NMR Studies of Plasticizer Motions in a Polymer Matrix

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Received July 2, 1991; Revised Manuscript Received March 6, 1992

ABSTRACT: ^{13}C NMR relaxation parameters have been used to compare the motional characteristics of di-*n*-hexyl adipate (DHA) in solution and in the solid state of a poly(vinylbutyral-*co*-vinyl alcohol) (PVB) matrix. The motional behavior of DHA is inherently anisotropic as seen from [13]C T_1 relaxation measurements in solution. This anisotropy is accentuated in solid PVB/DHA samples where α-carbons surrounding the DHA ester groups are found to exhibit less mobility than other DHA carbons. Scalar decoupled relaxation measurements of DHA carbons in the solid PVB/DHA matrix yield [13]C T_1 values which are similar to those measured with cross polarization (CP) and high-power decoupling, with the exception of carbons near the ester groups. Inversion–recovery cross polarization (IRCP) data are best fit by a biexponential model for all DHA carbons. However, biexponential behavior is most predominant for carbons near the ester positions. These results indicate that the DHA molecules exist in separate liquid and solid type environments in the PVB/DHA matrix, where the motion of DHA molecules in solid environments is most inhibited near the ester carbon positions, possibly by means of an association between PVB functional groups and DHA ester groups.

Introduction

Low molecular weight diluents are often blended with polymers to increase flexibility by effectively shifting the glass transition temperature to lower temperatures.[1] It is believed that plasticizer molecules can expand the total free volume in a polymer matrix, thereby making it possible for long-range segmental motions to occur at reduced temperatures.[2] However, little is known about the nature of plasticizer motions in such systems.

Solid-state NMR studies of plasticized polymers have revealed that these systems are not simple homogeneous blends but instead are complex multiphased matrices characterized by the existence of concentration gradients ranging from plasticizer pools to rigid polymer domains.[3] Schaefer and co-workers[4] have previously studied polymer motions and phase separation in poly(vinylbutyral-*co*-vinyl alcohol)/di-*n*-hexyl adipate (PVB/DHA) blends, but no studies of plasticizer motions have been accomplished for these materials.

As a first step toward understanding the motional behavior of plasticizers in systems like these, we have studied the motional characteristics of di-*n*-hexyl adipate (DHA) in a PVB matrix using solid-state CP/MASS NMR and solution NMR relaxation techniques. These techniques are particularly valuable since they allow for the study of intramolecular motional heterogeneities which may exist as a result of anisotropic modes of motion[5] and the study of intermolecular spin system heterogeneities which may exist as a result of microscopic phase separation.[6]

Experimental Section

PVB containing 32 phr DHA was obtained as the commercial product Saflex from Monsanto and was studied as received with solid-state and solution NMR procedures. DHA was extracted from the Saflex with *n*-hexane in a Soxhlet extractor. The *n*-hexane was removed by evaporation in a rotovap for 24 h at 60 °C.

^{13}C NMR studies were performed on a Bruker MSL 400 spectrometer at a ^{13}C frequency of 100.627 MHz. Samples for solid studies were cut into disks and packed into the ceramic

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MAS rotors with Kel-f caps. The rotors were spun at the magic angle with a spinning rate of 3000 Hz. Measurements of the ^{13}C spin–lattice relaxation times (T_1, $^C T_{1\rho}$), ^{1}H spin–lattice relaxation times ($^H T_{1\rho}$), and cross-polarization rates (T_{CH}) were accomplished at 25 °C under air bearing pressure and at –20 °C under precooled dry-nitrogen bearing pressure. Temperatures were maintained at ±3 °C with a Bruker temperature control unit.

All cross-polarization experiments were performed under Hartman–Hahn matching conditions with a contact time of 1.5 ms and with a proton radio-frequency (rf) power sufficient for providing a matching carbon pulse width of 4.4 μs, a condition which effectively provides a rotating-frame precession frequency of 57 kHz. Continuous proton rf power was also supplied during carbon signal acquisitions for the purpose of providing high-power decoupling of residual proton-dipolar broadening interactions.

T_1 experiments with cross polarization were performed using the pulse sequence of Torchia,[7] with a recycle time equal to $5^H T_{1\rho}$, a condition typically met with a value of 2 s. T_1 values were taken from the inverse slopes of semi natural log plots of intensity vs delay time.

