Effect of the processing temperature on the interaction between plasticizer and poly(vinyl chloride) as studied by solid state n.m.r. spectroscopy

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(Received 22 April 1992; revised 18 September 1992)

Solid state n.m.r. was used to investigate the effect of processing temperature on the interaction between poly(vinyl chloride) and diisodecyl phthalate plasticizer. Despite significant differences in the mechanical properties no clear trends emerged in the ^1H n.m.r. relaxation times or in the high resolution ^{13}C n.m.r. spectra.

INTRODUCTION

Plasticizers find extensive use with poly(vinyl chloride) (PVC) to convert rigid resins into workable compounds which exhibit a wide variety of properties depending on both the type and concentration of plasticizer used. Effective plasticization of PVC is of great importance to manufacturers not only to produce materials of the required flexibility but also to minimize phenomena such as plasticizer extraction, exudation and migration. Many researchers have studied the process of plasticization of PVC in varying detail[1] using theories of differing complexity. More recently[2] studies have attempted to relate the compatibility of plasticizers with PVC using interaction parameters and a knowledge of the molecular structure of the plasticizer. The precise nature of the factors governing plasticization remains an active area of study.

A wide range of plasticizers are used in PVC formulations, with the majority of those in use based on the esters of phthalic, adipic, trimellitic, sebacic and phosphoric acids. Equally, a number of plasticizer esters exist for each acid type, based on alcohols in the C_4–C_{13} range. The precise choice of plasticizer depends on the exact requirements of the final product and also on the processing conditions. Such requirements include viscosity, volatility and speed of gelation with PVC of the plasticizer as well as the product requirements such as high and low temperature performance, flame retardancy and also cost.

Recent advances in PVC processing technology have extended the range of applications. With these developments, new resins and new plasticizers are also being marketed. In order to gain a greater understanding of these applications we have recently been studying the fundamental action of plasticizers in terms of their precise effect on the PVC chains. The principal benefits from such a study would be:

1. a detailed molecular explanation for the observed changes in properties of the plasticized resin which occur when changes in plasticizer are made;
2. an explanation for the success of some plasticizers and failure of others; and
3. an indication of the events which take place when a plasticizer is heated with PVC in the processing operation.

The aim of this work in particular was to understand the differences in the distribution of plasticizer molecules in a PVC matrix when the PVC plastisol was subjected to different processing temperatures. PVC plastisols are a suspension of emulsion PVC and other formulation ingredients in plasticizer.

Solid state n.m.r. is a versatile method for investigating the effect of processing temperature on the nature of PVC and plasticizer mixtures[3-7]. Use can be made of a combination of ^1H nuclear spin relaxation times[8] and high resolution ^{13}C n.m.r. spectroscopy[9] to determine the phases present, their chemical composition and relative amounts, while the ^{13}C chemical shifts give information about any possible interaction between the PVC matrix and plasticizer molecules. Phase analysis by nuclear spin relaxation time measurements rests upon the assumption that each phase present will give a unique relaxation time which can be found by a multiexponential fit of a relaxation decay curve. On the whole this assumption is a valid one, mainly complicated by the presence of spin diffusion or an accidental equivalence of relaxation times. Spin diffusion, that is the transport of nuclear spin magnetization, acts as an averaging process causing closely adjacent phases with different intrinsic relaxation times to give a common averaged value[10]. Previous work has established that plasticized PVC yields a number of distinct ^1H relaxation times

depending on the precise conditions and the type of relaxation time studied[11]. In particular the presence of a long T_2 component in the free induction decay (f.i.d.) has been correlated with the plasticizer content, though no direct evidence in the form of the ^{13}C n.m.r. spectrum of this phase has been presented to confirm this[4-7].

