NMR Study of Crystalline and Amorphous Poly(ethylene oxide)

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ABSTRACT: The ^{13}C CPMAS NMR spectrum and the temperature dependence of the ^{1}H rotating-frame spin-lattice relaxation have been studied for poly(ethylene oxide) (PEO). Correlation times for the chain mobility have been derived from the relaxation data between the glass-transition temperature and the melting point of PEO. These data demonstrate that the rate of motion is about 100 times higher in the amorphous phase than in the crystalline phase. The very different ^{1}H relaxation behavior of amorphous and crystalline PEO is used to assign the two components observed in the ^{13}C spectrum and to study the phases separately. It is also shown that the width of the broad component in the ^{13}C spectrum assigned to crystalline PEO results from the rate of chain motion matching the precession frequency of the proton spins about the ^{1}H decoupling field.

Introduction

Solid polymers in general contain both amorphous and crystalline regions, and these regions are associated with very different polymer-chain dynamics. This difference in dynamics forms the basis for using NMR spectroscopy to observe selectively the two phases.[1] Poly(ethylene oxide) (PEO) has attracted considerable interest recently because of its ability to dissolve a wide variety of inorganic salts and thus producing a polymer material with high ionic conductivity.[2] The properties of these solid electrolytes are strongly dependent on the distribution of the constituent components among the various regions of amorphous and crystalline material and quite often macroscopic regions of pure PEO occur.[3] A systematic study of the polymer electrolytes is currently in progress in our department, and a first step in the understanding of these complex systems is clearly a proper understanding of pure PEO itself. Both ^{1}H NMR[4-8] and solid-state ^{13}C CPMAS NMR[9-11] have been used earlier for the characterization of PEO. The dynamic properties of PEO have been examined by Connor and Hartland[6] using ^{1}H spin-lattice relaxation measurements. In all these experiments the multiphase nature of PEO is evident, and two components corresponding to the amorphous and crystalline phases are observed, in both spectra and relaxation data.

The room-temperature ^{1}H-NMR spectrum, for example, contains two components with very different widths. It is generally accepted that the narrow component can be assigned, without ambiguity, to the mobile polymer chains in the amorphous phase, whereas the broad component is assigned to the more rigid molecules in the crystalline phase.

The interpretation of the two components observed in the ^{1}H rotating-frame spin-lattice relaxation data by Connor and Hartland[6] is less straightforward, however. In ref 6 the rapidly relaxing component is ascribed to the amorphous phase at all temperatures, and, consequently, the more slowly relaxing component, to the crystalline phase. This assignment has been disputed by Dechter,[9] who has pointed out that the assignment of the components in ref 6 should be reversed at room temperature, and he also suggests that a reassessment of the temperature dependence of $T_{1\rho}$ may be in order. Following the suggestion by Dechter, we will, in this paper, reexamine the temperature dependence of the ^{1}H rotating-frame relaxation rate, $1/T_{1\rho}$, to clarify the assignment and interpretation of the ^{1}H relaxation data over a wide temperature range.

Two components are also observed in the ^{13}C CPMAS spectrum of PEO, a narrow component as well as a broader one. Since the two phases in PEO exhibit very different rotating-frame spin-lattice relaxation behavior for the protons, it should be possible to design experiments that take advantage of this difference to separate and unambiguously assign the two components in the ^{13}C spectrum and study them for a better understanding of the dynamic properties of the different phases. We show in this paper that this is, indeed, possible.

Experimental Section

Preparation of Samples. PEO with MW = 4×10^6 (BHD) was studied both as obtained in the form of a powder and as a polymer film prepared essentially in the same way as the PEO-based electrolyte films, i.e., by dissolving the powder in anhydrous acetonitrile and then evaporating the solvent. The whole procedure was carried out in a glovebox with a dry atmosphere, relative humidity ≈3%, to prevent the uptake of water. Samples prepared under these conditions contain negligible amounts of water, as demonstrated by IR spectroscopy. This is important since water uptake will have a substantial effect on the chain dynamics, in both pure PEO and PEO-based solid electrolytes.[12] For the NMR experiments the samples were transferred to sample tubes which were sealed off prior to taking them out of the glovebox.

