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Studies of polymer morphology with ^{13}C inversion recovery cross polarization NMR

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SUMMARY

Inversion recovery cross polarization (IRCP) NMR was used to study the solid state morphologies of plasticized and neat poly(vinyl butyral-co-vinyl alcohol) (PVB), of polyether polyurethane elastomers (PU), and of low density polyethylene (LDPE). IRCP decay data for these polymers were best fit to a biexponential two-component model modulated by $T_{1\rho}H$ relaxation. These results clearly display the two-phase nature of these polymers, as well as the potential applicability of the IRCP technique.

INTRODUCTION

One of the most important variables affecting the physical properties of a solid polymer is its morphology (1). For this reason, the pursuit of this area has been of both industrial and academic interest. Because of the limited availability and expense of neutron scattering, and the limited applicability of X-ray techniques, solid state NMR with cross polarization and magic angle spinning (CPMAS) has been particularly useful for studying the morphology of amorphous and semi-crystalline polymers (2).

Cory and Ritchey (3) have recently shown that the IRCP technique can be used to elucidate multiple components in solid polymers when the components cross polarize at different rates. However, the biexponential decay that results from these experiments cannot always be interpreted in terms of a two component decay due to competing rotating frame proton spin lattice ($T_{1\rho}H$) processes. For this reason, we have followed the cross polarization equations presented by Mehring (4) in order to develop both single and dual component models for IRCP decay. Thus, we can now be more conclusive about the multiphase nature of polymers by comparing the fit of experimental IRCP data to the two models.

EXPERIMENTAL

The ^{13}C - NMR data was acquired on a Bruker MSL-400 spectrometer operating at 100.627 MHz. The proton decoupling and spin lock field strength was approximately 57 kHz. The magic angle sample spinner was a cylinder type made of Al_2O_3 and was spun at 3 kHz for most measurements (the PU samples were spun at 4kHz).

The IRCP experiments were run using the pulse sequence (3) shown in Figure 1. The cross polarization contact time (t_1) was held at 1.5 milliseconds for each experiment. The variable hold time (t_2) was varied from 0.0 to 1000 μsec.

The $T_{1\rho}H$ time constants were measured through the decay of carbon signals over extended contact times ranging from 0.1 to 10 msec. The $T_{1\rho}H$ values were

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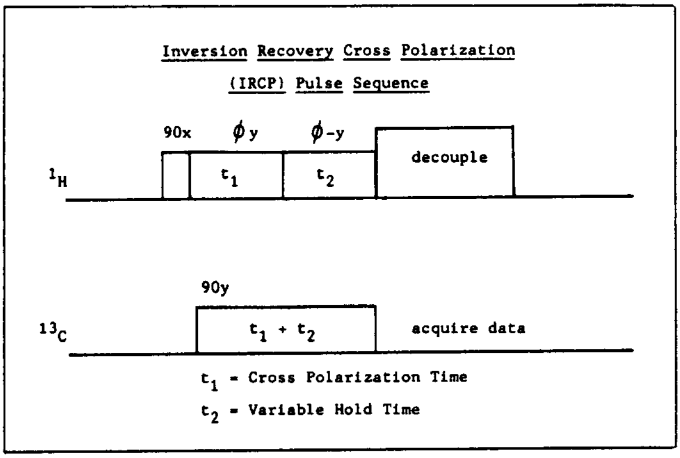
taken as the slope of M(t) vs. contact time beyond the cross polarization maxima (7).

Figure 1: IRCP Pulse Sequence



The plasticized PVB with 32 phr dihexyladipate (DHA) was obtained from Monsanto Co. as the commercial product Saflex. The neat PVB was obtained by extracting the DHA with n-hexane using a sohxlet extraction procedure. The PU samples were made from commercially available PTMEG/TDI prepolymers cured to solids by the diamine curative 4,4'-methylene-bis-2-chloroaniline (MOCA). The prepolymer used was Uniroyal Adaprene L-167.

RESULTS AND DISCUSSION

The cross polarization rate of ^{13}C nuclei with protons (T_{CH}) is believed to be modulated by the near static motional components of the respective nuclei (3,4,5). Thus, a rigid component in a multi-phased polymer system will cross polarize more quickly than the mobile components. This makes IRCP particularly useful since it can be used to elucidate separate motional environments for carbons having similar or nearly identical chemical shifts. This is accomplished by phase shifting the proton field (under Hartman-Hahn matching conditions) by 180 degrees for a delay time (τ), and by following the resulting decay and inversion of the carbon magnetization (M) as a function of time (t).

