^{2}H NMR Investigation of the Plasticization Effects Induced by High-Pressure Carbon Dioxide Gas on the Molecular Dynamics of Polymers

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Received September 13, 1989

ABSTRACT: ^{2}H NMR spectroscopy has been used to probe the effect of CO_2 gas pressure on the molecular dynamics of polymers used as membrane materials in gas separation. A special cell was constructed for the experiment which was capable of pressures from vacuo to at least 35 atm. The investigation showed that the molecular dynamics of the polymer were unequivocally enhanced by dissolved CO_2 (at relatively low pressures) for three polymers studied: polycarbonate, polyester carbonate, and polystyrene. In fact, the pressure dependence of the microscopic molecular dynamics of the polymer and the diffusivity of CO_2 were quite similar. Two conclusions are possible from this observation. First, CO_2 diffusion is directly related to the polymer dynamics monitored with ^{2}H NMR. If this conclusion is correct, then it suggests that concentration-dependent diffusion parameters are required to accurately model transport in these systems. However, an alternative conclusion is that CO_2 diffusion is not related to the polymer dynamics measured by ^{2}H NMR because the specific frequencies and motions monitored by NMR are not dominant in the CO_2 diffusion process. Instead, both the NMR determination and diffusion may be dependent on another process such as polymer swelling or plasticization.

Introduction

Polymeric materials are widely used as membranes for the separation of gases and liquids and as barrier materials in packaging. In general, the fundamental molecular level mechanisms of transport have only been inferred from bulk transport measurements, i.e., permeation and diffusivity experiments. This report describes a solid-state NMR investigation of the effects of dissolved carbon dioxide on polymer chain dynamics. Chain dynamics play a crucial, yet poorly understood role in the diffusional transport of small molecules through polymers. If the frequencies, amplitudes, and average separations of polymer chains were precisely known, a detailed molecular model of diffusional transport could be developed. This investigation's aim is to correlate the known "plasticization" effects of high concentrations of CO_2 on permeation with specific polymer chain motions. Three specific classes of polymeric materials were investigated. The classes, based on transport behavior, are listed below.[1,3]

(1) Permeability initially decreases slightly as CO_2 pressure increases. (Permeability is defined as flux normalized to unit pressure driving force and thickness.) Polystyrene is in this category (at least in the pressure regimes investigated).

(2) Permeability initially decreases slightly as CO_2 pressure increases. At higher pressures, however, it reaches a minimum and then increases dramatically as pressure continues to rise due to transport plasticization. Polycarbonate falls into this category.

(3) Permeability increases steadily as CO_2 pressure is increased. Poly(methyl methacrylate) and cellulose triacetate exhibit this behavior. This increase in permeability at high pressures is accompanied by simultaneous dramatic loss in separation selectivity.

In general, all of these materials are plasticized by CO_2. The T_g is lowered in all cases when samples are exposed to high-pressure CO_2. The degree of T_g depression does not seem to correlate with the classes defined above.[19] Therefore, the permeation process is not directly dependent on factors that influence "plasticization" behavior. The variation in permeation rate must be caused by subtle variations in polymer chain amplitudes, frequencies, or average spacings, which do not necessarily dominate T_g effects. These subtle variations may occur on a much more localized size scale than is typically associated with the glass transition.

This study focused on monitoring molecular level dynamics and correlating them with transport behavior. The results, although aimed at transport, provide a detailed picture of the changes that occur during plasticization of a polymer. The concepts developed are also certainly of interest for explaining plasticization effects on mechanical properties of commercial materials.

Background

Various theories have been proposed to model transport processes in glassy polymers, the most notable being the so-called "dual-mode" theory which describes transport and sorption of gases by polymeric systems in terms of two types of sites or modes.[2] The sites are described as Henry's law sites (dissolution sites) and Langmuir sites (hole-filling sites). According to the dual-mode theory, the two sites have different diffusion coefficients that are nominally independent of pressure. Both sites would also have different binding strengths for gas molecules. Therefore, gas molecules in the two sites would have different mobilities. The Langmuir sites, which provide stronger binding, would have more restricted mobility.

The dual-mode theory adequately describes the pressure dependence of such parameters as the solubility constant and permeability of a gas in glassy polymers of class 1, both of which are known to decrease with pressure for most polymeric systems. However, the dual-mode theory describes transport as a macroscopic phenomenon, neglecting the molecular properties of polymeric membrane. Plasticization of the polymer must be invoked in order to explain the increases in permeability with pressure observed in class 2 and class 3 polymers.

