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Study of Polymer−Plasticizer Interaction by ^{13}C CP/MAS NMR Spectroscopy: Poly(vinyl chloride)−Bis(2-ethylhexyl) Phthalate System

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ABSTRACT: Solid state ^{13}C CP/MAS studies of poly(vinyl chloride) (PVC)−bis(2-ethylhexyl) phthalate (DOP) have been carried out to elucidate the dynamics of polymer−plasticizer interaction at the molecular level. ^{13}C NMR spectra, spin−lattice relaxation time $T_1(C)$ and spin−spin relaxation time $T_2(C)$ were obtained for various PVC−DOP samples. Line widths of $\rangle CH{-}Cl$ show a sharp increase due to the strong hydrogen-bonding interaction between the $\rangle C{=}O$ (ester) group of DOP and $\rangle CHCl$ of PVC with various concentrations of DOP. The spin−lattice relaxation time $T_1(C)$ also confirms the presence of a strong interaction due to hydrogen bonding. The less mobile intermediate phase is mostly affected by the presence of plasticizer. The spin−spin relaxation time $T_2(C)$ shows that DOP is a mixed type plasticizer showing the features of both molecular and structural type plasticization.

Introduction

The properties of a plasticized poly(vinyl chloride) (PVC) have long been known to be a strong function of the interaction between the polymer and the diluent (plasticizer). A number of techniques have been used for the measurement of PVC-plasticizer interaction thermodynamics.[1] These techniques include the heat and volume of mixing, the Flory−Huggins interaction parameter, virial coefficients, inverse GLC, and empirical compatibility measurements. Surprisingly, relatively little attention has been paid to the use of spectroscopic techniques such as Fourier transform IR and NMR, which are powerful techniques for probing the molecular level interactions in PVC−plasticizer systems. Tabb and Koenig were the first to study the bis(2-ethylhexyl) phthalate (DOP) plasticized PVC by FT-IR spectroscopy.[2] They showed that the $\rangle C{=}O$ frequency in DOP is affected by plasticization while the methylene and methyl modes are essentially unaffected. The plasticizer was shown to solvate the amorphous chain segments possibly by complex formation of the type $\rangle C{=}O\cdots H\overset{|}{\underset{|}{C}}{-}Cl$. The miscibility of various polyester−PVC blends has also been studied by FT-IR spectroscopy.[3] A shift was observed in the carbonyl stretching vibration band which was attributed to a hydrogen-bonding interaction between the carbonyl group of the polyester and the methine proton of the halogenated polymer.

There exist only a few attempts in the literature to use ^{13}C NMR techniques to probe the interaction between PVC and plasticizer at a molecular level. Attempts have been made to relate the NMR line widths to the PVC−plasticizer interaction parameter.[4] Novikov et al. used the second moment of the NMR absorption line ΔH_2^2 to obtain some idea of the interaction between PVC and plasticizer.[5] The mobility of the plasticizer molecule in PVC was determined by measuring the spin−spin relaxation time, T_2, of plasticized PVC samples by the spin-echo method.[6]

Solid state ^{13}C CP/MAS NMR is a powerful tool for the study of molecular level interactions between polymer and diluent. In this paper we probe the nature of the dynamics of interaction of a model plasticizer DOP with PVC using solid state NMR spectroscopy.

Table 1. Formulations of Plasticized PVC Used in the Study

	blend code				
	P1	P2	P3	P4	P5
PVC	100	100	100	100	100
DOP (phr)	0	5	20	40	50
DOP (wt %)	0	4.8	16.7	28.6	33.3

Experimental Section

Materials. PVC, K-60, used in the powder form was received from Indian Pectrochemicals Corp. Ltd., Vadodara, India. A concentrated solution of the polymer was prepared by dissolving PVC in tetrahydrofuran (THF). The polymer was precipitated by addition of methanol and dried in vacuo at 60 °C. Bis(2-ethylhexyl) phthalate obtained from S. D. Fine Chemical Pvt. Ltd., was redistilled under vacuum prior to use.

The plasticized PVC samples used for analysis were obtained as cast films. The resin and the plasticizer were dissolved in THF, and films were cast on a mercury surface at 25 °C. The films were dried in air for 24 h followed by heating to 100−110 °C for 1 h. The absence of THF was confirmed by the absence of an IR absorption band at 1065 cm^{-1}. The samples used in the present study are listed in Table 1.