The IRCP decay curves for the polymers in this study could not be adaquatly fit by a single exponential decay. The curves showed biexponential character, and could be fit to the biexponential equation employed by Cory et. al. (3), shown as equation [1].

$$[1] \qquad M(t) = A \exp(-t/\ T_{CH1}) + B \exp(-t/\ T_{CH2}) + C$$

The prefactors, A and B, were interpreted by Cory to represent the fraction of each phase in a pre-supposed two-phase system. The time constants T_{CH1} and T_{CH2} represented the cross polarization constants for the respective phases, and C was interpreted to be a measure of the importance of $T_{1\rho H}$ to the relaxation process (3).

Equation [1] can provide some indication of the potential multi-phased nature of a polymer, but it is not free from ambiguity; especially when the time constant for the mobile component is on the same order of magnitude as $T_{1\rho}H$. When the experimental IRCP data are fit to the equation [1] model, five parameters are adjusted with only two of them, T_{CH1} and T_{CH2}, having true interpretational meaning. One might argue that the prefactors are valid components of this model, but it is apparent that these values, including the constant C, may contain undefined artifacts from the fitting process. It seems that the fitting of A, B, and C is a function of $T_{1\rho}H$, but there is no clear way to deconvolute the $T_{1\rho}H$ effect from these parameters.

In order to reduce this ambiguity, we have followed Mehring's description of cross polarization (4) to model IRCP decay for a one component system given by equation [2],

$$[2] \qquad M(t) = M_0\exp(-t/\ T_{1\rho}H)[2\exp(-t/\ T_{CH}) - 1]$$

and for a two component system as described by equation [3],

$$[3] \qquad M(t) = x\ \{M_0\exp(-t/\ T_{1\rho}H)[2\exp(-t/\ T_{CH1}) - 1]\} + (1-x)\{M_0\exp(-t/\ T_{1\rho}H)[2\exp(-t/\ T_{CH2}) - 1]\}$$

where M_0 represents the initial magnetization at the beginning of the IRCP delay sequence after a CP contact time. The variables (x) and (1-x) represent the fraction of each phase in the case of the two phase model, and $T_{1\rho}H$ is the time constant for apparent proton spin lattice relaxation determined in a separate experiment from carbon magnetization decay as a function of CP contact time (6).

We have made some assumptions in the use of these equations; namely that $T_{1\rho}H$ is averaged by spin diffusion and that both phases share the same $T_{1\rho}H$ value (this was observed experimentally from extended contact experiments where no bi-exponential $T_{1\rho}H$ decay is observed for these peaks), and that $T_{1\rho}C$ does not significantly affect the IRCP decay since $T_{1\rho}C > T_{1\rho}H$ for the polymers studied.

These equations remove ambiguity from the analysis of IRCP data since there are no undefined quantities in the expressions. In the case of the two component model (equation 3), the prefactors (x and 1-x) are more realistic estimates for the fraction of each component in the case of a two phase system.

The most important feature of these models is that they allow us to determine with more certainty whether a polymer is fairly homogeneous, or whether it is a heterogeneous system containing at least two motional environments. This is accomplished by comparing the quality of fit of the two models to the IRCP data for each polymer.

As shown in Table 1, the best fit for each polymer is obtained from the two phase model (the chi-square values are smaller). In general, the effect of $T_{1\rho}H$ on our experimental fit is least significant when the ratio of $T_{CH}/\ T_{1\rho}H$ approaches zero, and becomes more important as the ratio increases. This can be better visualized in Figures 2, 3, and 4 where the two models are fit to the experimental IRCP data.

PVB Results

All of the carbons in the PVB sample show biexponential character, but for this analysis, the 102 ppm butyral ring carbon is discussed since it provides a good representation of backbone motion. The effect of $T_{1\rho H}$ on the IRCP data for this

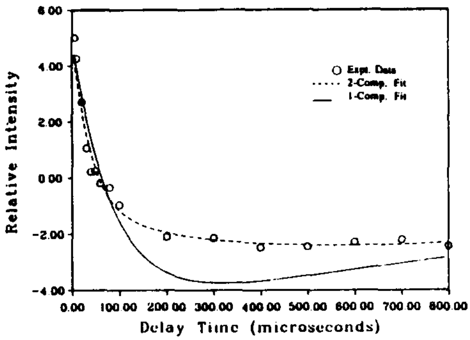
TABLE 1: IRCP Single-Phase vs. Two-Phase Model Fit

SAMPLE	δ (ppm)	χ^2 1-PHASE	χ^2 2-PHASE	(X)	TCH1 (μSEC)	(1-X)	TCH2 (μSEC)	T1ρH (mSEC)
PVB/NEAT	102	0.89	0.17	0.61	37	0.39	440	3.5
PVB/DHA	102	1.09	0.21	0.64	43	0.36	660	1.4
L-167 PU	71	0.99	8.4E^{-3}	0.38	79	0.62	4400	8.0
LDPE	33	1.14	0.27	0.75	33	0.25	550	30.0
LDPE	31	1.50	0.03	0.60	70	0.40	3400	30.0
LDPE[1]	33+31	2.01	0.16	0.66	39	0.34	2150	30.0

[1] from total area of amorphous + crystalline peaks

polymer is more pronounced than for the other polymers since its $T_{1\rho H}$ value (especially in the plasticized polymer) is closer to the T_{CH2} value for the mobile component.