A number of investigations have been reported using NMR to study the dependence of sorption and transport of gases on the molecular properties of polymeric materials. Assink studied the sorption of ammonia by

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polystyrene using ^1H NMR relaxation techniques to determine the mobility of ammonia in the polymer within the pressure limits of 0 and 5.5 atm.[4] In these experiments, only one population of ammonia molecules was observed, but the T_2 of the sorbed ammonia was observed to be pressure dependent. Assink interpreted these results as arising from ammonia molecules exchanging rapidly between two different sites (Henry and Langmuir sites) whose proportions varied with the pressure. Assink suggested (in accord with the proponents of the dual-mode theory) that the gas dissolved in the Henry sites was much more mobile than that in the Langmuir sites. Others have interpreted these results differently, suggesting that the diffusion coefficient of the gas molecule was pressure dependent.[5]

Sefcik and Schaefer conducted ^{13}C NMR $T_{1\rho}$ measurements of PVC in the presence of CO_2 in order to determine whether the polymer molecular motions were affected by the presence of the gas molecule.[5,6] The dual-mode theory assumes that the diffusion parameters of the sorbed gas are pressure and concentration independent. They proposed that if the dual-mode model was correct, the mobility of the polymer molecules could not be altered appreciably. In their experiments, the CO_2 pressure was varied from vacuo to 1.05 atm. ^{13}C NMR $T_{1\rho}$ measurements were utilized since this relaxation parameter probes molecular motions in the mid-kilohertz frequency range, the range believed to be of most interest for cooperative main-chain motions of the polymer backbone. A correlation between ^{13}C NMR $T_{1\rho}$ values and pressure was observed, although the change in $T_{1\rho}$ was small. The molecular motions of the polymer were observed to increase with the addition of CO_2 in contrast to the assumptions of the dual-mode theory. The authors concluded that their results "could not be reconciled with the dual-mode theory which claims that gas molecules preferentially occupy preexisting sorption sites in a conditioned polymer with no perturbation of the polymer matrix".

These investigations, while demonstrating that there was a gas/polymer interaction, were of limited value for the identification of the role that molecular dynamics played in transport because of the low pressures utilized, the small effects observed, and the difficulty of interpretation of the results. The investigation reported here is an attempt to define the change in molecular dynamics of the polymer as a function of CO_2 gas pressure in a more quantitative and detailed manner and to extend the experiment to much higher pressures.

^2H NMR spectroscopy was utilized for the determination because this technique has several advantages over conventional solid-state NMR techniques. First and most important, ^2H NMR spectroscopy does not require magic-angle sample spinning as do other solid-state NMR techniques. Therefore, a simple and safe apparatus could be designed for the determination of ^2H NMR spectra at pressures as high as 35 atm.[7] Second, the samples were deuterium labeled in specific locations so that the motions observed could be attributed to specific functional groups. Finally, the interpretation of ^2H NMR spectral and relaxation data is fairly straightforward with regard to dynamic information.

^2H NMR spectroscopy has been shown to be an excellent tool for the characterization of the molecular dynamics of polymeric systems.[8-13] It compares quite favorably to ^{13}C NMR methods for the measurement of molecular dynamics with the benefit that the ^2H NMR line shapes also define the type of motion present. The disadvantage of the ^2H NMR technique is that it requires deuterium-labeled analogues. The polymers of this study were deuterium labeled and included polystyrene-d_8 (PS-d_8), bisphenol A polycarbonate-d_8 (BPA-d_8), poly(methyl methacrylate)-d_8 (PMMA-d_8), and polyester carbonate-d_4 (PEC-d_4). Their structures are given in Figure 1.

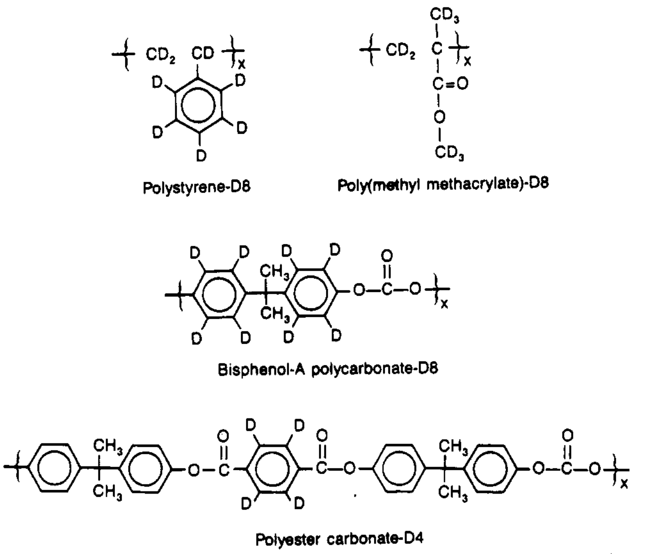

Figure 1. Structures of the polymers used in the investigation.

Experimental Section

The ^2H NMR spectra were obtained with the quadrupole echo pulse technique described elsewhere.[11] ^2H NMR spectra were obtained at 30.7 MHz on a Bruker CXP-200 spectrometer. The 90° pulse width was 6 μs, the delay time was 5.0 s (16 s for PS-d_8), the data acquisition size was 4096 points, the accumulation time was 0.001 s, the sweep width was 1.00 MHz, the apodization was exponential with 2-kHz line broadening, and the delay time between 90° pulses was 40 μs. Acquisition was begun at the top of the echo.

Before data collection was initiated, the sample was exposed to a given CO_2 pressure for 1-12 h, depending on the sample thickness. This allowed the system to reach a steady-state concentration of dissolved gas. The long-term relaxation of the glassy polymer toward equilibrium was not characterized. Relaxation effects will be the subject of another study.

