mass diffusion coefficient as T_g is approached from above. The slow change in the diffusion coefficient below T_g is related to the frozen-in segmental mobility, which results in a slower change of the average hole free volume in the system. A different-temperature behavior of the polymer above and below T_g is clearly manifested in the temperature dependence of the mass diffusion coefficient.

One also notes that the width in the transition region is closely related to the effect of physical aging. As previously shown by Zhang and Wang in PMMA,[7] the value of the mass diffusion coefficient in the transition zone (near T_g) depends on the time duration of the measurements. If it were possible to wait for true thermodynamic equilibrium before the LIHGR measurement was carried out, a more abrupt decrease in D, or a decrease over a narrower transition region, would be observed.[7]

In summary, we have carried out a laser-induced holographic grating relaxation study of camphorquinone in amorphous poly(bisphenol A carbonate). We have shown that the time dependence of the diffraction intensity of the reading beam is closely associated with the mass diffusion of camphorquinone and its photoproduct, which modulate the multiple grating effect. We have shown for the first time that by changing the temperature the shape of the diffraction intensity versus time curve can be changed drastically. The temperature dependence of the diffusion coefficients obtained for camphorquinone and its photoproduct can be described by the LWF equation, with constants C_1 and C_2. The C_2 constant is found in agreement with the dielectric relaxation data, suggesting that the same type of segmental motion is responsible for both processes. A rapid drop of the diffusion coefficient is observed as the temperature traverses across T_g from above. Below T_g the diffusion data only decrease very slowly with decreasing temperature.

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Registry No. PC (copolymer), 25037-45-0; PC (SRU), 24936-68-3; CQ, 465-29-2.

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Communications to the Editor

Interfacial Electron-Nuclear Polarization Transfer in Polymer Composites

In this paper, we report on a new NMR method for exploring the interfacial region in a multicomponent polymer mixture, one component of which contains unpaired electron spins. The samples used here consist of clusters of the electron-rich polymer several hundred angstroms in size dispersed in the bulk of a support polymer. The idea is to use the method of dynamic nuclear polarization (DNP), exploiting the short range of the electron-nucleus coupling to selectively polarize nuclei close to the clusters which contain the unpaired electron spins. The NMR spectrum of these nuclei is subsequently detected.

Nuclear polarization in nonmetals can be achieved via the Overhauser effect by saturation of the EPR accompanied by thermal relaxation processes which flip electron and nuclear spins simultaneously.[1] These processes are made possible by electron spin fluctuations at frequencies close to the EPR frequency. Nuclei can become polarized during saturation of the EPR if these fluctuations are transmitted through electron spin density at the site of the nucleus by scalar coupling or through space from a nearby electron by dipolar coupling. In either case the degree of polarization will depend strongly on the proximity of electron and nucleus, the property on which the selectivity of our method is based.

The sample we have used is a composite of 17% (w/w) polyacetylene in polyethylene. Preparation and characterization of these materials has been reported in detail elsewhere.[2] The polyethylene is low-density material, with ~70% crystallinity before impregnation, and is thought to become less crystalline as the polyacetylene is introduced.[2b] TEM measurements indicate that the polyacetylene in these composites forms islands with sizes ranging from ~600 to 2000 Å.[2b] Deuterium NMR studies confirm that domains of polyacetylene are present in a similar kind of composite formed with polystyrene.[3] EPR studies show that motion of the unpaired electrons in the polyacetylene formed in these composites exhibits correlation times of ~10^{-11} s, similar to those observed in the pure all-trans material.[4,5] These high-frequency fluctuations provide time dependence for the relaxation pathways required for DNP.

The DNP-NMR spectrometer, which operates at 1.4 T (40 GHz for electrons and 60 MHz for protons), uses a Fabry-Perot resonator for microwave saturation and has been described elsewhere.[6] The experiments reported here were carried out in a cryomagnet using a variable-temperature probe capable of operation from 4.2 to 300 K. All spectra shown result from Fourier transform of a proton signal excited by a $\pi/2$ pulse. In the DNP sequence, the microwave field necessary to saturate the EPR is kept on continuously. The power measured at the input to the resonator coupler is ~6 W.