NMR Studies. The NMR measurements were made in a Bruker MSL spectrometer with a 7-T magnet. The rotating-frame spin-lattice relaxation time $T_{1\rho}$ for protons was measured in the temperature range 170-390 K with the multiple-pulse method of Rhim, Burum, and Elleman,[13] allowing the registration of the full decay of the spin-locked magnetization in a single shot. The frequency, ν_1, corresponding to the effective spin-locking field was 18.5 kHz. The relaxation time $T_{1\rho}$ was also measured at room temperature with a standard spin-lock experiment, i.e., a 90° pulse immediately followed by a phase-shifted variable-length spin-locking pulse with ν_1 = 62 kHz. During cross polarization and for decoupling of the protons in the ^{13}C CPMAS experiments, ν_1 was 56 or 62 kHz.

Standard ^{13}C CPMAS spectra were recorded at 75 MHz, with contact times varying from 0.01 to 5 ms and with spinning rates between 1700 and 3000 Hz. To be able to separate and identify the two components observed in the ^{13}C spectrum, a series of CPMAS experiments was also performed where the protons were kept in a spin-locked state before beginning the cross polarization (Figure 1).

Results and Discussion

^{1}H-NMR Data. The rotating-frame spin-lattice relaxation data for protons in the PEO film (ν_1 = 18.5 kHz) are presented in Figure 2. Two relaxation components are clearly observed, with very different temperature de-

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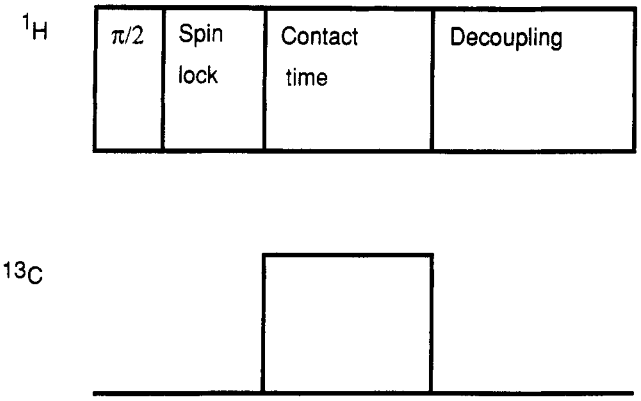

Figure 1. Pulse sequence for the CPMAS experiment with a prelocking pulse.

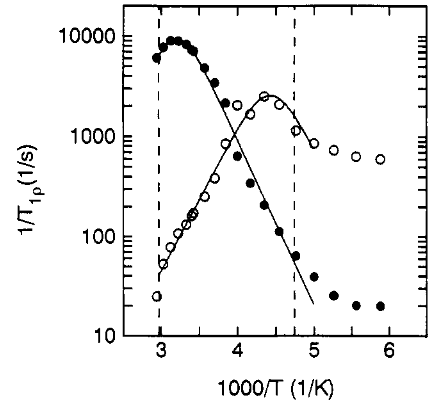

Figure 2. Rotating-frame spin–lattice relaxation rate, $1/T_{1\rho}$, for crystalline PEO (●) and amorphous PEO (○). The least-squares fits to eqs 1 and 2 in the text are represented by solid lines. The melting point and the glass transition temperature are marked with vertical lines.

pendence. The decomposition of a nonexponentially decaying magnetization into two or more components is often quite arbitrary. However, in the present case it is clear from the spectra in Figure 3 that the broad (crystalline) and the narrow (amorphous) components decay with different rates.

Rotating-frame spin–lattice relaxation data have also been reported by Connor and Hartland[6] at a somewhat higher effective spin-locking field (ν_1 = 64 kHz). The interpretation in ref 6 of the data is very different from ours, though. The relaxation rate for crystalline PEO is claimed to be slower than for the amorphous phase over the whole temperature range. This is clearly incorrect, which is most easily seen in the room-temperature spectrum by noting the change in shape obtained after spin-locking the protons for periods of varying length (cf. Figure 3). The broad component, corresponding to the crystalline component, decays much more rapidly than the narrow component. This is in agreement with Dechter,[9] who has pointed out that the assignment in ref 6 of the two components should be reversed at room temperature. Thus, at and above room temperature the relaxation rate is faster for protons in crystalline PEO than for those in the amorphous phase.

