has a T_g of 100 °C.[3] The ^{2}H wide-line spectrum of atactic polystyrene-d_3 narrows from a full powder pattern to a motionally narrowed signal over the range 30–60 °C above T_g. Of course, this narrowing does not occur at the thermal (DSC) T_g because the ^{2}H NMR measurement is at a higher frequency compared to the thermal test; hence, the molecular motions associated with T_g are displaced to a higher temperature. Similar behavior was seen for deuterated polyacrylates.[4]

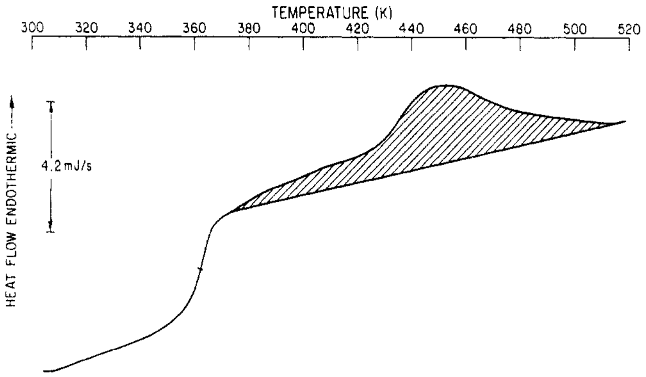

Figure 2. DSC scan (second heat) for PVC-d_3. The sample was first heated to 100 °C to remove the thermal history below T_g.

Table I
TGA and DSC Results for PVC-d_3

(A) TGA

	thermal history	
wt % loss at	virgin	140 °C (NMR)
200 °C	0.15	0.10
250 °C	0.31	0.15
275 °C	1.06	1.08

(B) DSC

	thermal history	melting range, °C	ΔH_m,[a] kJ/kg
1	(a) annealed for 15 min at 140 °C to simulate NMR run (b) 1st heat to 100 °C (c) 2nd heat to 252 °C	100–247	15.8 ± 0.08
2	same as above	140–247	13.8 ± 0.24
3	3rd heat to 252 °C	100–247	12.4 ± 0.32
4	(a) NMR sample after run at 140 °C (b) 1st heat to 100 °C (c) 2nd heat to 252 °C	100–247	15.6 ± 0.16

[a] Average of two runs.

In addition to the motionally narrowed portion, a small fraction remains which exhibits the quadrupole powder pattern. The splitting of 122.1 kHz is only slightly reduced from that seen at low temperature. The powder pattern is too weak to be seen in its entirety under our conditions. We assign this remaining quadrupole powder pattern to the immobile crystalline fraction remaining at 140 °C, which is consistent with the extensive thermal, infrared, and rheological evidence indicating the existence of crystallinity in commercial PVC at this temperature.[12-14] When the temperature is reduced, the full static powder pattern is again obtained.

Figure 2 shows the DSC curve for the deuterated PVC sample. To eliminate the thermal history below T_g, the sample was first heated to 100 °C. The DSC curve of Figure 2 is similar in shape to that of a commercial PVC, except that the area of the melting peak is larger. The glass transition is observed under these conditions (third heat) at 90 °C, and the melting peak occurs over the range 100–247 °C. A broad melting range in PVC has been attributed to the presence of a relatively wide range of crystallite sizes, with smaller crystallites having lower melting temperatures.[15,16] The DSC results for this sample under several conditions are shown in Table I. The heat of melting of the as-prepared PVC-d_3 is about 5 kJ/kg higher than that of a virgin, commercial PVC.[10]

The TGA results also are given in Table I. The sample is significantly more stable than a commercial (protio)

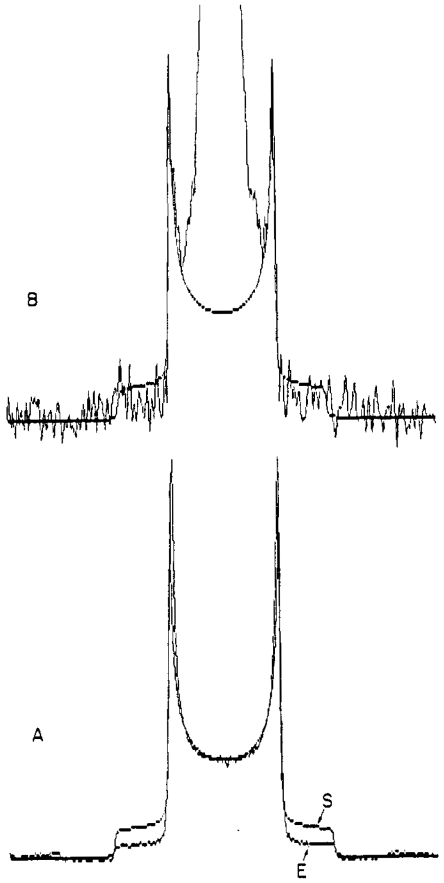

Figure 3. Simulation of the broad component of the ^{2}H spectrum of PVC-d_3. (A) Ambient temperature, phase-alternated quad-echo sequence, $\Delta\omega_Q$ = 123.153 kHz, 0.7-kHz line broadening in simulated spectrum; (B) 140 °C, phase-alternated quad-echo sequence, $\Delta\omega_Q$ = 117.53 kHz, 0.8-kHz line broadening in simulated spectrum. E, experimental spectrum; S, simulated spectrum.