Measurements. ^{13}C CP/MAS NMR spectra were measured with a Bruker MSL-300 NMR spectrometer (75.5 MHz) with a CP/MAS accessory at 25 °C. The sample (ca. 200 mg) was placed in a cylindrical ceramic rotor and spun at 3 kHz. The contact time and repetition time were 2 ms and 5 s, respectively. The spectral width and data points were 27 kHz and 8 K, respectively. The ^1H field strength was 2.0 mT for both the CP and decoupling processes. The number of accumulations was 160−200. ^{13}C chemical shifts were calibrated indirectly with reference to the higher field adamantane peak 29.5 ppm relative to tetramethylsilane ($(CH_3)_4Si$). The Hartmann−Hahn condition was matched using adamantane in each case. The experimental errors for the chemical shifts were within ±0.1 ppm for the broad peaks.

The spin−spin relaxation times (T_2) were obtained using the $90°{-}\tau{-}180°$ pulse sequence, the amplitude of the spin echo (occurring at 2τ) being measured as a function of pulse separation. Care was taken to ensure that there arose no contribution to the T_2 decays from self-diffusion in the field gradient caused by inhomogeneities in the static magnetic field. Again, plotting $A(t)/A(0)$ versus delay time τ, the slope $-1/T_2$ was calculated by using a least-squares method.

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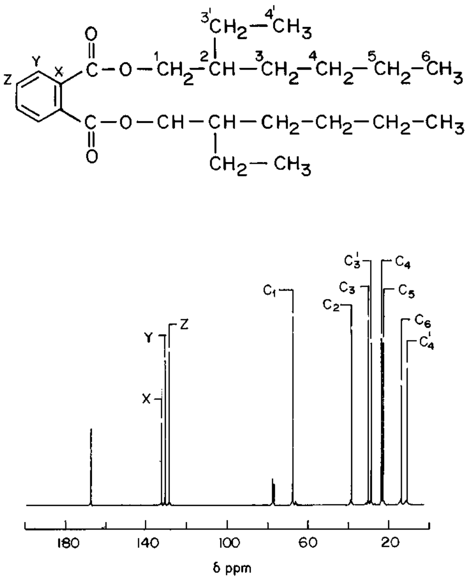

Figure 1. ^{13}C NMR spectrum of bis(2-ethylhexyl) phthalate in $CDCl_3$ at 25 °C.

Table 2. ^{13}C NMR Chemical Shifts of DOP, P1, P2, P3, P4, and P5 Samples[a]

	^{13}C NMR chemical shifts, ppm					
^{13}C atoms	DOP	P1	P2	P3	P4	P5
C=O (ester)	167.2		168.9	167.2	166.8	166.8
aromatic	128.4		130.4	132.0	130.0	130.0
	130.4					
	132.2					
C1	67.6	67.5	67.4			67.2
C2	38.5				38.6	38.5
C3′	28.6		29.3	29.2	28.9	28.8
C5	22.6			23.0	23.0	22.9
C3	30.0				30.0	30.0
C4	23.5					
C6	13.6		14.4	14.0	13.9	13.8
C4′	10.6		11.4	11.0	10.8	10.7
⟩CHCl of PVC		56.7	56.8	56.8	57.1	57.8
⟩CH_2 of PVC		46.2	46.2	45.7	45.7	45.5

[a] Chemical shifts of all carbons of DOP and plasticized PVC are assigned from refs 7–10.

DSC measurements were performed on a Perkin-Elmer thermal analyzer model DSC-7 in a nitrogen atmosphere. T_g's of the samples were taken as the midpoint of the step in the scan, run at a heating rate of 5 °C min^{-1}.

The infrared spectra were obtained on a 1600 PC Perkin-Elmer Fourier transform IR spectrometer. Each spectrum was recorded in double precession at a resolution of 4 cm^{-1} with a total of 10 scans.

Results and Discussion

Structure of Bis(2-ethylhexyl) Phthalate (DOP). The ^{13}C NMR spectrum of DOP in $CDCl_3$ at 25 °C is shown in Figure 1. The chemical shift assignments were based on the literature data for *n*-alkanes, as determined by Van der Hart,[7] and are shown in Table 2.

Structure of P1. The ^{13}C CP/MAS spectrum of solid sample P1 is shown in Figure 2a. The solution spectrum of PVC in nitrobenzene-d_5 is shown in Figure 2b. The chemical shifts were assigned on the basis of earlier literature[8,9] and are shown in Table 2. The peaks appearing at 57.9, 56.9, and 55.9 ppm in the solution spectra (Figure 2b) are assigned to syndiotactic, heterotactic, and isotactic placement of ⟩CHCl groups.[10] Similarly, the peaks due to the ⟩CH_2 groups of PVC appeared at 45.8 and 46.8 ppm, for which no assignment as to sequence configuration could be made.[10] The solid state spectrum of the same sample (Figure 2a) shows only two broad peaks at 56.7 and 46.2 ppm corresponding to the ⟩CHCl and ⟩CH_2 groups, respectively. Apparently, in the solid state, the tacticities are not resolved.