However, according to our interpretation of the data, the relaxation rates for the two components cross at about 250 K. Below this temperature the relaxation rate for crystalline PEO is, in fact, slower than that for amorphous PEO. This is also confirmed by comparing the relative amounts of the two phases, as reflected in the least-squares-fitted parameters of the two-component decomposition of the relaxation data. The interpretation of Connor and Hartland would lead to a dramatic change in the relative amounts of the phases at 250 K, from 70 and 30% for the crystalline and amorphous phases just above 250 K to the opposite relative amounts at 250 K. However, at 230 K the proton spectrum still consists of two components with very different widths (about 65- and 10-kHz full width at half-height), and the broad component from the crystalline phase clearly has a considerably larger area than the narrow component. In order to obtain an estimate of the relative amounts of the two components, a sum of Lorentzian and Gaussian bandshapes was fitted to the spectrum. The best fit was obtained with a Lorentzian narrow component and a Gaussian broad component. This gave about 20 and 80% for the narrow and the broad components, respectively. Although these numbers cannot be taken too literally because of a certain arbitrariness in the choice of line shape, they show quite unambiguously that no dramatic phase-composition reversal occurs at 250 K.

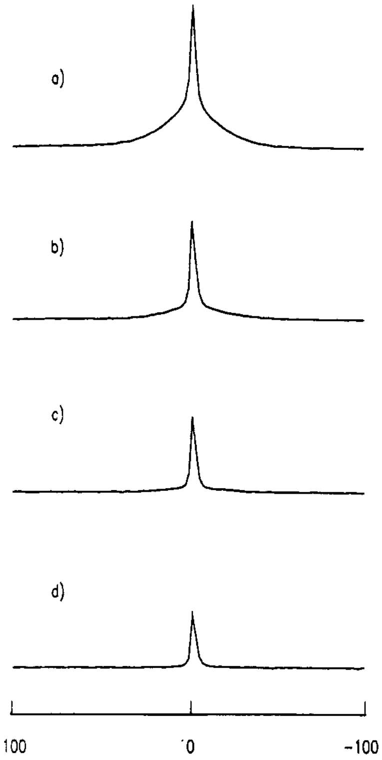

Figure 3. Room-temperature proton spectra after spin-locking for (a) 0.01, (b) 0.8, (c), 2, and (d) 5 ms.

The component in Figure 2 corresponding to crystalline PEO reaches a relaxation rate maximum at a higher temperature, 310 K, than the amorphous component, 230 K. This is consistent with the fact that the mobility of the polymer chains is expected to be higher in the amorphous phase of PEO than in the crystalline phase.

The source of the ^{1}H relaxation is the random fluctuation in the ^{1}H–^{1}H dipole–dipole interaction caused by the movements of the polymer chains. In the analysis of the relaxation data we assume the correlation time, τ, of this polymer-chain motion to be related to the rotating-frame spin–lattice relaxation rate, $1/T_{1\rho}$, via an equation of the form[14]

$$\frac{1}{T_{1\rho}} = C\left\{\frac{3}{2}\frac{\tau}{1+4\omega_1^2\tau^2} + \frac{5}{2}\frac{\tau}{1+\omega_0^2\tau^2} + \frac{\tau}{1+4\omega_0^2\tau^2}\right\} \quad (1)$$

Here, C is a constant proportional to the mean-square amplitude of the fluctuating dipole–dipole interaction and ω_1 and ω_0 are the angular Larmor frequencies of the protons, in the effective spin-locking field and the static magnetic field, respectively. Using eq 1 with ν_1 = 18.5

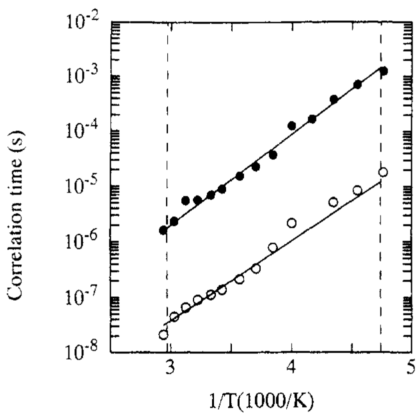

Figure 4. Temperature dependence of the correlation time, τ, for crystalline PEO (●) and amorphous PEO (○), calculated from the experimental $T_{1\rho}$ using eq 1. The melting point and the glass transition temperature are marked with vertical lines.

kHz, we find that the relaxation rate maximum observed occurs for $\tau = 1/2\omega_1$, that is, for $\tau = 4.3 \times 10^{-6}$ s in the present case.