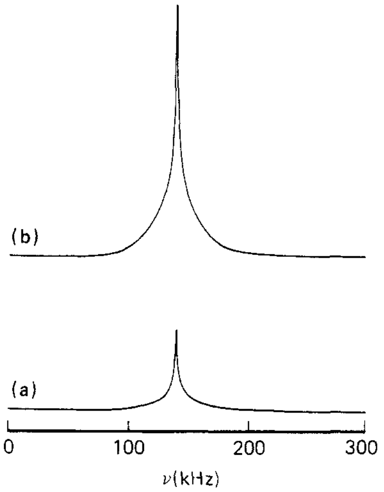

Figure 1. ^{1}H NMR spectrum of a 17% polyacetylene in polyethylene composite material (a) without and (b) with saturating microwave irradiation at the center of the polyacetylene EPR line. The amplitude of the narrow component (noncrystalline polyethylene) is increased by 2.8 due to dynamic polarization, i.e., $\epsilon = +1.8$ (vide infra).

The 40-GHz EPR spectrum of the 17% polyacetylene/polyethylene composite consists of an intense, narrow line (width = 7.4 G). EPR at X-band on a wider sweep shows that this narrow line is superposed on a broad line (width = 50 G). The narrow EPR line is due to electrons in the polyacetylene,[5] while the fine structure on the broad line indicates that it arises from unpaired electrons associated with the Ziegler–Natta catalyst used to produce the polyacetylene.[7]

The results of a proton DNP experiment on the composite sample are shown in Figure 1. The proton spectrum obtained without microwave irradiation (Figure 1a) consists of a narrow line superposed on a broad line. The broad component arises from polyacetylene and crystalline polyethylene, while the narrow line is from noncrystalline polyethylene.[8] The signal is enhanced when the polyacetylene EPR line is saturated as shown in Figure 1b. The proton enhancement is defined as

$$\epsilon = (A_p - A_a)/A_a = A_p/A_a - 1 \qquad (1)$$

where A_p and A_a are the amplitudes of the ^{1}H signal in the presence and absence of saturating microwave irradiation, respectively. The proton enhancement measured from the spectra in Figure 1 is +1.8. Since the amplitude of the transformed signal is due mainly to the narrow line from noncrystalline polyethylene, the DNP results show enhancement of the protons in polyethylene via the electrons in polyacetylene, thus demonstrating interfacial polarization transfer between two components in a polymer composite. As in pure polyacetylene at ambient temperature, the maximum enhancement is achieved with the microwave frequency centered on the EPR line, showing that the dynamic polarization arises through an Overhauser effect.[5]

Several factors contribute to the sign as well as the magnitude of an Overhauser enhancement:[9]

$$\epsilon = (\gamma_e/\gamma_H)f\xi s \qquad (2)$$

where γ_e/γ_H is ratio of the electron to proton magnetic moment, the leakage factor f reflects the fraction of proton relaxation due to the electrons responsible for the DNP ($0 < f < 1$), ξ denotes the nature of the electron–nucleus coupling (ranging from $+^1/_2$ for a pure dipolar to -1 for a pure scalar interaction), and s indicates the degree of saturation of the EPR ($0 < s < 1$).

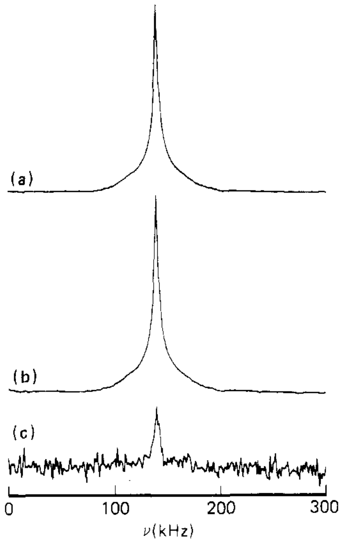

Figure 2. ^{1}H NMR spectrum of a composite of 6.7% *fully deuteriated polyacetylene in protonated polyethylene* (a) without and (b) with saturating microwave irradiation at the center of the polyacetylene EPR line. Spectrum c is obtained by subtracting spectrum a from spectrum b.

Since we have measured a positive value for ϵ, eq 2 shows that ξ must be negative, indicating scalar coupling between the electrons in polyacetylene and protons in polyethylene.[9] One possible mechanism explaining this enhancement is that there is some electron spin density from polyacetylene on the polyethylene protons and this further implies bonding between the polyacetylene and polyethylene; although possible, there is no evidence for such chemistry.[2]

Another explanation is a scalar Overhauser enhancement of the protons in polyacetylene[5] followed by spin diffusion to the protons in polyethylene.[10] We tested this idea by carrying out ^{1}H DNP-NMR experiments on a sample of fully deuteriated polyacetylene in protonated polyethylene. The results are shown in Figure 2. In contrast to the results obtained with fully protonated material, a very small proton enhancement shown in Figure 2c ($\epsilon = +0.03$) is observed when the microwave field is applied. This result confirms the role of intermolecular proton spin diffusion, since the enhancement is reduced by over an order of magnitude in the deuteriated sample in which spin diffusion is no longer a viable pathway.