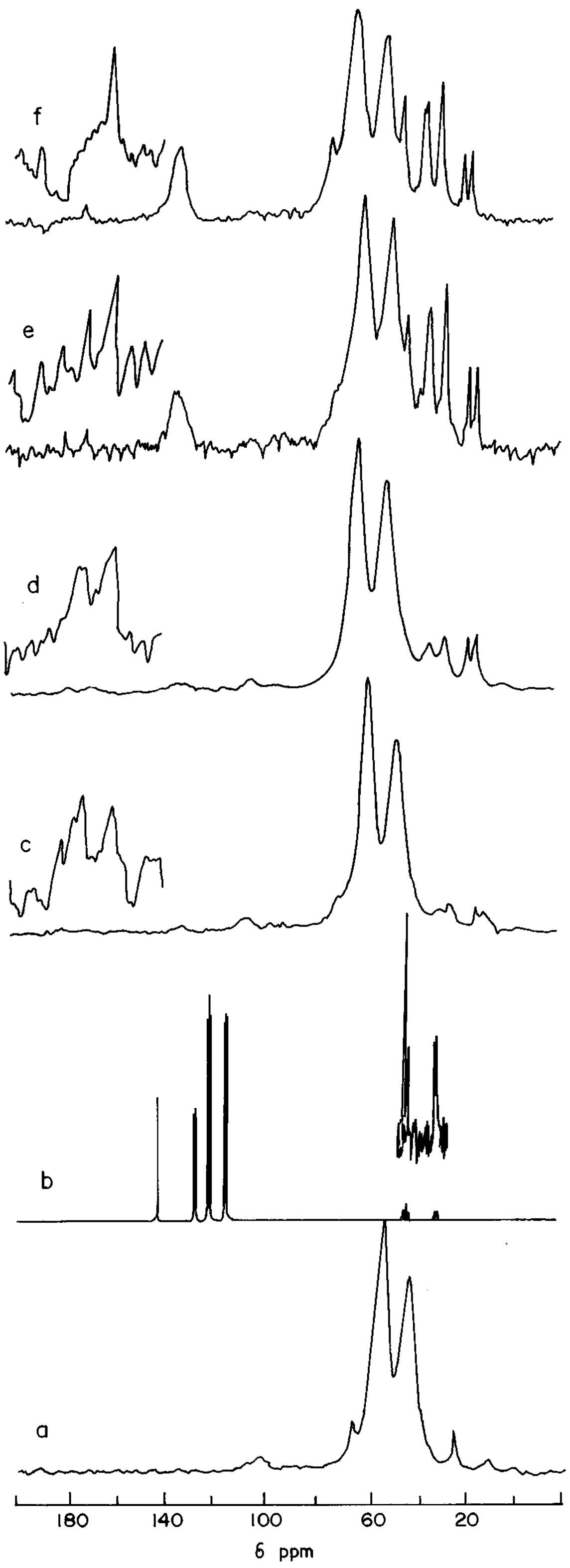

Figure 2. ^{13}C CP/MAS NMR spectra of (a) PVC (P1), (b) solution spectra of PVC in nitrobenzene-d_5 at 25 °C, and PVC–DOP samples with (c) 5 phr (P2), (d) 20 phr (P3), (e) 40 phr (P4), and (f) 50 phr (P5).

^{13}C CP/MAS of Plasticized PVC. ^{13}C CP/MAS NMR spectra of plasticized PVC samples (P2, P3, P4, and P5) are shown in Figure 2c–f. The amplified and expanded spectra of the carbonyl signal in all spectra (P2, P3, P4, and P5) are also given in Figure 2c−f. The assignments of chemical shifts were given in Table 2. To observe whether any overlapping of side bands with chemical shift signals in ^{13}C CP/MAS spectrum occurred, two spectra of sample P3 were obtained at different rates of magic angle spinning (i.e. 3.4 and 4.0 kHz). It was confirmed that in all cases no overlapping of side bands with chemical shift signals occurred.