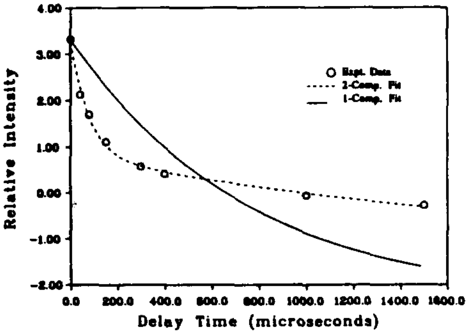
Figure 2: IRCP, PVB/32 phr DHA, 102 ppm



However, we are still able to resolve the data into two components as can be seen from our fit to the two component model (Table 1). Thus, both the plasticized and unplasticized polymers seem to exhibit bi-phasic behavior. This is further verified by the poor fit to the single component model.

It must be realized that this conclusion is by no means absolute. For example, PVB may actually be composed of more than two phases, but certainly no less than two. It is interesting to note that this is consistent with the results from Schaefer's (7) neutron scattering experiments on plasticized and unplasticized PVB, and that this is the first time to our knowledge that the multi-phased nature of PVB has been verified with NMR data.

Figure 3: IRCP, L-167 PU, 71 ppm



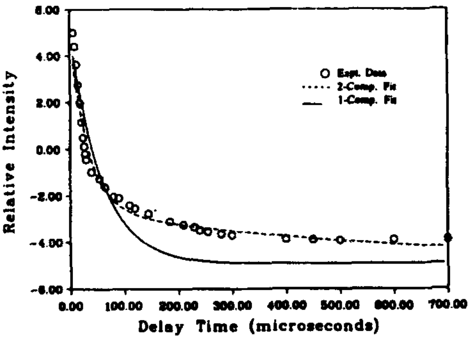
Polyurethane Results

The two-phase morphology of polyurethane elastomers first suggested by Cooper and Tobolsky (8) has become a widely accepted model for these materials. The two-phases are readily seen in the measurement of T_{CH} for the PU sample.

The IRCP data for the oxymethylene carbon (71ppm) of the flexible segment of the elastomer was fit to both models. As can be seen in Figure 3 and Table 1 the fit is best for the two-component model where T_{CH1} and T_{CH2} are the cross polarization constants for the rigid and the mobile components respectively.

The effect of $T_{1\rho}H$ on the estimated T_{CH} values is smaller for T_{CH1} than for T_{CH2} which is consistent with the observation that $T_{1\rho}H$ has a greater influence over relaxation kinetics when the sample or (phase in this case) is highly mobile. The other carbons observed and measured for this polymer (but not reported in this paper) are also best fit by the two component model.

Figure 4: IRCP, LDPE, 33 ppm



PE Results

The difference in chemical shifts of the two overlapped components in polyethylene is close to 1.8 ppm with the crystalline resonance at 33.2 ppm, and the amorphous at 31.4 ppm. The IRCP data for LDPE shows that the integrated area of the overlapped peaks fits the two component model well. The short T_{CH1} of 40 μsec corresponds to the cross polarization time for the rigid crystalline domains which comprise about 66 mole % of the polymer, while the T_{CH2} at 2150 μsec represents the non-crystalline components comprising about 34 mole % of the polymer.

The percent crystallinity from this data is in agreement with previously measured values obtained from a 60 MHz spectrometer (3). An analysis of the data from crystalline peak heights (not area) indicates that there are probably two different structures (packings) involved. The results imply that there are at least three motional environments that can be resolved: a rigid crystalline region (50%), a transition region which may be tied to the rigid crystallites (16%), and a very mobile non-crystalline component (34%).

Since the very mobile non-crystalline component showed a broad T_{CH} dispersion, we did not try at this point to resolve it into further structural regions. A variety of structures within this 34% component may become apparent with further study.

The more mobile carbons take longer to cross polarize from protons than the less mobile carbons due to the attenuation by molecular motion of the carbon-proton and proton-proton dipolar interactions. It is difficult to quantify T_{CH} values in semi-crystalline polymers since the measurement is complicated by differing degrees of molecular mobility even within the same phase. However, it is this function of the relative differences in molecular motion which makes the IRCP technique so useful and allows it to be used for the determination of fraction crystallinity.

The crystallinity values measured by the IRCP technique may differ from values obtained by other techniques because the technique places more emphasis on molecular motion rather than on direct differences between crystalline and amorphous character. Also, it probably tends to yield lower values as compared to those obtained from X-ray diffraction measurements which tend to be longer range in nature. (10)

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