The ^2H NMR T_1 values were determined by using the $180°-\tau-90°$ pulse sequence followed by the 40-μs delay and refocusing pulse, with acquisition at the top of the echo. The delay times were varied from milliseconds to 16 s.

The high-pressure cell (shown in Figure 2) is made from a $^3/_8$-in. heavy-wall glass elbow of dimensions given in the figure. The cell is connected to a $^1/_8$-in. copper tube through a Swagelok fitting in which the copper tubing is soldered to the male portion of the fitting. Nylon ferrules are utilized for the seal. The fitting is constructed of brass and copper so as not to interfere with the NMR experiment. The copper tube is connected to a $^1/_8$-in. Teflon tube by a $^1/_8$-in. Swagelok union. The flexible Teflon tube is fed through the magnet bore and connected to a manifold with suitable valves and connections to a regulated gas cylinder, a vacuum pump, and a vent. A pressure gauge is placed between the sample cell and the manifold. Gas pressure is supplied from a regulated gas cylinder.

The sample cell is loaded with the sample (as a powder) and connected to the manifold as described above. The cell is placed into the NMR probe, which is then loaded into the magnet. (The cell and magnet bore are shielded in case of accidental cell explosion.) The cell can then be evacuated or pressurized with the operator shielded from accidental explosion by the probe and magnet assemblies. The cells have been pressure tested to 1000 psig of CO_2 without failure. However, the recommended pressure limit for these cells is 500 psig. The estimated limits of temperature for the probe are 0-60 °C, but a Dewared sys-

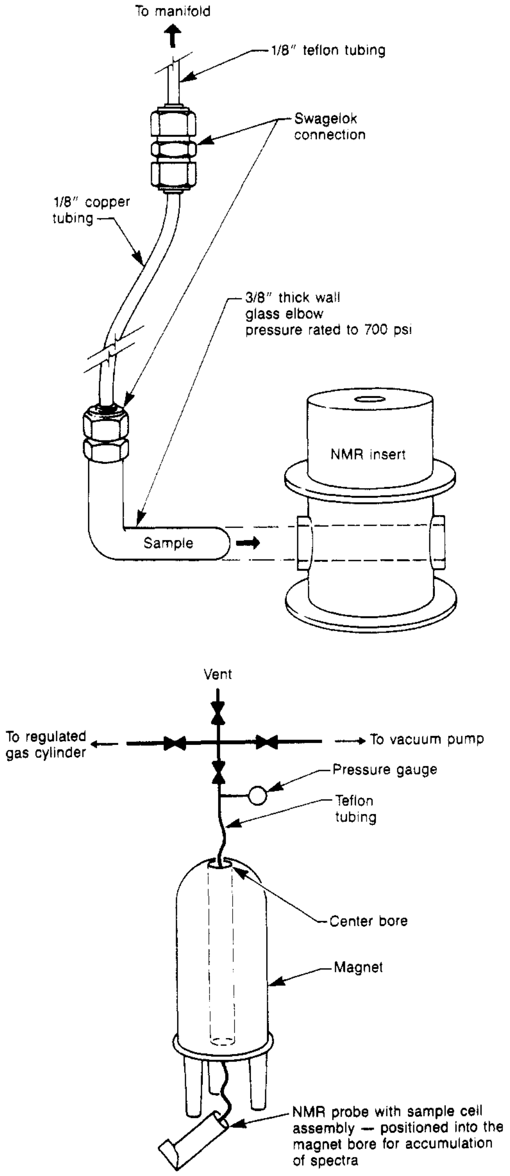

Figure 2. High-pressure NMR cell design.

tem would allow extension of this range.

Results

(A) Temperature Dependence of T_1 Values. There are a number of ^{2}H NMR parameters that can be utilized to determine molecular dynamics, including line shape and T_1 values.[10,17,18] An analysis of the ^{2}H NMR line shapes was attempted first with little change in this parameter with CO_2 pressure. The T_1 values were found to have a much larger dependence upon CO_2 pressure and were, therefore, utilized for the characterization of molecular dynamics. More will be said subsequently about the reasons for the stronger dependence of T_1 than line shape. In polymeric systems, it is difficult to relate an NMR relaxation parameter such as the T_1 value to molecular dynamics because the motions are not simple reorientations such as in small molecules but are often more complex segmental motions. Also, the glassy state of a polymer gives rise to a complex distribution of motional correlation times for even the simplest motion, leading to nonexponential relaxation.[17] Therefore, it is difficult to relate the measured relaxation times quantitatively to a correlation time for motion. To estimate the effect that gas pressure has on the T_1 value (and thus the molecular motions), we studied the temperature dependence of the T_1 value for the polymers. These values are given in Figure 3.

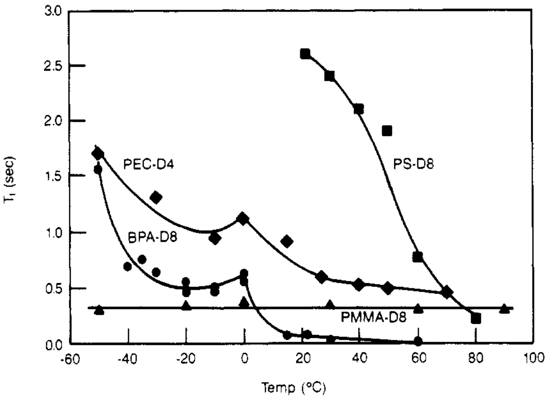

Figure 3. Temperature dependence of the T_1 values.