A comparison of Figure 1 with Figure 2a−f shows that the chemical shifts of plasticized PVC (Figure 2c−f) are similar except that the $\rangle$C=O (ester) of DOP moves downfield from 167.2 to 168.9 ppm as 5 phr of DOP is added to PVC (Figure 2c). This is due to the entrapment of DOP in the PVC matrix and its consequent loss of mobility. Upon a further increase of the DOP content in PVC (samples P3, P4, and P5), the chemical shift of the $\rangle$C=O (ester) moves upfield (Figure 2d−f) from 168.9 to 166.8 ppm. The upfield chemical shift of the ester group implies that the ^{13}C shielding component changes monotonously to upfield. The hydrogen-bonding interaction between $\rangle$CHCl of PVC and the $\rangle$C=O group of DOP ($\mathrm{Cl{-}\overset{|}{\underset{|}{C}}H\cdots O{=}C\langle}$) which appears in the ^{13}C shielding component dominates the relative ^{13}C chemical shift.[11] The sharpness and intensity of this peak increased due to further addition of DOP to PVC. The increased intensity of the $\rangle$CH−Cl group may occur due to CP dynamics. At ambient temperature, CP techniques for generating ^{13}C signals fall victim to molecular motion in two ways. Not only are the lines broadened, but also the generation of the ^{13}C signal is rendered very different because $T_1^{\mathrm{H}} \approx T_{\mathrm{CH}}^{\mathrm{SL}}$ (SL spin-locked), where the latter quantity is the time constant characterizing the equilibrium of the carbons and protons in the CP experiments.[12] Therefore, signals are distorted since the ^{13}C spin-locked carbons do not have time to equilibrate with spin-locked protons.[13] Longer $T_{1\rho}^{\mathrm{H}}$'s allow stronger ^{13}C signals to be generated by CP. The sharpness and intensity of the $\rangle$CH−Cl peak of PVC increase due to the increase of $T_{1\rho}^{\mathrm{H}}$'s, which are shown in Figure 2d−f. For mobile solutions, $T_{1\rho} = T_1 = T_2$ under most circumstances, though not necessarily when chemical exchange occurs. For viscous solutions and solids $T_{1\rho}$ differs substantially from both T_1 and T_2 and depends on the spectral density governed by $\omega_1 = \tau_1\beta_1$ (which is of the order of tens of kilohertz). This is attributed to the subsequent increase of sharpness and intensity of the $\rangle$CH−Cl peak in Figure 2c−f. $T_{1\rho}$ is the rotating frame relaxation time for a proton which is sensitive to motions with correlation frequencies, ν_{c} in the kilohertz range. The spin−lattice relaxation times T_1 respond to much more rapid motions in the megahertz region, whereas spin−spin relaxation time T_2 is sensitive to the low-frequency motion. The line width of $\rangle$C=O broadens in P2 as compared to DOP and then becomes narrower as the proportion of DOP is enhanced (samples P3−P5).

The aromatic carbon of DOP appeared as a broad peak at 130 ppm for samples P2−P5. Some peaks due to DOP were not observed in the plasticized PVC below 20 phr concentration.

A comparison of the chemical shifts of the carbon atom located in the C3 position of free DOP and plasticized PVC indicates that they appear in the same region, viz. at 30 ppm. This peak did not appear in P2 and P3, indicating that it overlaps with the C3′ atom (at 28.9 ppm) due to the restricted mobility of C3, the $\mathrm{CH_2}$ group. The peak at 28.9 ppm of P4 (Figure 2e) splits into a doublet where $\mathrm{CH_2}$ appears at 30.0 ppm. Similarly, in P5, this doublet is very prominent. This implies that C3′ and C3 groups of DOP are able to split the amorphous region of PVC resin. The C1, C2, C4, and C5 atoms of DOP in PVC resin appear unchanged. However, the C6 and C4′ atoms of DOP in PVC show a gradual upfield shift from 14.4 to 13.8 ppm and 11.4 to 10.7 ppm, respectively, due to an increase in the shielding effect.

The chemical shift of the $\rangle$CH−Cl group of PVC moves downfield, i.e. from 56.7 to 57.8 ppm, as the concentration of DOP is increased. This downfield shift of $\rangle$CH−Cl can be attributed to the hydrogen bonding between $\mathrm{Cl{-}\overset{|}{\underset{|}{C}}H\cdots O{=}C\langle}$. A similar downfield chemical shift of NH in the ^{1}H NMR signal in the complex between uracil and 2,6-diaminopyridine has been observed.[14] The $\rangle\mathrm{CH_2}$ peak of PVC moved upfield from 46.0 to 45.5 ppm as the concentration of DOP increased. Apparently, the adjacent $\rangle\mathrm{CH_2}$ group is also affected due to the strong hydrogen-bonding interaction between $\mathrm{\rangle C{=}O\cdots H\overset{|}{\underset{|}{C}}{-}Cl}$ and an upfield shift is obtained due to a gradual increase of the shielding effect in samples P3, P4, and P5 (Figure 2d−f). Again, the noncrystalline component of linear polyethylene is, on the average, chemically shifted upfield 2 ppm from the crystalline resonance, possibly because the noncrystalline carbons can participate in both gauche and trans conformations whereas the crystalline carbons are confined to the trans conformations.[15,16] In general, the conformation of the polymer changes due to the solvent interaction. Here, the conformation of PVC changes due to the hydrogen-bonding interaction between PVC and DOP, where DOP solvates the PVC.