One important result of our reassessment of the temperature dependence of the experimental spin–lattice relaxation data is that we now can fit eq 1 combined with an Arrhenius expression for τ

$$\tau = \tau_0 e^{E_a/RT} \qquad (2)$$

to the data for both components, between the glass transition temperature, 210 K, and the melting point of PEO, 336 K. As a result an activation energy, E_a, for the chain motion can be determined, for both the crystalline phase and the amorphous phase. In the crystalline phase the least-squares-fitted value of E_a is 32 kJ/mol and in the amorphous phase is 28 kJ/mol. Although the relative size of the two activation energies is consistent with the greater mobility of the polymer chains in the amorphous phase compared to the crystalline phase, it is interesting to note that the difference is rather small. Also, for both phases of pure PEO the activation energy is considerably smaller than the one associated with the chain mobility in some of the polymer electrolytes where the chain motion appears to be constrained by ether oxygen coordination to the cations. In, for example, $Pb(CF_3SO_3)_2{\cdot}(PEO)_9$ this activation energy is about 80 kJ/mol.[5] Below the glass transition temperature of pure PEO the slope of the curves in Figure 2 decreases. The reason for this is unclear, and we have made no further attempt to interpret the data.

The correlation time τ can be calculated directly from the observed spin relaxation times using eq 1, provided a relaxation rate maximum is observed, allowing a calculation of the constant C in eq 1. This is the case for the present data, and the resulting correlation time as a function of the inverse temperature between the glass transition and the melting point of PEO is presented in Figure 4.

The spin–lattice relaxation data by Connor and Hartland[6] were acquired at a spin-locking field corresponding to $\nu_1 = 64$ kHz. Using our fitted parameters E_a, τ_0, and C in eqs 1 and 2, we have, for comparison purposes, calculated the expected relaxation rate as a function of temperature for $\nu_1 = 64$ kHz. The relaxation rate maximum, thus calculated, for the crystalline PEO occurs at 350 K and 2700 s^{-1} and for the amorphous phase occurs at 250 K and 780 s^{-1}. In the experiments done by Connor and Hartland the maxima occur at 300 K and 3500 s^{-1} and at 240 K and 1200 s^{-1} for the crystalline and the amorphous components, respectively. The results based on our calculation and on the experiments reported in ref 6 differ somewhat, and there are several possible reasons for this. One conceivable explanation is some contribution from dipolar relaxation, $1/T_{1d}$, in our data because of the rather low effective spin-locking field. Another possibility is a non-Lorentzian spectral density for the polymer-chain motion, leading to a deviation from eq 1. Yet another possibility is an actual difference in the chain mobility because of the slight difference in molecular weight in the two cases, MW = 2.8×10^6 in ref 6 and 4×10^6 in our case.

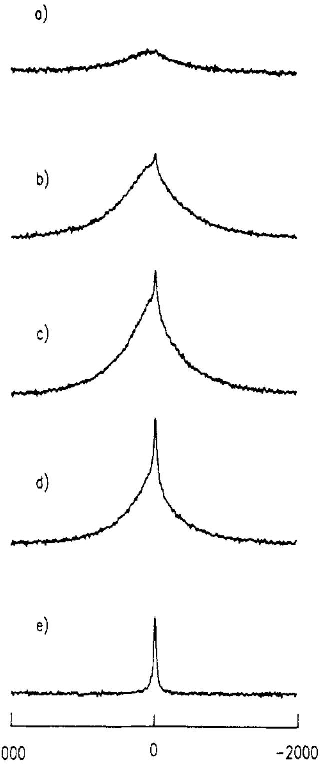

Figure 5. Room-temperature ^{13}C CPMAS spectra from a PEO powder with a contact time of (a) 0.01, (b) 0.06, (c) 0.2, (d) 0.6, and (e) 5 ms.

^{13}C-NMR Data. A selection of ^{13}C CPMAS spectra from a PEO-powder sample is shown in Figure 5. The shape of the spectrum varies strongly with the contact time. At very short contact times the spectrum consists of a single, broad peak. As the contact time increases, a narrow peak appears superposed on the broad peak. The relative area of the two peaks varies with the contact time, due to the difference between the two components, both in the ^1H–^{13}C cross-polarization rate and in the ^1H rotating-frame spin–lattice relaxation. Some spectra were also recorded on a PEO film, but no significant differences were observed.