More sophisticated experiments, of the Goldman–Shen type[12], based on the monitoring of spin diffusion across a prepared magnetization gradient indicate that the plasticizer phase identified by the long T_2 component and PVC matrix, short T_2 component, are heterogeneous on the 50 Å scale[3,10]. This interpretation appears to be at variance with commonly accepted models for PVC and plasticizer which involve plasticizer molecules distributed throughout the PVC matrix and not clustered into specific domains. However, should the long T_2 phase not be pure plasticizer but contain PVC we can continue to maintain the idea of large scale heterogeneity but now in terms of regions of plasticized and, at the extreme, unplasticized PVC. This uncertainty highlights the potential problems of testing the accepted models for PVC–plasticizer interactions by solid state n.m.r. and demonstrates the importance of characterizing the chemical species giving rise to a particular ^1H nuclear spin relaxation time. The two objectives of the work described below were as follows. First, to test the picture of the PVC–plasticizer interaction found by n.m.r. against models proposed in the literature and secondly, to see whether n.m.r. could shed light on the morphological changes which take place when the processing is carried out at different temperatures. To this end the ^1H nuclear spin relaxation times, T_1, $T_{1\rho}$ and T_2 were measured for four PVC–plasticizer samples corresponding to an unprocessed sample, processed at 130, 170 and 200°C. In addition a sample of unprocessed PVC polymer, in the absence of plasticizer, was also studied. For each ^1H relaxation time where more than one component was observed a selective high resolution ^{13}C n.m.r. spectrum was obtained to identify the composition of the corresponding phase. Goldman–Shen spin diffusion experiments were carried out on the samples processed at 130 and 200°C. As noted above the ^{13}C chemical shifts can give information about any potential interaction between the plasticizer molecule and the PVC; this can then be compared with data from vibrational spectroscopic work on similar systems[13-16].

EXPERIMENTAL

Sample preparation

Plastisols based on the EVC 'Corvic' emulsion resin P72/754 and ICI Hexaplas diisodecyl phthalate (DIDP) were spread onto release paper and processed in a Werner-Mathis oven at 130, 170 and 200°C. Physical tests, tensile strength evaluation, elongation measurements and d.s.c. all suggest the achievement of maximum physical properties at a processing temperature of 170°C. DIDP is a mixture of isomers of the ester of phthalic anhydride with iso-decanol. A plasticizer content of 80 parts per 100 of PVC resin was used, equivalent to 35% w/w.

N.m.r. measurements

Solid state n.m.r. spectra and relaxation times were obtained on a Bruker MSL 200 NMR spectrometer operating at 200.13 MHz for ^1H and 50.32 MHz for ^{13}C.

Prior to the ^1H relaxation time experiments the radiofrequency pulse amplitudes and phase orthogonality were optimized using a standard multiple pulse tune up procedure[17]. The ^1H $\pi/2$ pulse was set to be 1.9 μs giving a spin-locking field of 102.6 kHz in the $T_{1\rho}$ experiment. T_1 was measured using the saturation recovery method in a single point acquisition manner, including 20 baseline points to estimate the error arising from the experimental signal-to-noise. A similar, single point acquisition method was used to collect the $T_{1\rho}$ relaxation decay curve, though in this case 40 points were used to define the baseline and estimate the experimental error as it was found that the fitting process was more sensitive because of the greater number of exponentials required to fit the data. Free induction decays, used to find T_2, were acquired following a solid echo with an interpulse spacing of 8 μs and a dwell time of 0.2 μs. Again the last 40 points in the relaxation decay curve were used to estimate the experimental error. Loss of magnetization from a highly mobile species because of it not rephasing to form an echo will be negligible given the short echo delay. Non-linear least squares fitting based on the Levenberg–Marquardt algorithm was used to extract the ^1H relaxation times from the appropriate decay curve[18].

High resolution ^{13}C n.m.r. spectra were obtained using magic angle spinning (MAS) and high power proton decoupling. In certain experiments aimed at selecting particular phases cross-polarization (CP) was also employed. Phase selection based on $T_{1\rho}$ differences was achieved by the delayed contact pulse experiment where the contact pulse on the ^{13}C spins is delayed until all the magnetization associated with the shorter $T_{1\rho}$ component has decayed away; in this way only the phase with the long $T_{1\rho}$ will be seen. Variations in T_2 were exploited in three ways: first by delaying decoupling in a ^{13}C single pulse excitation for a time of the order of five times the shorter T_2; secondly using a similar dipolar dephasing period in a CP experiment; and thirdly by delaying the spin-locking pulse in a ^{13}C CP experiment for a similar time. In all three cases only the phase giving the long T_2 will be seen.