Carbon $T_{1\rho}$ experiments were performed with a standard spin-lock sequence followed by a variable proton delay period.[8] The carbon $T_{1\rho}$ values were then calculated from the inverse slopes of semi natural log plots of intensity vs delay time.

Apparent proton $T_{1\rho}$ values were measured from the decays of carbon signal intensities over sustained spin-lock periods ranging from 1 to 10 ms.[9] These values were then used in the fitting of inversion–recovery cross-polarization (IRCP) data to models which account for $T_{1\rho}$(H) decay.[10] IRCP experiments were performed with the pulse sequence of Cory et al.[11] using 180° phase-inverted contact times ranging from 10 to 800 μs.

Solution-state spectra were obtained with low-power scalar decoupling for DHA with 10% CDCl$_3$ (by volume) added as a reference and field lock. T_1 values were measured using a standard inversion–recovery pulse sequence[5] with delay times ranging from 0.5 to 10 s and a recycle time of 45 s. Scalar-decoupled solution spectra and T_1 values were also obtained for solid PVB/DHA samples using a procedure similar to that of Jelinski et al.,[12] where solid samples were placed in a 10-mm-outside-diameter glass tube along with a sealed capillary containing DMSO-d_6 as a reference solvent and external lock.

Results and Discussion

Table I lists chemical shifts for DHA carbons from high to low field for solution, "solid" solution, and solid CP-MAS spectra, while Figure 1 shows the corresponding DHA
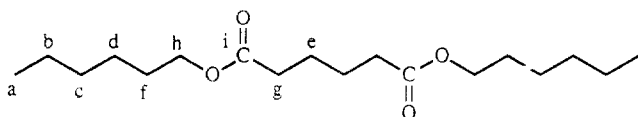
Figure 1. Structural assignments for di-*n*-hexyl adipate (DHA).

Table I
Chemical Shift Assignments for DHA Carbons (ppm)

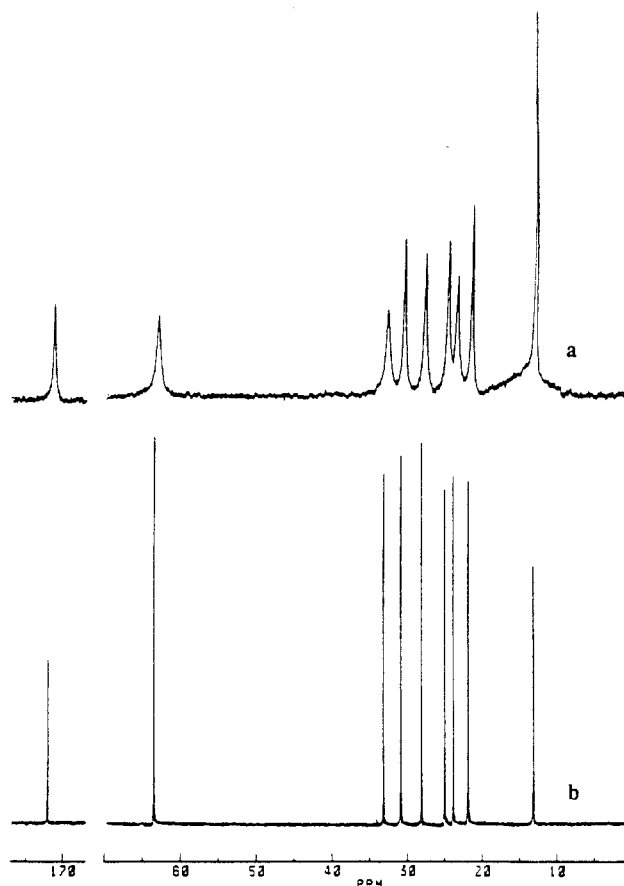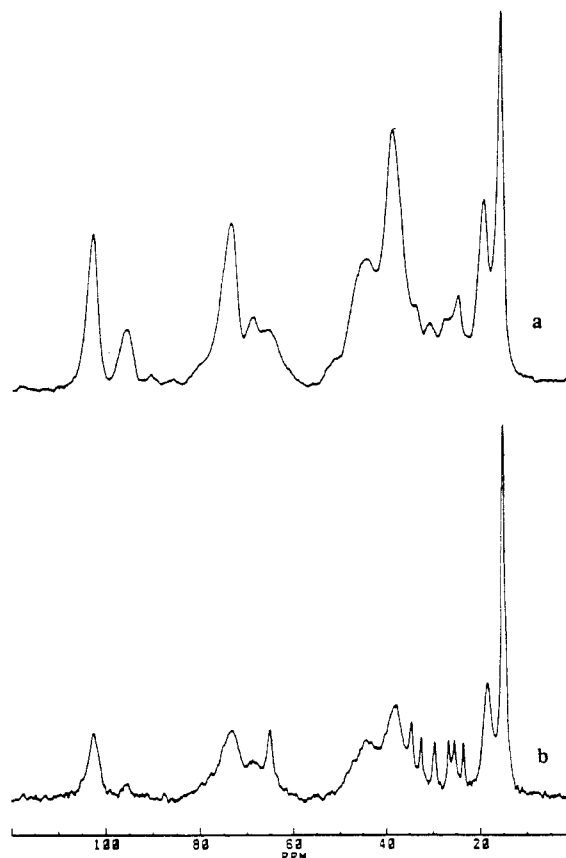|		PVB/32 phr DHA	
carbon	DHA/CDCl₃: solution	"solid" solution	CPMAS solid
A	13.2	12.8	
B	21.9	21.3	23.7
C	23.9	23.2	25.6
D	25.0	24.5	26.8
E	28.1	27.5	29.9
F	30.9	30.3	32.7
G	33.2	32.5	34.9
H	63.5	62.8	65.0
I	172.0	171.0	