PVC, Geon 103EP-F76 (BFGoodrich Co.). A sample of the latter gave a weight loss of 3.0% at 275 °C, whereas the deuterated PVC sample, both virgin and after NMR testing at 140 °C, gave only a 1.1% loss at 275 °C. At 250 °C, the maximum temperature to which the PVC-d_3 was heated in the DSC runs, the polymer showed only a 0.3 wt % loss.

Approximate spin–lattice relaxation times were measured for PVC-d_3. At 37 °C, the value for the entire pattern was found to be about 1.5 s. No effort was made to detect T_1 differences across the powder pattern or to detect nonexponentiality in the free induction decay. The T_1 of the narrow peak from the amorphous regions was found to be about 5.5 ms at 130 °C. The T_1 of the crystalline pattern at 130 °C could not be measured due to its weak intensity.

We can calculate the degree of crystallinity by ^{2}H NMR only at temperatures above 140 °C because it is necessary for the signal of the amorphous portion to be motionally narrowed. Hence, part of the crystalline fraction existing at ambient temperature, but which is melted at 140 °C, is not a factor in the NMR determination. This amounted to about 2.0 kJ/kg or 13% of the total crystallinity.

The degree of crystallinity of the PVC-d_3 at 140 °C was estimated by numerically fitting the line shape of the rigid portion to a pattern of idealized shape with the peak splitting observed in the spectrum. This is demonstrated in Figure 3A for the full static pattern at ambient temperature. Note that the experimental spectrum E has lower intensity in the wings than the best simulation S. This drop-off in intensity in the experimental spectrum is due to the problem of finite pulse power.[11] Figure 3B shows the simulation for the rigid portion remaining at 140 °C. This latter simulation is with 0.8 kHz of line broadening added and a splitting of 117.53 kHz, which is slightly reduced from the value at ambient temperature. To estimate the area of the broad component, the best powder pattern obtained from the simulation was adjusted in scale to visually fit the data. The crystallinity remaining at 140 °C was estimated to be 18.7% by this method. Considering the noise level and the ability to distinguish differences between the experimental and simulated spectra, we estimate the accuracy to be on the order of 3–5%. This could be improved significantly by increasing the signal-to-noise ratio by additional signal averaging or probe improvements. On the basis of the NMR results, the estimate the degree of crystallinity at ambient temperature is 21.5%.

The above analysis assumes that the motionally narrowed spectral component arises from only the amorphous fraction and the broad component from only the crystalline fraction. It is possible that, as for polyethylene, there is a motionally rigid amorphous component, presumably an interfacial fraction at the crystallite surface. For PVC, the relatively low degree of crystallinity has made characterization of PVC crystallites difficult, although it seems generally agreed that they are small.[6] The relatively small fraction of syndiotactic sequences available for crystallization in commercial atactic PVC has led to suggestions that isotactic or heterotactic sequences can be incorporated into PVC crystallites.[6] Thus, what constitutes a PVC crystallite and its interfacial region is still the subject of debate.

We measured the syndiotacticity of the PVC-d_3 by 200-MHz ^{1}H NMR (of the residual ^{1}H in the deuterated polymer) in THF-d_8. The α-proton region of the spectrum of the perdeuterated polymer was assigned by comparison to the spectrum obtained with specific decoupling of the β-methylene protons.[17,18] This yielded the fraction of syndiotactic triads (rr = 0.33, mr = 0.49, mm = 0.18), and a syndiotactic diad fraction of 0.57. This value is slightly higher than the 0.54 obtained for a commercial PVC (Geon 103EP-F76)[10] and undoubtedly accounts for the higher heat of melting of the PVC-d_3, 15.8 vs 11.2 kJ/kg.