RESULTS AND DISCUSSION

^1H n.m.r. results

Plasticized PVC can be expected to be heterogeneous consisting of regions of plasticized and unplasticized polymer. Within each region there may well be a degree of heterogeneity arising from the local distribution of the plasticizer molecules. Of especial interest, given the high plasticizer content of the samples studied, is whether the plasticizer has been able to penetrate the more ordered regions of the polymer. An indication of heterogeneity, albeit motional, within the plasticized polymer is provided by the ^1H f.i.d. which has components decaying with different time constants. At this stage it is not possible to say whether this range in molecular motions is a consequence of phase heterogeneity. The f.i.d. of pure PVC on the other hand is well described by a single Gaussian function with a short T_2 despite being largely an amorphous material. This is a reflection of the rigid and brittle nature of the matrix in the absence of plasticizer which explains the fundamental need for PVC to be plasticized. Accurate fitting of the ^1H f.i.d. of PVC plasticized with DIDP proved to be difficult because when the data have a low
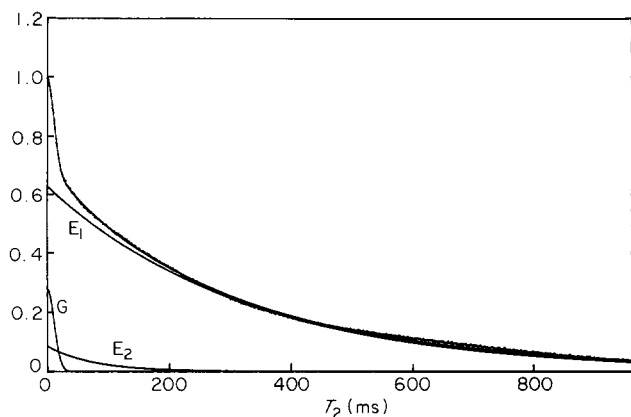
Figure 1 Solid echo ^{1}H n.m.r. f.i.d. of PVC and DIDP processed at 170°C showing the fit to two exponential functions and one Gaussian function

Table 1 Components derived from a fit of the solid echo f.i.d. using two exponential functions and one dipolar function

Sample and processing temperature	Exponential		Exponential		Dipolar	
	I	T_2 (ms)	I	T_2 (μs)	I	T_2 (μs)
PVC^a	–		–		1.0	11.7
PVC + DIDP 130°C^b	0.65	0.29	0.08	89.2	0.27	11.6
PVC + DIDP 170°C^c	0.64	0.32	0.08	74.9	0.28	10.7
PVC + DIDP 200°C^d	0.64	0.29	0.10	74.3	0.26	11.5

All the f.i.d.s were acquired at ambient temperature. An echo delay time of 8 μs was used and 4000 data points collected with a dwell time of 0.2 μs. PVC corresponds to an unprocessed PVC polymer without plasticizer while PVC + DIDP signifies PVC with diisodecyl phthalate and the stated temperature was used for processing
$^a \chi^2 = 27\,264.6$; $^b \chi^2 = 20\,797.9$; $^c \chi^2 = 54\,655$; $^d \chi^2 = 79\,871$. The expected value for χ^2 is 3954

noise level simple functions are not sufficient to fit a complex f.i.d. generated by a material containing ^{1}H spins undergoing a range of motions from restricted small amplitude motions to large amplitude quasi-isotropic motion. However, the f.i.d. fits do indicate that three components are necessary to describe the decay regardless of the temperature used to process the material (Figure 1, Table 1). Two of these components have an exponential decay with a long time constant, T_2, while the third component is Gaussian and has a short T_2. The combination of an exponential functional form and a long T_2 are consistent with a high degree of dynamic freedom both in terms of frequency and amplitude leading to a substantial averaging of the dipolar coupling through rotational motion. In contrast, a Gaussian form and short T_2 are expected for a rigid lattice where the full dipolar coupling is still present. Despite the poor χ^2 obtained, all fits gave an error of <0.8% indicating that the three function model is a good approximation to the f.i.d.