The line splitting of the methylene carbon resonance was not observed in samples P1−P5. The line shape and the position depend on the tacticity of each sample. Thus, when the line width is larger than the splitting, the line shape of the methylene carbon resonance is expected to be symmetric for atactic and asymmetric for isotactic and syndiotactic with a steeper slope in the upfield side and downfield side. The $\rangle\mathrm{CH_2}$ group became steeper and steeper in slope in both sides from P1 to P5 as shown in Figure 2a,c−f which is attributed to the participation of the syndiotactic configuration of PVC.

The line width plot of the $\rangle$CHCl carbon in hertz versus the DOP/PVC ratio is shown in Figure 3a. The ^{13}C line widths have been measured in organic solids by means of high-power proton decoupling and magic angle sample spinning. VanderHart et al.[17] have elucidated the importance of the ^{13}C line-broadening mechanism in solid polymers. They have suggested that ^{13}C line widths, usually expressed in hertz, show a linear dependence on magnetic field B_0 which corresponds to equivalent resolution at different static fields. The ^{13}C line width broadening occurs in solid polymers due to several factors such as insufficient proton decoupling fields, off-resonance decoupling, imperfections in magic angle spinning, and motional modulation of both the carbon−proton dipolar coupling and carbon shift anisotropy. In the present study, the line broadening arising out of the above factors was eliminated by combination of cross polarization (CP), the actual rotation of the sample at the magic angle of 54.7° (MAS), and dipolar decoupling (DD) of the ^{1}H nuclei from the ^{13}C nucleus.[18] Thus, the broadening observed during the present study can be attributed only to strong interaction occurring at the $\rangle$CHCl carbon. The plot

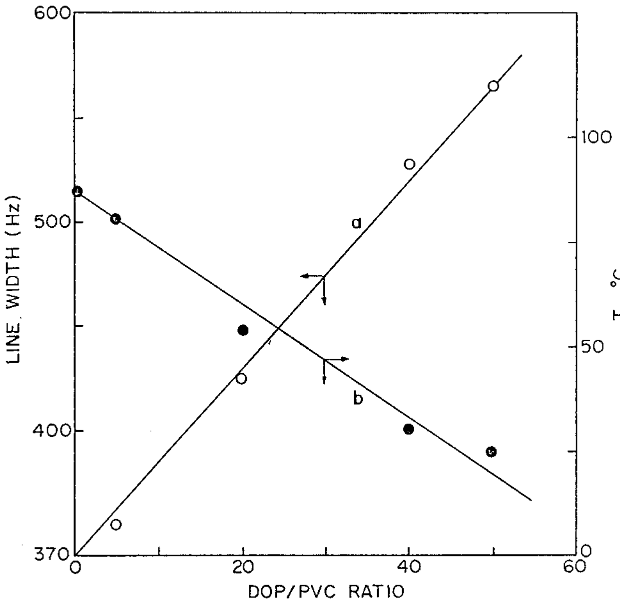

Figure 3. (a) Effect of hydrogen bonding on line width of the ⟩CHCl carbon of PVC. (b) Glass transition temperature (T_g) versus plasticizer amount.

(Figure 3a) shows an essentially linear relationship, indicating the degree of hydrogen-bonding interaction between the ⟩C=O (ester) group of DOP with ⟩CHCl of PVC increases with the DOP/PVC ratio. Terao et al.[19] have suggested that intermolecular hydrogen bonds have caused the line width of the resonance to broaden to some extent. Below the glass transition temperature, the conformational and packing disorder lead to relatively broad lines for amorphous samples. Line widths between 300 and 500 Hz (Figure 3) are typical at 75 MHz (^{13}C). Similar line widths between 100 and 500 Hz have been observed[18] which are typical at 75 MHz (^{13}C). The glass transition temperature of plasticized PVC also shows a steady decrease as the proportion of DOP is increased in samples P2–P5. FT-IR data are also consistent with these observations. The ⟩C=O frequency of DOP is affected by plasticization (1730–1725 cm^{-1}). There is a decrease in the frequency of the C–Cl stretching mode which shows a frequency shift from 695 to 692 cm^{-1}, respectively, as the plasticizer content is increased from P2 to P5. These shifts in frequencies reflect an increase in a more stable conformation in amorphous regions.

Dynamics of Plasticized PVC Polymers. The physical properties of PVC are profoundly modified by plasticization. This in turn depends on the molecular mobility of DOP in plasticized PVC. T_1 (spin–lattice relaxation time) measurements reflect the fast motions in the megahertz region while $T_{1\rho}$ (spin–lattice relaxation in the rotating frame) is sensitive to the kilohertz region. The spin–spin relaxation time T_2 is much more sensitive to the low-frequency motion. We therefore undertook a study of T_1(C) and T_2(C) measurements of plasticized PVC in the solid state with varying contents of DOP.