Various attempts to determine $\Delta H°_m$, the heat of melting of 100% crystalline PVC, have measured values ranging from 40 to 181 kJ/kg.[19] The techniques have included (1) melting point depression using plasticizer,[20–23] (2) the heat capacity increment at T_g in combination with heat of melting,[10] and (3) X-ray diffraction in combination with heat of melting values.[24] Each method involves assumptions. The calculation from melting point depression data involves a diluent–polymer interaction parameter, the value of which is very critical. Heats-of-melting data, particularly in the case of PVC, which has a very broad peak, depend on how the amorphous heat capacity baseline is determined.[10,24] Assumptions inherent in the X-ray diffraction technique are associated with the uncertainty in the area of the amorphous phase.[26–28]

The solid-state NMR technique, on the other hand, probably affords a more direct measure of PVC crystallinity because of less uncertainty in the area of the amorphous peak. Thus, in combination with the DSC heat-of-melting data, one should obtain a more accurate estimate of the heat of melting of 100% crystalline PVC than has been possible before by other methods. From the crystallinity (18.7%) and the heat of melting (13.8 kJ/kg) above 140 °C, the heat of melting of 100% crystalline PVC is calculated to be 74 ± 4 kJ/kg. This result is higher than many reported values[10,21–23] but comparable to the 78.6 kJ/kg value determined by Gouinlock.[24] Agreement with the latter is probably accidental

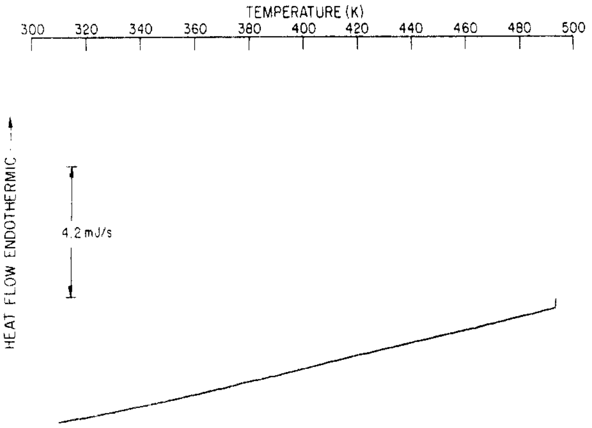

Figure 4. DSC scan (second heat) of urea–clathrate PVC-d_3.

because of compensating factors in the determinations, which were based on the second heats of melting, whereas the X-ray crystallinity measurements were made on the virgin samples. This previous work was criticized by Baker et al.,[26] who concluded the degree of crystallinity of the PVC was 50% instead of 43%.

The calculation of the heat of melting of 100% crystalline PVC also depends on assumptions regarding the amorphous heat capacity baseline. We have attempted to minimize this uncertainty as follows: (1) the onset of melting at 100 °C was taken just above T_g because the slope of the specific heat capacity (dC/dT) at this temperature indicates melting,[10,29] and (2) the end of melting was taken at about 250 °C because the specific heat capacity resumed its endothermic trend expected for amorphous materials.[10] Normally with protio PVC one can expect thermal instability in the 200–250 °C range.[30,31] Our experience has shown that when decomposition of protio PVC is significant, as shown by dark discoloration and weight loss (>1%), heat is evolved and manifested as an exothermic bias in the apparent amorphous baseline above 200 °C, which, depending on the degree of degradation, may have a zero or negative slope (dC_p/dT). The result of all this is to produce an apparently greater melting area. However, our deuterated PVC was significantly more stable than protio PVC as shown by TGA weight loss data and the sample color. Thus, after the third DSC heat run (Table I), our PVC-d_3 had only changed to a light orange, whereas under the same conditions a protio PVC turned dark brown. Even the PVC-d_3 powder used for the NMR analysis at 140 °C (Table I) and subsequently tested by DSC turned only a slight orange and showed no detectable (<1%) weight loss.

A deuterated PVC prepared in urea–canal complex was also examined by solid-state ^{2}H NMR. The spectrum at both ambient temperature and 140 °C consisted of the full static quadrupole powder pattern. No narrow component was seen at 140 °C to indicate an amorphous fraction. This is consistent with the DSC results which showed no T_g up to 220 °C (Figure 4). The latter agrees with other thermal results on a urea–clathrate protio PVC.[7] According to X-ray diffraction analysis on a similar PVC, the crystallinity was determined to be 63–78% depending on thermal history.[26] The absence of any motionally narrowed component at 140 °C in our solid-state NMR analysis suggests that our deuterated sample may have had a higher crystallinity or that the T_g of the amorphous fraction lay above 140 °C. The absence of a T_g by DSC below 220 °C might be a consequence of too little and too diffuse an amorphous fraction to cause a significant endothermic event. Unfortunately, because the urea–clathrate PVC is insoluble in all known solvents, its syndiotactic diad fraction cannot be determined by NMR, and it is difficult to characterize by other methods.

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Registry No. PVC (homopolymer), 9002-86-2; $H_2NC(O)NH_2$, 57-13-6.