Having identified three components in the ^{1}H f.i.d. it is essential that we can assign these to particular species within the material, perhaps only to molecular entities but also, if applicable, to specific phases. It must be noted that phase information will only be obtained if the f.i.d. component can be associated with different phases. Earlier work, both on stabilized PVC and on a PVC with

a lower plasticizer level, has shown that a rigid lattice type T_2 component is expected for unplasticized PVC up to temperatures in excess of 100°C while plasticized polymer has a more variable behaviour depending on the level of plasticizer and its nature[3]. Experimentally it is found that the majority of the very short T_2 component in the present series of plasticized samples shows a marked increase in T_2 at temperatures as low as 70°C (Figure 2). This observation suggests that most of the short T_2 component is actually plasticized polymer. At the highest temperature used, 90°C, roughly 6% of the total signal remains in a short T_2 component, showing that little unplasticized PVC is present. On the basis that this component represents ordered PVC and given that 46% of the ^{1}H signal arises from the PVC, we can estimate that upwards of 13% of the PVC is ordered which is in line with levels found by X-ray diffraction. However, the precise nature of the order of crystallinity in PVC is open to question as d.s.c. results have been interpreted as indicating a crystallinity of over 20%[19]. It is perhaps surprising that plasticized PVC should have such a short T_2 at room temperature, but this is by no means incompatible with an improvement in the mechanical properties since higher frequency motions are required to cause a lengthening of T_2 than those thought to be important in dissipating mechanical energy under impact conditions[20]. Judging from previous work we can reasonably assign the long T_2 components to the plasticizer molecule though it is by no means clear whether there is also a contribution from the plasticized polymer chains.

Partial confirmation of these assignments can be made by combining a selective ^{1}H n.m.r. relaxation time with a high resolution ^{13}C n.m.r. detection or by measuring the ^{1}H n.m.r. relaxation time using the ^{13}C n.m.r. spectrum. In this way we can identify the particular moiety giving rise to the selected ^{1}H n.m.r. property through the characteristic chemical shifts in the ^{13}C n.m.r. spectrum. Thus by using the ^{13}C resonances assigned to the PVC and a delayed spin-lock CP pulse sequence we can measure the ^{1}H T_2 for the PVC indirectly. For the PVC–plasticizer sample processed at 170°C a good fit was obtained to a Gaussian decay with $T_2 = 14\,\mu$s for the PVC resonance, in excellent agreement with the short T_2 component found in the ^{1}H f.i.d.
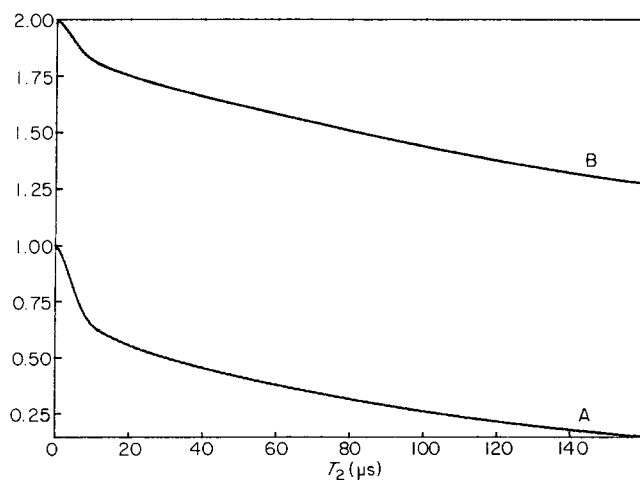

Figure 2 Solid echo ^{1}H n.m.r. f.i.d.s of PVC and DIDP processed at 170°C: (A) at ambient temperature; (B) at 70°C showing the increase in T_2 of the plasticized PVC matrix

Moreover, there was no evidence for any PVC having a longer T_2 and thus contributing to the exponential decay. Despite the seemingly conclusive nature of this result it can only provide partial confirmation because of the possibility, albeit remote, that any PVC sufficiently highly plasticized to give a $T_2 > 0.1$ ms, will not readily cross-polarize. Set against this, though, is the fact that plasticizer molecules which do have a long T_2 appear in the CP n.m.r. spectra. Indeed if we select a long enough delay in the delayed spin-lock experiment to pick up only ^{1}H spins with a T_2 in excess of 20 μs we just see DIDP. Thus it would appear that both long T_2 components arise from plasticizer. Two possible explanations for this are as follows. First, the shorter of the two components with a T_2 of $\sim 80 \mu$s corresponds to plasticizer molecules at the interface with the ordered regions of PVC. Secondly, there is an intramolecular variation in rotational motion. At one extreme we have the aromatic end of the plasticizer molecule, which is thought to interact with the PVC chain, held quite rigidly while the ends of the aliphatic groups are highly mobile. This will give rise to a distribution in T_2 along the molecule with the f.i.d. analysis only representing a limiting case. Since the ^{13}C CP dipolar dephasing spectrum of PVC and DIDP gave little evidence for a preferential loss of signal from the aromatic resonances we can conclude that the extreme case of rigidly held aromatic groups cannot be true in general, though this does not discount the idea of different T_2 for various parts of the plasticizer molecule.