The T_1 values of PS-d_8 monitor both the backbone motions and phenyl motions because the polymer is completely deuterium labeled. Therefore, it is difficult to define the type of motion giving rise to the decrease in T_1 value from these spectra alone. However, the predominant motion in this temperature regime has been defined by others as restricted phenyl vibrational motions.[15,16] The T_1 values are ca. 3.0 s at low temperatures. Above 0 °C, they decrease dramatically to ca. 0.2 s at 90 °C. Thus, in this temperature range, an increase in molecular dynamics causes a large decrease in T_1.

PMMA-d_8 shows very little temperature dependence because the experiment primarily monitors the motion of the methyls. The backbone deuteriums contribute little to the T_1 measurement because their pattern is so broad. The motion of the methyl groups is fast at all temperatures and is, therefore, perturbed little by temperature (and, as shown later, by CO_2 pressure).

The temperature dependence of the T_1 values of the PEC-d_4 and BPA-d_8 polymers is much more interesting. The T_1 values for both polymers go through a minimum at ca. −20 to 0 °C and then decrease sharply at still higher temperatures (see Figure 3). This trend was verified with the BPA-d_8 system by determining several T_1 values in the area between −40 and 0 °C. The same trend is observed with the PEC-d_4 system but is less dramatic. The fact that the precision of the T_1 data is quite good (about 0.1 s) supports the existence of the double minimum in the PEC-d_4 T_1 data as does the analogy with the BPA-d_8 system, which undergoes the same types of phenyl motions. The powder patterns help the interpretation of these data because they indicate that above 0 °C, the motions accessible to the rings (at the NMR time scale) change.[8] Below 0 °C, the rings undergo only rocking motions at the NMR sampling frequency, whereas at temperatures above 0 °C phenyl ring flips also narrow the lines. It appears, therefore, that the T_1 minima in the plots are due to rocking motions in the range of −20 to 0 °C and to phenyl ring flips above 0 °C.

The temperature dependence of the line shapes for the four polymers studied is given in Figures 4–7. A more thorough discussion of the interpretation of these shapes is given elsewhere.[8,17]

(B) Pressure Dependence of the T_1 Values. The dependence of the ^{2}H NMR T_1 value upon CO_2 pressure was measured using the cell described above. This cell was constructed of thick-walled glass tubing to withstand the high pressures utilized. Therefore, the sample size contained in the cell was reduced relative to that of the thin-wall cells used for the temperature study. In so doing, the sensitivity was also reduced relative to that of

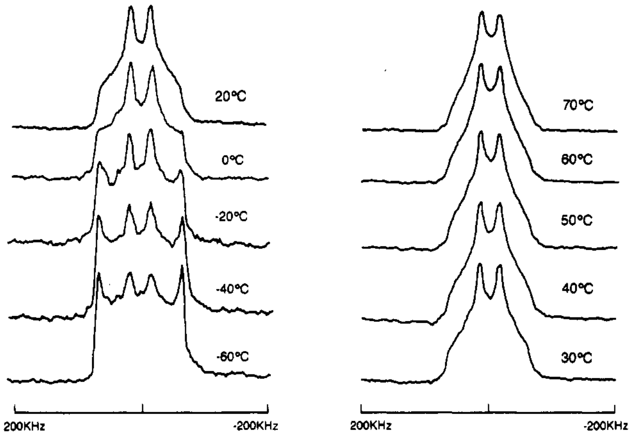

Figure 4. Temperature dependence of the ^2H NMR line shapes of PC-d_8.

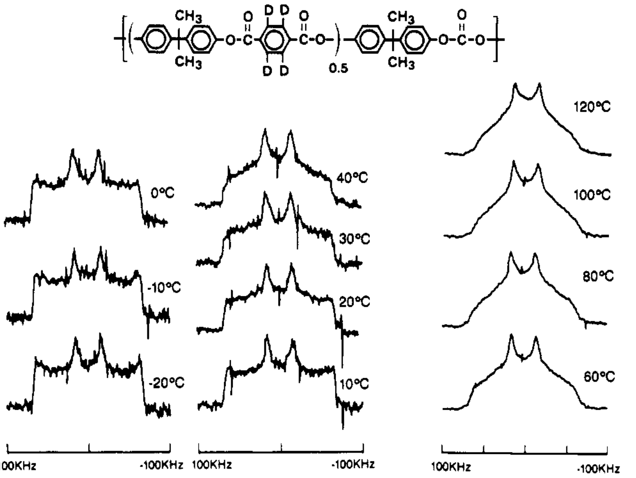

Figure 5. Temperature dependence of the ^2H NMR line shapes of PEC-d_4.

the temperature data and the uncertainty in the measured values of T_1 was greater. The pressure dependence of the ^2H NMR powder pattern of PS-d_8 is given in Figure 8. The powder pattern of this polymer, as well as that of the others, shows very little change as a function of CO_2 pressure.