Table II
DHA nT_1 Values (s) from CPMAS, "Solid" Solution, and Solution Experiments

			PVB/32 phr DHA	
			CPMAS solid	
carbon	DHA/CDCl₃: solution	"solid" solution	+25 °C	−20 °C
A	15.8	6.8		
B	8.6	1.8	1.6	0.7
C	2.8	0.4	0.9	0.6
D	4.6	1.1	1.0	0.5
E	3.5	1.0	1.0	0.6
F	6.7	1.5	1.6	0.7
G	2.8	0.5	2.0	
H	2.9	0.6	2.2	
I	10.2	5.6		

structure. Table II lists T_1 values (listed as n times T_1 where n is equal to the number of directly bonded protons) for DHA carbons obtained from the three techniques. Comparison of CPMAS T_1 values at +25 and −20 °C indicates that most of the DHA carbons reside on the high-temperature or fast motional sides of their T_1 minima at room temperature (indicated by a decrease in T_1 with a decrease in temperature[5]). Plasticizer molecules would be expected to exhibit high levels of mobility even in the polymer matrix. Figure 2 shows the solution spectra of DHA and the "solid" solution spectra of PVB/32 phr DHA. Figure 3 shows the CPMAS spectra of PVB/32 phr DHA at −20 and +25 °C. The carbonyl carbons and the methyl carbons do not appear in the CPMAS spectra. Also, the CPMAS spectrum of DHA is broadened at −20 °C (Figure 3) with little or no cross polarization of the carbon atoms surrounding the DHA ester group (34 and 65 ppm).

T_1 **Relaxation Experiments.** The motions of DHA methylene carbons (particularly H, G, and C) are inherently anisotropic, with solution T_1 values varying by as much as 3-fold. This anisotropy can be expected since motion in the megahertz region is likely to involve coupling between oscillatory combinations of rotational and translational motions.[13] Methylene carbons H and G (64 and 34 ppm, respectively) appear to be less mobile than the other methylene carbons as seen from the T_1 values of the DHA both in solution and in the PVB matrix. Thus, there seems to be a tendency for DHA molecules to exhibit more rigidity in the vicinity of ester groups, which would follow from the lower degree of translational and rotational freedom that would accompany the higher mass of a collective ester unit. Further inspection of T_1 values in Table I shows that DHA carbons are more mobile in the CDCl₃ solution (longer T_1 values), while mobility is

Figure 2. ¹³C NMR solution spectra obtained at 25 °C: (a) PVB/32 phr DHA; (b) DHA in CDCl₃.