Figure 4a,b shows the results of ^{13}C spin–lattice relaxation time measurements by the T1CP method.[20] Actually, the T1CP method is best suited for measurements of two-phase systems though it is used in a solid sample. The T1CP method provides a set of relaxation spectra of the gelled material in which the unwanted signal is suppressed.[20] It has also been verified that the T1CP method yielded measured relaxation times which agreed with those obtained by the T1IR (inversion-recovery) method. So the T1CP method was adopted by us to measure T_1(C). The recovery of magnetization does not obey a single exponential but two overlapping exponentials. Conventional poly(vinyl chloride) is an essentially amorphous material which possesses sufficient paracrystallinity to be detectable by X-ray diffraction.[21] Thus PVC could be considered as a heterogeneous blend of three phases, namely, a paracrystalline, which remains essentially rigid (R), a less mobile, intermediate phase (I), and a mobile phase (M).

The ability to detect a second relaxation component, assuming a sufficiently different T_1, is limited by the signal/noise ratio. In these experiments a second component with an intermediate T_1 of 2–8 s might go undetected if it were present at a level of less than 2–8%. Nevertheless at least 92% of the ⟩CHCl– groups appear to be concentrated in one phase, which is most probably the amorphous phase. The values of T_1(C) for P1–P5 samples at 56.08 ppm obtained from the second exponential are 46.77, 58.98, 65.32, 63.68, ad 44.32 s, respectively. The rise of T_1(C) values from P1 to P3 is due to the increasing mobility of the ⟩CHCl– groups due to the increasing DOP concentration in the PVC matrix. A similar observation has been reported by Kelusky et al.[22] in ethylene–1-octene copolymer. They have shown that the transport of magnetization through spin diffusion for ^{13}C nuclei at natural abundance is very slow as a result of the high degree of isotropic dilution, the T_1(C) is determined by high-frequency components of the local molecular dynamics along the side chain of an ethylene–1-octene copolymer. The T_1(C) maximum value at the P3 sample is 65.32 s, which suggests a stronger interaction between the ⟩CHCl group of the PVC resin and the ⟩C=O group of the DOP molecule. Again, the increased molecular mobility in the amorphous substance partially averages out the dipole–dipole interaction necessary for the transfer of magnetization from ^{1}H to ^{13}C and leads to a slower transfer rate of $1/T_{CH}$ for the mobile (amorphous) components.[18] The T_1(C) values of P4 and P5 decrease monotonously with a further increase of DOP concentration. These results are attributed to a lesser interaction between the PVC matrix and DOP as compared to the DOP–DOP and PVC–PVC intermolecular interaction.

The T_1(C) values of the ⟩CH$_2$ group of the PVC backbone chain obtained from second exponentials are 63.94, 67.87, 62.73, 69.30, and 48.93 s, respectively. The T_1(C) value of the CH$_2$ group increases from 63.94 to 67.86 s due to its mobile nature. The T_1 value of P3 is 62.73 s, which is indicative of a decrease in mobility due to the proximity of the ⟩CHCl carbon in the main chain. It is also apparent from this study that there is a strong interaction at the molecular level in the PVC sample at P3.[22] The T_1(C) value of P4 increases from 62.73 to 69.30 s, which is attributed to the mobility of the ⟩CH$_2$ group. There is a decrease in the T_1(C) value of sample P5 (48.93 s). The reason for this decrease is not apparent at the moment.

The addition of plasticizer produces dramatic effects on the relaxation behavior of the I and M phases. The I phase shows a greater dependence on intermolecular hydrogen bonding in the presence of plasticizer than the M phase. The mobile phase (M) is not seen by the CP technique. The R phase is almost totally insensitive to the CP technique. This behavior demonstrates the heterogeneous nature of the system and points to the presence of a strong hydrogen-bonding interaction between the I phase of PVC and DOP.