The pressure dependence of the T_1 values for the polymers at 27 °C is given in Figure 9. Only PS-d_8 shows a correlation of T_1 with CO_2 pressure. The T_1 value of PS-d_8 is almost at its largest value at 27 °C (see Figure 3). Therefore, increases in motion induced by either temperature or dissolved CO_2 cause a marked decrease in the T_1 value. Thus, as the pressure is increased, the T_1 value is observed to decrease from the value of 3.0 s in vacuo to a value of ca. 0.7 s at 35 atm of CO_2 pressure. (The value of T_1 measured in vacuo is in good agreement with that measured at 25 °C in the study of Figure 3, indicating that the configuration of the cell has little effect on the measured T_1 value. An estimate of the standard deviation of these values is 0.05 s.) The largest change is observed between vacuo and ca. 7 atm of CO_2 pressure. Above 7 atm of pressure, the decrease in T_1 is much less pronounced.

It is obvious from Figure 3 why PMMA-d_8 shows no pressure dependence. The same arguments used to explain its lack of temperature dependence also apply to its pressure dependence. The PEC-d_4 and BPA-d_8 samples also show no pressure dependence because at 27 °C the T_1 values for these samples are already at a minimum (see Figure 3), and increases in motion do not have a measurable effect. At 0 °C, the T_1 values of both BPA-d_8 and PEC-d_4 are at the upper limit of the second minimum of the plot of T_1 versus temperature. Therefore, the pressure dependence for these polymers was determined at 0 °C so that an increase in the molecular dynamics could be most readily observed. A plot of the pressure dependence of the T_1 value for these two polymers at 0 °C is given in Figure 10, together with PS-d_8 at 27 °C for comparison. The T_1 values were observed to

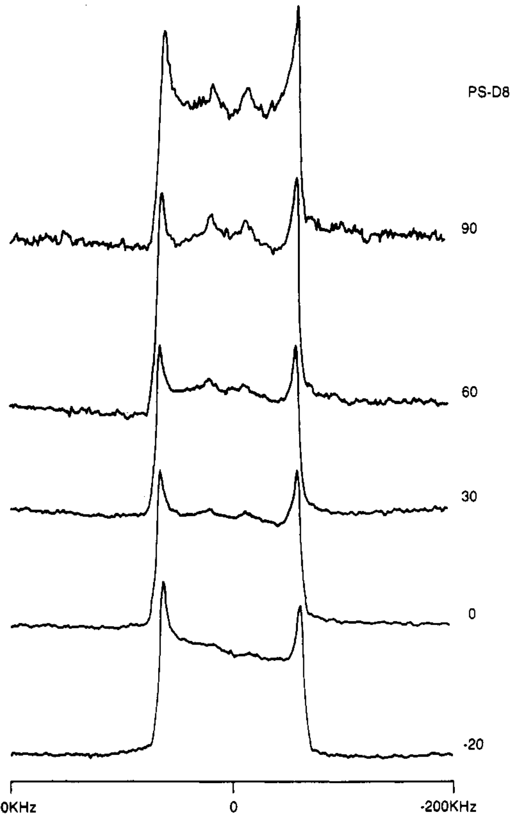

Figure 6. Temperature dependence of the ^2H NMR line shapes of PS-d_8.

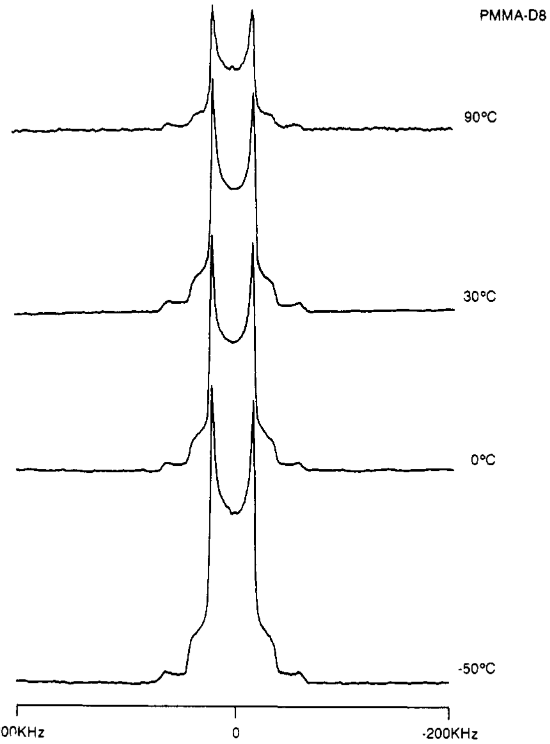

Figure 7. Temperature dependence of the ^2H NMR line shapes of PMMA-d_8.