From the ^{1}H f.i.d. we can observe motional heterogeneity which gives evidence for constrained motion of the plasticizer and indicates little high frequency segmental motion in the PVC chains at room temperature. T_2, however, is a very local measurement and gives no clues about the morphology except in conjunction with spin-diffusion experiments. These experiments, based on the Goldman–Shen pulse sequence, can give information on the sizes of domains and will be considered in detail later. Before we turn to the spin-diffusion experiments we can get a qualitative idea about the order of magnitude of any domains present from the ^{1}H T_1 and $T_{1\rho}$. The key idea when using relaxation times to provide a rough estimate of the domain size is that two phases with intrinsically different relaxation times will give a common averaged value if the nuclear spin magnetization can diffuse between the two regions in a time of the order of the longer relaxation time[21]. Assuming three-dimensional diffusion gives the root-mean-square distance, $\langle r^2 \rangle^{1/2}$, as:

$$\langle r^2 \rangle^{1/2} = (6DT_i)^{1/2} \qquad (1)$$

where D is the spin-diffusion coefficient, typically 5×10^{-12} cm^2 s^{-1} [22,23] and T_i is the relaxation time.

Looking at the spin-lattice relaxation times, T_1, shown in *Table 2* we see only a single value for all the samples, regardless of the processing temperature used or whether plasticizer is present or not. Accidental coincidence of the T_1 values is of course possible but the more likely explanation given the disparity in motions evident from the T_2 is that we are seeing a value averaged by spin diffusion. Before we can estimate the domain size consistent with an averaged T_1 of ~ 0.5 s from equation (1) we must know the appropriate D since each phase will have a different one depending on the magnitude of the dipolar coupling within the phase. In a highly mobile part of the sample, molecular motion will greatly reduce

Table 2 ^{1}H spin-lattice relaxation times, T_1, at ambient temperature for PVC without plasticizer (PVC) and PVC plasticized with diisodecyl phthalate (PVC + DIDP) processed at the stated temperatures

Sample and processing temperature	T_1 (s)	$\chi^{2\,a}$
PVC	1.9	132.4
PVC + DIDP 130°C	0.3	114.3
PVC + DIDP 170°C	0.34	107.9
PVC + DIDP 200°C	0.58	133.1

^{a} 128 data points. The expected value for χ^2 is 127

Table 3 ^{1}H rotating frame spin-lattice relaxation times, $T_{1\rho}$, at ambient temperature using a spin-lock field of 102.6 kHz for PVC without plasticizer (PVC) and PVC plasticized with diisodecyl phthalate (PVC + DIDP) processed at the stated temperatures

Sample and processing temperature	A I	A $T_{1\rho}$ (ms)	B I	B $T_{1\rho}$ (ms)	C I	C $T_{1\rho}$ (ms)
PVC^a	0.29	2.9	0.76	16.2	–	–
PVC + DIDP 130°C^b	0.28	1.6	0.57	4.0	0.26	12.9
PVC + DIDP 170°C^c	0.23	1.2	0.65	4.0	0.24	13.0
PVC + DIDP 200°C^d	0.32	1.4	0.63	3.5	0.21	12.6

$^a \chi^2 = 322.5$; $^b \chi^2 = 147$; $^c \chi^2 = 211.9$; $^d \chi^2 = 299.6$: 150 data points. The expected value for χ^2 is 144

the dipolar coupling and hence the transition probability for the spin flip-flop process, the mechanism for spin diffusion. As a consequence, D will be smaller than in a rigid part which has the same proton density. To a good approximation D is inversely proportional to T_2 (ref. 24), consequently if we assume a D of 5×10^{-12} cm^2 s^{-1} for a rigid lattice with a T_2 of 10–20 μs then a plasticizer phase with a T_2 of 200 μs will have a D of 5×10^{-13} cm^2 s^{-1}. Note that this will only be true for a pure plasticizer phase. In a mixed plasticizer–PVC phase we would need to take into account the relative proportions of each component and their respective D values.