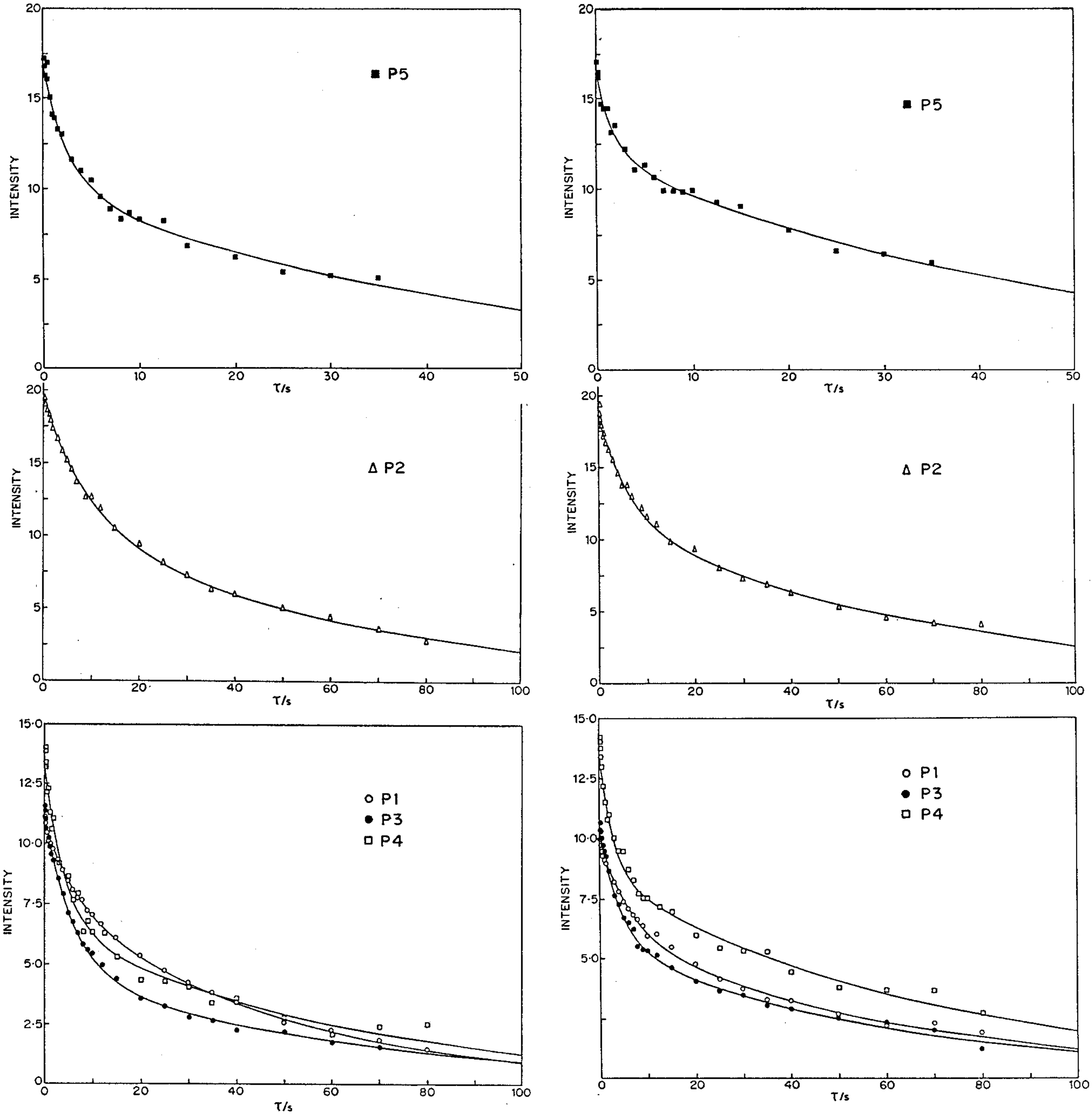

Figure 4. ^{13}C plots of PVC by the T1CP method at room temperature at (a) 56.0 ppm and (b) at 46.0 ppm.

The dimensionless value $T_2/T_2°$ was selected to compare the interaction between polymer and plasticizer. T_2 is the spin−spin relaxation time of the plasticizer inside the polymer whereas $T_2°$ is that of pure plasticizer. A plot of dimensionless value $T_2/T_2°$ versus DOP concentration is shown in Figure 5. This curve is best understood in terms of two parts, namely, AB and BC. Up to 20 phr DOP in PVC, the mobility of plasticizer molecules quickly decreases compared with that of pure DOP, indicating strong interaction of the plasticizer with the macromolecules. The plasticizer molecules cannot penetrate any further into the spaces between molecules once point B is reached. In the range of DOP concentration 20−50 phr (BC) the mobility of plasticizer molecules rapidly increases causing effective plasticization of PVC. Any attempt to increase the DOP concentration above 50 phr will progressively lead to phase separation, leading to coalescing of DOP droplets on the surface of polymer. The range AB signifies intraspherulitic or molecular plasticization where BC indicates interpherulitic or structural plasticization.[6]

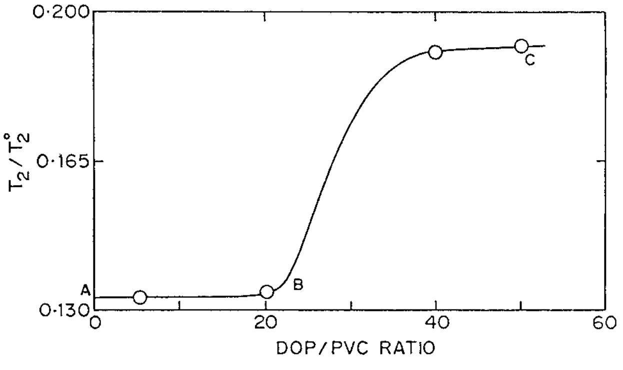

Figure 5. Curve of the concentration dependence of $T_2/T_2°$: (AB) molecular and (BC) structural plasticization.