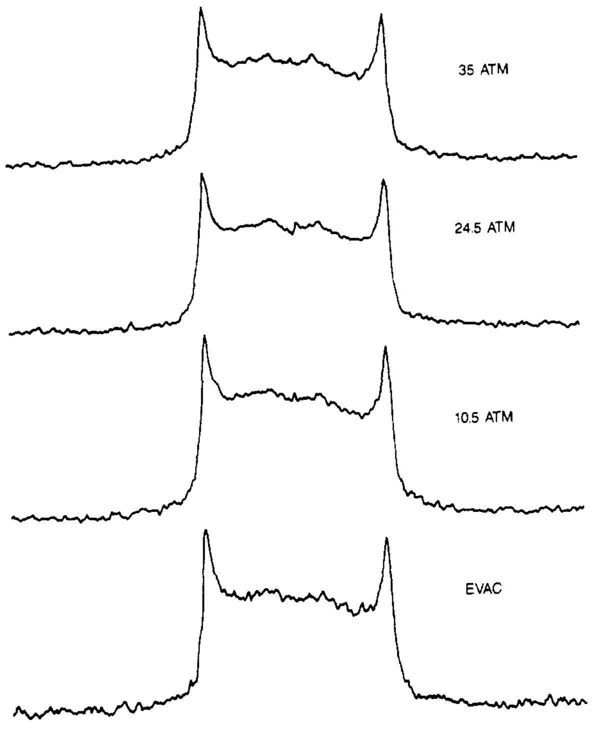

Figure 8. CO_2 pressure dependence of the ^2H NMR line shapes of PS-d_8.

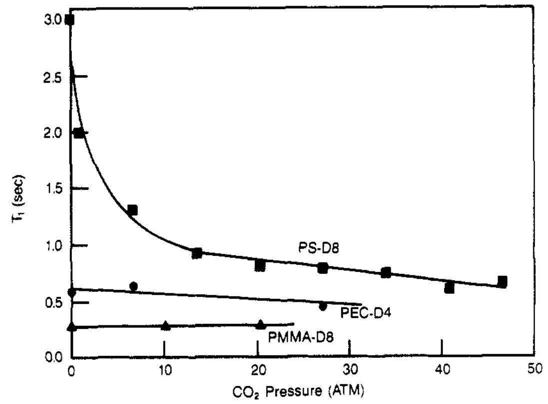

Figure 9. Pressure dependence of the ^2H NMR T_1 values at 27 °C.

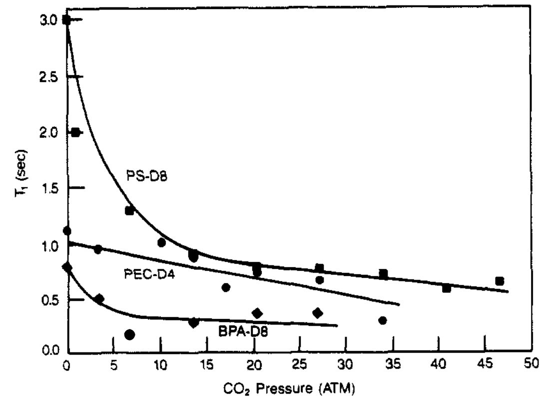

Figure 10. Pressure dependence of the ^2H NMR T_1 values for PEC-d_4 and BPA-d_8 at 0 °C and PS-d_8 at 27 °C.

decrease with CO_2 pressure even though the uncertainty in the measured T_1 values was too large (about 0.1 s) to be as definitive about the trend as with PS-d_8. The T_1 of PEC-d_4 appeared to decrease almost linearly with pressure while that of BPA-d_8 followed a behavior similar to that of PS-d_8.

Unfortunately, there are no pressure-dependent diffusivity data for BPA at 0 °C. Therefore, it is not clear at what pressure transport plasticization occurs under the conditions of the NMR experiments. Transport measurements at 0 °C are needed to determine the correlation between transport plasticization and polymer dynamics.

Discussion

It was shown that the changes induced in the polymers by CO_2 pressure were much easier to observe by ^2H NMR T_1 measurements than by line-shape measurements. The reason for this observation is not certain, but some comments can be made. The line shapes are less sensitive to vibrational motions than to two-site jumps or continuous rotational motions. In PS-d_8, vibrational motions are the predominant motions in the temperature regime of interest.[15,16] Phenyl ring flips give rise to a narrowed ^2H NMR powder pattern which was not observed in the spectra of PS-d_8 (except for a very small fraction of the population which are more labile due to the nonequilibrium nature of the glass). On the other hand, T_1 measurements are equally sensitive to vibrational and rotational motions. The changes in the motions in BPA and PEC induced by temperature between 0 and 20 °C give rise to a change of ca. 15% in the ^2H NMR line widths. The change in the T_1 values in this temperature range is at least 50%. Since the changes are proportionately larger for the T_1 values, they are also easier to detect.

The changes in the T_1 for PS-d_8 as a function of pressure are larger than that of the other polymers. However, this does not imply that the pressure-induced changes in motion are the largest for polystyrene. The changes in the T_1 values of PS-d_8 induced by temperature were also much larger than those for the other polymers. Thus, the temperature dependence of the T_1 can be used to estimate the change in dynamics associated with a pressure-induced T_1 change for any given polymer but not to compare one polymer to another. The T_1 value for PS-d_8 ranged from 3.0 s in vacuo to 0.7 s at high pressures. This corresponds to a change in dynamics associated with roughly a 30 °C increase in temperature. Figure 3 can be compared to Figures 9 and 10 for these values. The pressure-induced dynamics changes for PEC and BPA were very similar to this also. The T_1 value of these polymers did not level off at the minimum observed in the T_1 versus temperature plot of Figure 3, but at some value substantially larger than this. The plasticization of the polymer by dissolved gas apparently only enhances the molecular dynamics of the polymer a given amount. The increased dynamics caused by dissolved CO_2 are clearly not correlated directly with the dynamics induced by increased temperatures.