The spectrum has been fitted to a sum of two Lorentzians. The result is that the shape of the two component peaks is close to independent of the contact time. The shift difference for the two peaks has been determined to approximately 0.8 ppm; this is in agreement with what has been found earlier.[9]

The most reasonable interpretation of the two peaks is that they correspond to amorphous and crystalline PEO. It would be tempting to attribute the broad peak to the amorphous phase, the width then reflecting the dispersion of chemical shifts often observed in amorphous systems because of the distribution of the local structure experienced by the molecules. This is, in fact, opposite to the assignment suggested by Dechter.[9] As discussed above, the rotating-frame spin–lattice relaxation of protons is much slower for the amorphous phase than for the

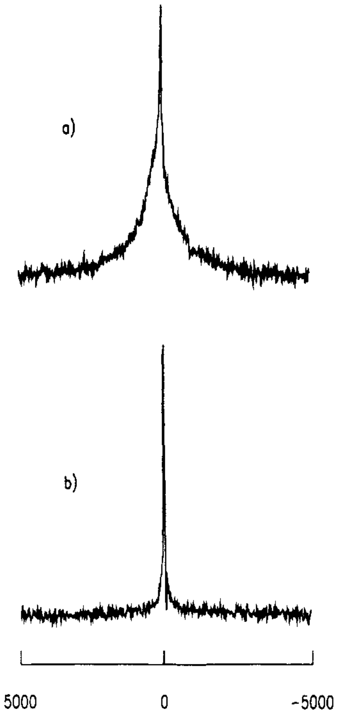

Figure 6. Room-temperature ^{13}C spectra for a PEO film from (a) a CPMAS experiment and (b) a CPMAS experiment with a prelocking pulse of 2 ms. The contact time is 0.8 ms in both cases.

crystalline phase at room temperature. Therefore, by first spin-locking the protons for a suitably selected period before initiating the cross polarization in the CPMAS experiments, the magnetization of the protons in the crystalline phase will have decayed almost completely, while still a substantial fraction of the magnetization in the amorphous phase will remain. The subsequent cross polarization between ^1H and ^{13}C will then produce a ^{13}C magnetization in the amorphous phase only. We have reexamined the ^{13}C spectrum for PEO using both the standard CPMAS experiment and the variety with a proton prelocking pulse in an attempt to account quantitatively for the difference in the width between the two components. For a contact time of 0.8 ms the standard CPMAS spectrum consists of two components (Figure 6a). In the prelock experiment ($\nu_1 = 62$ kHz), using the same contact time and a prelock period of 2 ms, a single, narrow peak was obtained (Figure 6b). This demonstrates, unambiguously, that the narrow peak corresponds to amorphous PEO and the broad peak to crystalline PEO, as suggested by Dechter.[9]

A possible source of the ^{13}C peak broadening for the crystalline phase is the mechanism discussed by Rothwell and Waugh for heteronuclear decoupling in the presence of molecular motion:[15] line broadening occurs when the average rate ($1/\tau$) of the random molecular motion in a sample is close to the rate of the coherent precession imposed on the spin system in the rotating frame by the decoupling field, i.e., when $\omega_1\tau$ is on the order of 1.[10,15] The correlation time required to test this suggestion can be taken to be that derived from the $T_{1\rho}$ data and associated with the fluctuating ^1H–^1H dipole–dipole interaction, because of the strongly correlated motion of the carbons and the protons in the polymer chain. It follows that, at room temperature where $\tau_1 = 9 \times 10^{-6}$ s, $\omega_1\tau \approx 3$ and the condition for line broadening is, indeed, fulfilled for crystalline PEO. The full width at half-height for the crystalline peak due to motionally induced broadening can be calculated by the relation[10]

$$\text{fwhh} = \frac{1}{T_{2m}\pi} = 0.5M_2\frac{J_m(\omega_{1H})}{\pi} \tag{3}$$

where the spectral density is expressed as

$$J_m(\omega_{1H}) = 2\frac{\tau}{1 + \omega_{1H}^2\tau^2} \tag{4}$$

We find that the calculated value is fwhh ≈ 2 kHz. This is in reasonable agreement with 1-kHz width that is found experimentally.

For the amorphous phase, τ is smaller by a factor of about 100 (Figure 4) and $\omega_1\tau \approx 0.03$, implying that the broadening due to this mechanism should be considerably less, as is observed.

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