Figure 3. ¹³C NMR CPMAS spectra of PVB/32 phr DHA: (a) obtained at −20 °C; (b) obtained at 25 °C.

decreased in the environments which are elucidated by both the "solid" solution and the solid CPMAS experi-

Table III
Carbon $T_{1\rho}$ (ms) Values for Selected DHA Carbons at -20 and +25 °C

carbon	$^{C}T_{1\rho}$ at -20 °C	$^{C}T_{1\rho}$ at 25 °C
B	2.9	11.0
C	2.1	6.8
E	1.9	7.6

Table IV
IRCP Parameters for DHA Carbons in PVB/32 phr DHA at 25 °C

carbon	X (fraction of rigid component)	$^{a}T_{CH}$ (μs)	$^{b}T_{CH}$ (μs)	$^{H}T_{1\rho}$ (ms)
B	0.06	26	4400	9.0
C	0.06	18	3900	8.6
D	0.05	47	3700	15
E	0.11	19	4000	14
F	0.23	55	5200	17
G	0.32	41	4400	5.7
H	0.27	50	3100	6.5

ments. Also, the T_1 values for methylene carbons from the "solid" solution experiments are similar to those obtained from the CPMAS experiments, with the exceptions of the 65, 34, and 25 ppm lines (carbons H, G, and C, respectively). The relative rigidity of carbons H and G remains the same in both the solution and "solid" solution experiments as seen from a proportional decrease in their T_1 values relative to other methylene carbons. However, carbons H and G exhibit anomalously different behavior in the CPMAS experiments where T_1 values are observed to increase.

Since cross polarization in the CPMAS experiment is more efficient for carbons with higher levels of motional rigidity, we would expect the carbons from our CPMAS experiments to be at least as mobile or less mobile than carbons observed under "solid" solution (scalar-decoupled) conditions.[4] Thus, the increase in CPMAS T_1 values for carbons H and G could be due to a different dipolar environment or a shift in the T_1 minima. However, no direct evidence for a shift in the T_1 minima for carbons G and H is observed since they do not cross polarize at -20 °C.

Note that the T_1 values exhibited by the methyl and carbonyl carbons are anomalously long in both the solution and "solid" solution experiments. The high mobility of the methyl carbon and the low concentration of protons in carbonyl environments also hinder the efficiency of cross polarization in a CPMAS experiment, which results in poor signal intensity. For these reasons, intramolecular motional trends among methyl, carbonyl, and methylene carbons are difficult to evaluate. This is probably due to the observation that methyl and carbonyl relaxation times are often dominated by spin rotation and chemical shift anisotropy, respectively, while methylenes are more strongly influenced by proton dipolar interactions.[5] However, intramolecular comparisons of methylene carbons in all three experiments can be accomplished since methylene relaxation rates are most strongly influenced by proton dipolar interactions.

$T_{1\rho}$ **Relaxation Experiments.** Figure 3 shows that, as the temperature is lowered in the CPMAS experiments, the resonance lines for carbons H and G are broadened, which indicates that the kilohertz regime mobilities of these carbons are approaching the high-power decoupling frequency of our experiment (57 kHz).[14] The other methylene carbons have a higher level of kilohertz regime mobility, but they are also broadened at -20 °C.

Despite the broadening, relative intensity measurements at -20 °C were taken at the same chemical shifts as those
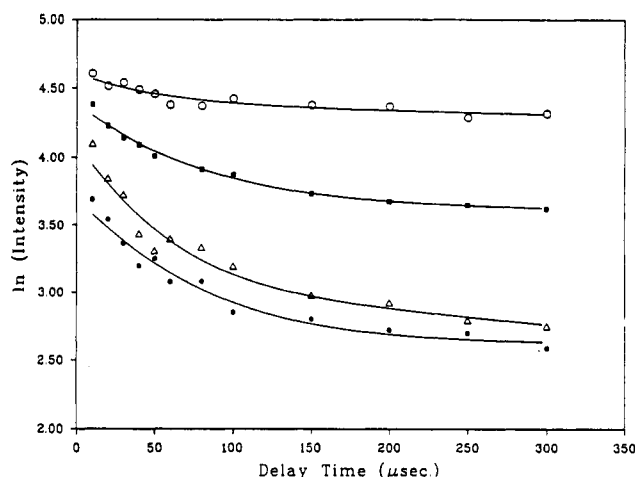