The trends observed in the pressure dependence of the ^2H NMR T_1 values appear to correlate with the pressure dependence of the diffusivity of the CO_2 in the polymer.[21] This is shown for PS-d_8 in Figure 11 and for BPA-d_8 in Figure 12. Thus, it appears that the diffusivity of the CO_2 is enhanced by the molecular motions of the polymer. However, there is an alternate conclusion that can be drawn: that the two observables are dependent on the same parameter but are mutually independent. Increases in the unoccupied volume of the polymer or in the long-range backbone motions which could result from either plasticization or swelling of the polymer by the sorbed CO_2 could also give rise to the increase in molecular dynamics of the polymer and the enhanced diffusivity. It has been shown that the T_g of the polymers is

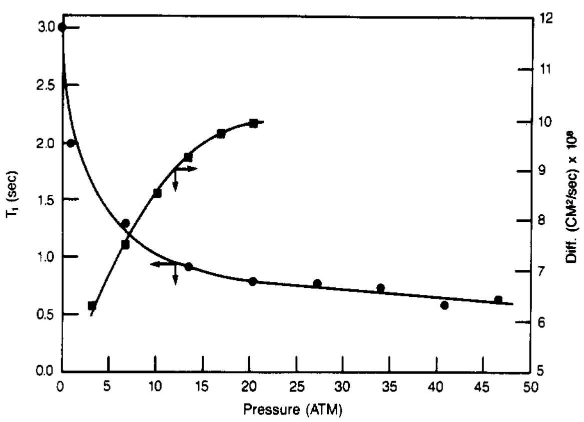

Figure 11. CO_2 pressure dependence of the CO_2 diffusivity and ^2H NMR T_1 value for PS-d_8.

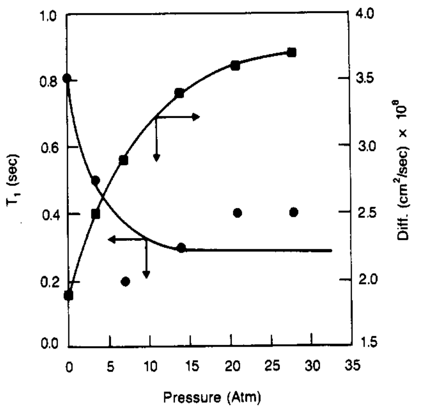

Figure 12. CO_2 pressure dependence of the CO_2 diffusivity and the ^2H NMR T_1 value for BPA-d_8.

depressed as a result of sorption of CO_2 and that the polymer swells upon exposure to CO_2.[19-20] The swelling of the polymers has been shown to depend upon several factors, including the temperature, solubility of the gas in the polymer, and, most importantly, the conditioning pressure and time.[19] However, the level of swelling of polycarbonate with CO_2 is nearly a linear function of pressure when the polymer is not conditioned by preexposure to CO_2. In contrast to this behavior, the changes in diffusivity and NMR T_1 are not linear with increased pressure but rather show considerable curvature at lower pressures. Also, the behavior of the ^2H NMR T_1 value for PS-d_8 did not show the hysteresis effect observed for polymer swelling as a function of conditioning pressure. The T_1 values of PS-d_8 on the plot of Figure 9 did not depend on the previous pressure to which the sample had been exposed. Thus, polymer swelling is probably not the predominant cause of the enhanced diffusivity and molecular dynamics.

Plasticization of the polymer, which gives rise to enhanced amplitudes of long-range chain motions, may be the cause of the enhanced diffusivity and microscopic dynamics. The distinction between microscopic dynamics as measured by NMR and the longer range, macroscopic motions affected by plasticization is an important one. The suppression of T_g follows a pressure dependence similar to that of the diffusivity and NMR T_1 values. Therefore, it is possible that diffusivity and the microscopic molecular dynamics are both a function of these enhanced chain motions.

The time scale of the two processes (diffusion of the gas and dynamics measurements by ^2H NMR T_1 values) may be very different. This NMR measurement samples frequencies at ca. 10–100 MHz, whereas the passage of a gas molecule between two polymer chains could be significantly faster. Spin–lattice relaxation measurements of gases dissolved in polymers suggest motional correlation times of 10^{-12} s.[22] Therefore, polymer dynamics in the 10–100-MHz frequency regime, as measured by NMR, may be too slow to be important to diffusional processes.