In any transport process the rate-limiting step will be diffusion of magnetization into or out of a plasticizer domain because of its order of magnitude smaller diffusion coefficient. This restricts the size of any pure plasticizer domain to ~ 100 Å while any heterogeneity involving the PVC matrix must have a domain size of < 300 Å. From the common values of T_1 it is evident that the longer range probe T_1 is not sensitive enough to pick up any heterogeneity arising from differences in the processing conditions. If we wish to observe structure on a smaller scale we must turn to a shorter n.m.r. relaxation time so that the magnetization decays before it has time to diffuse as far. One such relaxation time is $T_{1\rho}$ which is typically of the order of milliseconds. Now in contrast to T_1, all the plasticized PVC samples show a $T_{1\rho}$ relaxation decay curve which can be analysed in terms of two or more components, their values being shown in *Table 3*. Probably the most important aspect of this analysis is the qualitative one, namely that the

multiexponential form of the decay clearly demonstrates phase heterogeneity. However, we cannot deduce from the $T_{1\rho}$ results alone whether the phases differ in order or plasticizer content. If we look at the $T_{1\rho}$ results for pure PVC where typically 10% is thought to be crystalline, or at least in more ordered regions, we might expect to see two components, as indeed we do. Yet the proportions of the two phases are not consistent with one representing an ordered region. This suggests averaging of the $T_{1\rho}$ of the ordered and disordered regions by spin diffusion, indicative of a small domain size for the ordered region. From equation (1) we can estimate that any ordered domains must be of the order of 95 Å or less. As an illustration we can compare this with small angle X-ray scattering (SAXS) estimates of 65 Å for the crystalline phase of unplasticized PVC[25,26]. A naive interpretation of the $T_{1\rho}$ results for the PVC–plasticizer samples, based on the similarity between the long $T_{1\rho}$ value seen in these samples and the pure PVC, is that the long $T_{1\rho}$ component corresponds to unplasticized PVC. We must bear in mind though, as the pure PVC result demonstrates, that the $T_{1\rho}$ behaviour of plasticized PVC will, in all likelihood, be complicated by spin diffusion. Indeed, in these circumstances it may well prove to be impossible to establish a particular phase model. We can attempt to identify the long $T_{1\rho}$ component by looking at the ^1H f.i.d. at the end of a long spin-lock pulse and from the f.i.d. components to say whether this phase does contain just PVC, or whether plasticizer is present as well. However, to minimize the effects of spin diffusion a temperature or spin-locking field must be used where the shorter $T_{1\rho}$ value is of the order of a millisecond or so. Under these conditions it should be possible to remove essentially all of the magnetization associated with the short $T_{1\rho}$ by a shorter spin-lock pulse of only 3 ms during which time the amount of spin diffusion will be negligible. A comparison of the f.i.d.s after a short locking pulse and a long pulse using a B_1 field of 59 kHz demonstrates a marked increase in the short T_2 component (*Figure 3*). Thus when the effects of spin diffusion are reduced it becomes clearer that the long $T_{1\rho}$ component is mainly PVC, although we cannot rule out the presence of plasticizer in the limiting case when spin diffusion is fully quenched.
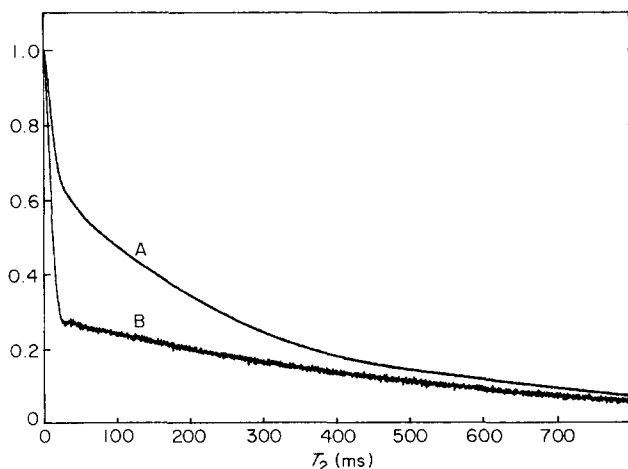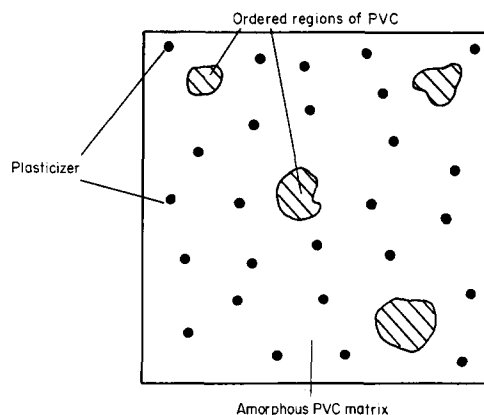
Note that we must be careful when talking about the