The interfacial proton NMR signal can thus be viewed as originating from a proton magnetization gradient created during saturation of the EPR. This gradient arises from a difference in polarization of the polyacetylene protons at the surface of the polyacetylene clusters and nearby polyethylene protons. Spin diffusion smooths out this gradient and propagates the magnetization generated locally at the intermolecular boundary into the bulk of the polyethylene.

The magnitude of the observed enhancement is over 2 orders of magnitude less than the theoretical maximum of 657. Examination of eq 2 indicates that there are three factors that may account for this loss. Measurement of the enhancement as a function of microwave power has shown that the power used in these experiments approached saturation of the EPR ($s = 0.8$). Since coupling in all-trans polyacetylene is purely scalar,[5] the coupling factor (ξ) should be close to -1. Therefore, the most likely source of loss in the enhancement lies in the leakage factor, i.e., f may be close to zero. Leakage results from relaxation pathways that sap dynamic nuclear polarization through losses to the lattice. Two sources of leakage that are suggested by experimental evidence are proton dipole–dipole relaxation and proton relaxation by unpaired electrons that are not involved in the DNP. Proton dipole–dipole relaxation requires molecular motion in polyethylene with correlation times ~(60 MHz)$^{-1}$; such motion is well documented at ambient temperatures.[11] Leakage due to other mechanisms becomes important at low temperatures where we have also measured very small enhancements ($\epsilon = +1.4$ at 90 K) and where the motions so crucial to dipole–dipole relaxation are quenched. At these temperatures, we believe that relaxation of the protons by unpaired electrons in pockets of unreacted catalyst is the dominant source of leakage.

The source of the small but reproducible enhancement found in the composite containing deuteriated polyacetylene (Figure 2c) is intriguing. There are three possible explanations for this signal: (1) direct surface polarization of polyethylene protons by electrons in polyacetylene due to electronic overlap between the two components; (2) residual protons in the deuteriated polyacetylene; (3) enhancement of catalyst protons left in the polyacetylene during sample preparation.

This investigation shows that it is indeed possible to use DNP to polarize the nuclei in a matrix surrounding clusters which contain unpaired electrons. In the particular composite we have studied, rapid ^{1}H spin diffusion in the polyethylene matrix propagates the polarization induced by the DNP, thus reducing the initially selective interfacial polarization transfer from the polyacetylene clusters. Possibilities for overcoming this limitation include restricting the extent of spin diffusion either by polarizing for short times or by using rotating-frame DNP.[12] Another alternative is to probe with rare nuclei, such as ^{13}C, for which spin diffusion is very slow. Experiments are currently under way to explore these alternatives.

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Registry No. Polyacetylene, 25067-58-7; polyethylene, 9002-88-4; deuteriated polyacetylene, 28265-43-2.

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Hypercross-Linked Organic Solids: Preparation from Poly(aromatic diacetylenes) and Preliminary Measurements of Their Young's Modulus, Hardness, and Thermal Stability

We are engaged in a program intended to establish relationships between the microscopic structure of highly cross-linked organic solids and the Young's modulus, thermal stability, and hardness of these solids. This program was stimulated by an interest in the physical properties of diamond.[1] Diamond is the hardest substance known, is the best thermal conductor, and has the highest known Young's modulus. These properties undoubtedly reflect, in some way, the high volume density of strong, directional carbon–carbon bonds that characterize the structure of diamond. Our objective is to prepare organic solids with a high and controllable density of carbon–carbon bonds, to characterize the bonding in these solids, to establish their physical and materials properties (especially Young's modulus, thermal stability, and hardness), and to correlate their microscopic structures with these macroscopic properties.

Our approach has been to prepare organic oligomers containing a high proportion of acetylenic groups capable of forming carbon–carbon bonds, to mold these oligomers into macroscopic objects, and to cause the cross-linking reaction to occur in the solid state (eq 1). It was our hypothesis that a high ratio of carbon to hydrogen in these oligomers and, thus, a high density of carbon–carbon bonds in the solids derived from them, would result in a high modulus and thermal stability. This paper summarizes the preparation of polymers from five aromatic diacetylenes (**1a**–**5a**)[2] and the conversion of these polymers to highly cross-linked solids (**1c**–**5c**). These structures were chosen to survey the response of the physical properties of the final cross-linked solid to variation in the structure