Figure 4. IRCP decay for ^{13}C DHA plasticizer resonances: ln (^{13}C intensity) vs delay time (μs); (O) carbon B, (■) carbon F, (△) carbon G, (●) carbon H. Solid lines are a theoretical fit to the data.

taken at 25 °C. Like the T_1 values, the $^{C}T_{1\rho}$ values of the B, C, and E methylenes reside on the fast motional sides of their minima at room temperature (Table III). On the other hand, carbons H and G at -20 °C must residue near their $T_{1\rho}$ minima as measured at 57 kHz. This indicates that carbons H and G are motionally restricted in the environments for which the CPMAS experiment is sensitive.

IRCP Relaxation Experiments. T_{CH} values taken from the best fit of inversion–recovery cross-polarization (IRCP) data are presented in Table IV along with $^{H}T_{1\rho}$ values. The best fit was achieved with a two-component model accounting for $^{H}T_{1\rho}$ relaxation, where $^{a}T_{CH}$ and $^{b}T_{CH}$ represent the cross-polarization rates for "rigid" and "mobile" components, respectively, and X represents the fraction of "rigid" material.[10] Figure 4 depicts the enhanced biexponential behavior of carbons F, G, and H, which parallels the observation that these carbons exhibit the highest rigid fractions (X) of all the DHA carbons.

Since the rate of cross polarization follows a $1/r^6$ proton spatial dependence, it is predominantly influenced by directly bonded protons,[15] with the process being most efficient in rigid systems.[8] The CP process is also a function of the second moment of the carbon–proton heteronuclear dipolar coupling distribution (M_2^{CH})[15] which itself is a function of dipolar reorientation rates, intermolecular packing tendencies, and structural features such as tacticity in vinyl polymers. Given that DHA is a structurally simple molecule, the biexponential cross-polarization behavior must be a result of a bimodal distribution in the near static portion of the motional spectrum. This phenomenon could be related to the natural tendency for carbons near the ester groups to be more rigid as seen from the T_1 experiments (intramolecular motional heterogeneity), or it could be related to the presence of intermolecular motional heterogeneity as a result of different motional environments (phase heterogeneity).[11,16]

The fact that IRCP experiments are able to resolve biexponential components while T_1 and $T_{1\rho}$ experiments display monoexponential behavior simply illustrates that the manifestation of motional heterogeneity depends on the frequency range of observation.[4,8] Thus, the biexponential IRCP behavior indicates that motional heterogeneity exists in the "near static" frequency regime[8] while the mega- and kilohertz regimes (as observed through T_1 and $T_{1\rho}$ experiments) appear to be more homogeneous.

Furthermore, it is also likely that the "character" of molecular motion may differ in the three frequency regimes.

Conclusion

In light of previous data, *inter*molecular motional heterogeneity as a result of DHA phase separation seems to be the likely reason for the biexponential IRCP behavior. In fact, the β/α anomeric ratio of this PVB sample is approximately 0.3 (ratio of peaks at 95 and 102 ppm). Previous studies by Schaefer et al.[4] suggest that 25% of the DHA plasticizer will be immobilized within a solidlike environment when PVB has this anomeric ratio. This is in good agreement with the rigid fraction ($X = 0.23$–0.32) as identified by IRCP for carbons near the ester position.

Given that the relative intramolecular mobilities of DHA carbons are more drastically reduced among α-carbons surrounding the ester groups in the solid state as compared to the solution state (from T_1 experiments), and given that all carbons exhibit spin system heterogeneity (from IRCP experiments), it is reasonable to suspect that DHA molecules are associating with PVB molecules in the solid state. An obvious means of association would involve hydrogen bonding between PVB hydroxyl groups and DHA carbonyl groups. Other secondary associations are possible, one of which may include the solvation of DHA hydrocarbon moieties by PVB butyral side chains. However, regardless of the exact nature of association, it is apparent that the morphologies of plasticized polymers like the PVB/DHA blend are complex but can nevertheless be evaluated with NMR techniques.

References and Notes

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