In summary, there are two explanations for the apparent correlation between the macroscopic diffusivity of CO_2 in polystyrene and polycarbonate and their microscopic molecular dynamics as determined by ^2H NMR spectroscopy. First, the diffusion is aided by the microscopic dynamic processes such as phenyl ring flips and oscillatory motions. As these molecular processes occur, they facilitate diffusion of the penetrant in the polymer matrix. A second explanation for the correlation concerns the fact that the presence of the dissolved gas molecule causes plasticization of the polymer, giving rise to increased molecular dynamics and gas diffusivity. Thus, the two processes (molecular dynamics and diffusivity) are both a function of the plasticization of the polymer by the sorption of the gas but are mutually independent. This explanation must be considered because the relative frequencies of diffusivity and the NMR dynamics measurement are so different. Therefore, the molecular processes observed by NMR may be too slow to affect the diffusivity of the gas. Either explanation would lead to the conclusion that the presence of the gas in the polymer does alter its molecular dynamics. The commonly used dual-mode transport model for penetrants dissolved in glassy polymers attributes changes in overall diffusivity to shifts in population between Langmuir and Henry's law sorption environments. This suggests that concentration-dependent diffusion parameters may also be required to accurately model transport in these systems.

Acknowledgment. We acknowledge the assistance of Drs. D. Hasha, A. Burmester, R. Bubeck, J. Heeschen, R. Wessling, J. Berdasco, and S. Martin.

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High-Resolution Solid-State ^{13}C NMR Study of Isotactic Polypropylenes Isothermally Crystallized from the Melt

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Received May 3, 1989; Revised Manuscript Received December 28, 1989

ABSTRACT: The phase structure of isotactic polypropylenes isothermally crystallized from the melt has been examined at different temperatures by solid-state high-resolution ^{13}C NMR spectroscopy using VT/MAS (variable temperature/magic angle spinning). On the basis of ^{13}C spin-lattice relaxation and computer line-shape analyses, it has been found that polypropylene samples are composed of not only crystalline and amorphous components but also another noncrystalline component with 3_1-helical conformation. Similar NMR analyses at different temperatures have revealed that a reversible structural change between the 3_1-helical and random conformations occurs in the noncrystalline region at 60-110 °C.

Introduction

Solid-state high-resolution ^{13}C NMR spectroscopy is a powerful technique for characterizing the crystalline and noncrystalline regions of semicrystalline polymers.[1-13] Recently we found on the basis of the measurements of ^{13}C spin-lattice and spin-spin relaxation times and computer line-shape analyses for the total dipolar decoupling/magic angle spinning (DD/MAS) spectra that polyethylene samples crystallized from the melt were composed of not only crystalline and amorphous phases but also crystalline-amorphous interphase.[1] The thickness of the interphase was estimated to be about 30 Å, which corresponds well to the theoretical value calculated using a lattice model by Flory et al.[14]

Isotactic polypropylene, which is also a highly crystalline polymer, has already been studied by several groups using solid-state high-resolution ^{13}C NMR spectroscopy. Bunn et al.[11] measured CP/MAS spectra of annealed and quenched α-form (monoclinic) and β-form (hexagonal) samples at room temperature. The doublets with 1:2 intensity were observed for CH_2 and CH_3 resonance lines of the annealed α-form sample. They supposed that these doublets were derived from the presence of two different packing sites in crystals on the basis of the arrangement of the molecular chain in a unit cell of α-form. They also suggested that disappearance of these doublets for quenched α-form and β-form samples was due to the decrease in crystalline perfection and the absence of the different sites, respectively.

Lyerla et al.[12] measured ^{13}C spin-lattice relaxation times (T_{1C}) over a wide temperature range from room temperature down to 105 K. They concluded that T_{1C}'s of not only CH_3 but also CH_2 and CH resonances depended on CH_3 rotational motion, and the broadening of the CH_3 resonance around below -100 °C was also due to modulation of CH_3 rotational motion at the frequency of proton nutation in the presence of the decoupling field. Recently Tonelli et al.[13] also reported solid-state high-resolution ^{13}C NMR spectra of isotactic polypropylenes. They used samples that were carefully characterized by X-ray crystallography and reconfirmed the results obtained by Bunn et al.

In this paper, we report new results on the solid-state structure and molecular motion for isothermally bulk-crystallized isotactic polypropylenes. We have particularly paid attention to the crystalline-noncrystalline structure (phase structure) of this polymer and its dependence on temperature. For this purpose we have used some isotactic polypropylenes isothermally crystallized from the melt and measured solid-state high-resolution ^{13}C NMR spectra and different spin relaxation parameters at various temperatures using the VT/MAS system.

Experimental Section

Isotactic polypropylene (Showa Denko K. K. MA510) was purified by Soxhlet extraction with toluene to remove low molecular weight compounds and the atactic polypropylene. The molecular weight and isotacticity of the purified sample were $M_w = 2.30 \times 10^5$ from GPC and (mm) = 98.0% from the analysis for the methyl region of the ^{13}C NMR spectrum in solution, respectively.

After melting at 230 °C the sample was isothermally crystallized at 100 °C for 1 h or at 140 °C for 6 days (hereafter abbreviated to PP100 and PP140, respectively). It was confirmed by X-ray analysis that the crystal structure was α-form (monoclinic) for both samples. The degree of crystallinity was determined from density measurements and DSC. Here, the values 0.936 and 0.850 g/cm^3 were assumed for the crystalline and amorphous densities and 2.10 kcal/mol for the heat of fusion of crystals.[15]

0024-9297/90/2223-3256$02.50/0