Conclusion

^{13}C CP/MAS NMR spectra of plasticized PVC have been studied in terms of the chemical shift displacement, line width, and $T_1(C)$ and $T_2(C)$ measurements. The chemical shift displacement and line width of the $\rangle C{=}O$ group of DOP and the $\rangle CHCl$ group of the P3 sample confirm that plasticizer solvates more in the amorphous chain segments by hydrogen-bonded interaction of the type $\rangle C{=}O\cdots H\overset{|}{\underset{|}{C}}{-}Cl$. The spin–lattice relaxation time ($T_1(C)$) of the $\rangle CHCl$ and $\rangle CH_2$ groups in sample P3 is more affected by the hydrogen-bonded interaction compared to that of P1, P2, P4, and P5 samples. The behavior of PVC is best understood in terms of a heterogeneous blend of three phases, namely, the rigid (R), intermediate (I), and mobile (M) phases. The I phase is more affected by the presence of the plasticizer whereas the mobile phase is not detectable by the CP technique and the rigid phase remains totally insensitive to the CP technique. The spin–spin relaxation time ($T_2(C)$) of the $\rangle C{=}O$ group in DOP is also influenced in the P3 sample compared to other samples. $T_2(C)$ is affected by both short-range and long-range frequency motion. The plot $T_2/T_2°$ versus DOP concentration suggests that DOP is a mixed type plasticizer, namely, molecular and structural.

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References and Notes

(1) Foss, P. H.; Shaw, M. T. *J. Vinyl Technol.* **1985**, *7*, 160.
(2) Tabb, D. L.; Koenig, J. L. *Macromolecules* **1975**, *8*, 929.
(3) Cousin, P.; Prud'homme, R. E. In *Multicomponent Polymer Materials*; Paul, D. R., Sperling, L. H., Eds.; Advances in Chemistry Series No. 211; American Chemical Society: Washington, DC, 1986; p 87.
(4) Tager, A. A.; Yushkova, S. M.; Bessonov, Y. S.; Guzeyev, V. V.; Rafikov, M. N.; Yezhov, V. S. *Vysokomol. Soedin.* **1979**, *A21*, 1051; *Chem. Abstr.* **1979**, *91*, 21688z.
(5) Novikov, N. A.; Shashkov, A. S.; Galil Ogly, F. A. *Vysokomol Soedin.* **1970**, *B12*, 323; *Chem. Abstr.* **1970**, *73*, 46379r.
(6) Chenborisova, L. Ya.; Ionkin, V. S.; Maklakov, A. I.; Voskresenskii, V. A. *Vysokomol. Soedin.* **1966**, *8*, 1810; *Chem. Abstr.* **1966**, *64*, 9891b.
(7) VanderHart, D. L. *J. Magn. Reson.* **1981**, *44*, 117.
(8) Inoue, Y.; Ando, I.; Nishioka, A. *Polym. J.* **1972**, *3*, 246.
(9) Wilkes, C. E. *Macromolecules* **1971**, *4*, 443.
(10) Carman, C. J.; Tarpley, A. R.; Goldstein, J. H. *J. Am. Chem. Soc.* **1971**, *93*, 2864.
(11) Ando, S.; Ando, I.; Shoji, A.; Ozaki, T. *J. Am. Chem. Soc.* **1988**, *110*, 3380.
(12) Demco, D. E.; Tegenfeldt, J.; Waugh, J. S. *Phys. Rev.* **1975**, *B11*, 4133.
(13) Look, D. C.; Lowe, I. J. *J. Chem. Phys.* **1966**, *44*, 2995.
(14) Brienne, M. J.; Gabard, J.; Lehn, J. M.; Stibor, I. *J. Chem. Soc., Chem. Commun.* **1989**, 1868.
(15) Earl, W. L.; VanderHart, D. L. *Macromolecules* **1979**, *12*, 762.
(16) Fyfe, C. A.; Lyerla, J. R.; Volksen, W.; Yannoni, C. S. *Macromolecules* **1979**, *12*, 757.
(17) VanderHart, D. L.; Earl, W. L.; Garroway, A. N. *J. Magn. Reson.* **1981**, *44*, 361.
(18) Voelkel, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1468.
(19) Terao, T.; Maeda, S.; Saika, A. *Macromolecules* **1983**, *16*, 1535.
(20) Torchia, D. A. *J. Magn. Reson.* **1978**, *30*, 613.
(21) Brunner, A. J. *J. Polym. Sci., Part B* **1972**, 379.
(22) McFaddin, D. C.; Russel, K. L.; Kelusky, E. C. *Polym. Commun.* **1986**, *27*, 204.

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