Figure 4 Schematic representation of the PVC–plasticizer phase structure. Ordered regions of PVC lie within a disordered PVC matrix with an essentially homogeneous distribution of plasticizer

long $T_{1\rho}$ phase as being a PVC phase since we have in fact only established that the PVC resonance has a long $T_{1\rho}$ and not that it forms a distinct phase. Usually the observation of a distinct $T_{1\rho}$ would be sufficient to conclude that a particular phase is present; however, in the present case we need to consider whether this is justified. The reason for the uncertainty is that the plasticizer molecules have a long T_2 indicating that rotational motion has significantly reduced the dipolar coupling between the plasticizer and rigid PVC matrix. As a consequence any averaging effects of spin diffusion will be severely limited. Indeed plasticizer molecules dispersed at a molecular level throughout a rigid PVC matrix may in all probability show an intrinsic $T_{1\rho}$ rather than any spatially averaged value. As a consequence it is conceivable that plasticizer may well appear in the long spin-lock f.i.d. regardless of spin diffusion because some ^1H spins in the plasticizer molecule actually have a long $T_{1\rho}$.

A model for the structure of plasticized PVC which is consistent with the $T_{1\rho}$ results is shown schematically in *Figure 4*. The long $T_{1\rho}$ component is identified as being intrinsic to the PVC chains, thus accounting for the similarity between this value and that seen for pure PVC. We identify the short $T_{1\rho}$ component as being the intrinsic $T_{1\rho}$ of plasticizer molecules dispersed throughout the PVC matrix, except for the more ordered region. The explanation for the similar ^1H f.i.d.s seen in the short and long spin-locking fields, when a spin-lock field of 102.6 kHz is used, is that because of the small domain size of the plasticizer, essentially the size of molecule, spin diffusion obscures the phase information despite the inefficient coupling between the plasticizer and PVC. At lower spin-locking fields with the reduction in $T_{1\rho}$ the inefficient coupling becomes manifest and spin diffusion is no longer able to compensate for the differences in $T_{1\rho}$ and the long $T_{1\rho}$ selective pulse sequence now shows more of the PVC resonance. Overall the $T_{1\rho}$ results for PVC and plasticizer processed at 130°C are little different from those of the sample processed at 200°C. In part this may reflect a genuine similarity between the materials but in addition any differences may be obscured by spin diffusion effects. If the latter is the case then we can say that the differences between samples processed at different temperatures must be on the 20–100 Å level. The $T_{1\rho}$ results are complex and require further examination with a greater range of temperature and locking fields. They are consistent with both a heterogeneity on the 100 Å

Figure 3 Effect of a spin-lock of variable duration on the solid echo ^1H n.m.r. f.i.d. of PVC and DIDP processed at 170°C with a spin-lock time of: (A) 10 µs; (B) 20 ms. The effective spin-locking field was 59 kHz

scale and at the other extreme an intimate dispersion of plasticizer throughout the PVC matrix where plasticizer mobility decouples the plasticizer from the PVC.

We can attempt to distinguish between these possibilities by using the Goldman-Shen experiment[12]. In this experiment a magnetization gradient is created by allowing complete dephasing of the magnetization associated with the phase with the short T_2, that is the rigid PVC matrix, whilst preserving the long T_2 magnetization, that is the plasticizer. The proximity of the PVC matrix and the plasticizer is then studied by monitoring the diffusion of the magnetization from the plasticizer back into the PVC. From a knowledge of D it is possible to calculate the domain size. A number of treatments have been presented for the analysis of spin diffusion in polymeric systems involving greater or lesser degrees of sophistication in the modelling[27-29]. Initial semiquantitative estimates of the domain size can be made using the limiting analytical expressions given for the case of n-dimensional diffusion with amorphous domains of characteristic length b with a Poisson distribution in a long period of a polymer[27]. For one-dimensional diffusion the recovery of the magnetization $R(t)$ is given by:

$$R(t) = (2/\pi^{1/2})(Dt/b^2)^{1/2} \qquad t \ll b^2/D$$

$$= 1 - \pi^{-1/2}(b^2/Dt)^{1/2} \qquad t \gg b^2/D \qquad (2)$$

The recovery curve based on the analytical expressions is shown in *Figure 5*. A linear dependence on $t^{1/2}$ is seen for short t as expected while the long term behaviour, whilst not in the true limit of $t \gg b/D$, is best represented by three-dimensional diffusion. From the initial gradient of the graph we can determine the characteristic length of the diffusion process, but as noted above we must be careful to use the appropriate value for D. In this case the magnetization remains in the highly mobile phase with the long T_2 and small D, consequently the rate-limiting step will be diffusion of magnetization out of this phase with subsequent transport in the rigid matrix expected to be rapid. Thus to a first approximation we can only get information on the thickness of the plasticizer
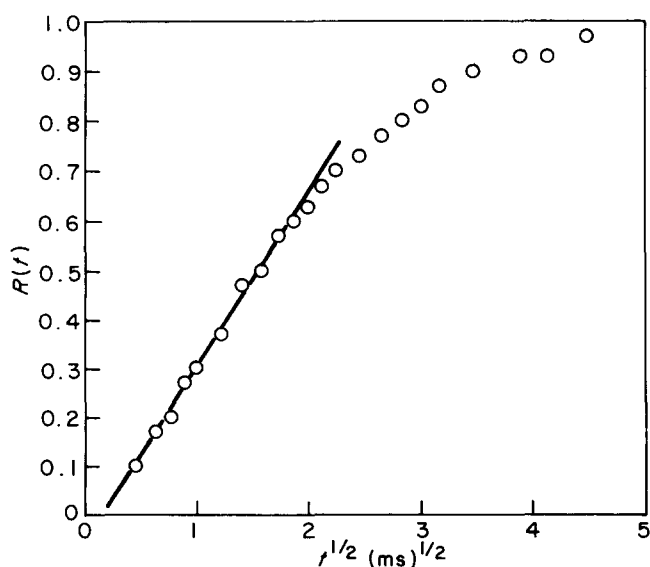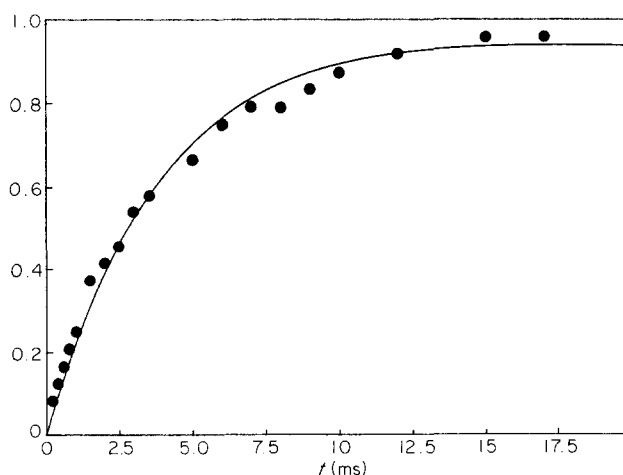

Figure 6 Variation in the magnetization of the PVC resonance in a Goldman-Shen experiment modelled as a CP process. The solid line represents the calculated magnetization based on a rise time constant of 6.4 ms

containing phase. Even here we have two possibilities corresponding to different PVC-plasticizer models, thus in one case the limiting step may be at the interface, in the actual transfer of magnetization from the mobile to rigid phase. This corresponds to the physical model of a completely homogeneous dispersion of plasticizer within the PVC matrix. In the other case, consisting of domains of plasticizer, the rate-limiting process is transport of the magnetization from the bulk of this domain to the interface. However, with such domains the physical diffusion of plasticizer molecules provides a more efficient transport mechanism to the interface as can be seen from the self-diffusion coefficient of n-decyl phthalate at 25°C, 50 wt% plasticizer[30] which is 60×10^{-10} cm^2 s^{-1}. Thus even with domains of plasticizer the rate-limiting step must be coupling between the ^{1}H spins of the plasticizer and the PVC at the interface. Using the D of 5×10^{-13} cm^2 s^{-1} we can calculate b to be only 20 Å, i.e. very small domains of the order of the size of one molecule. A small domain size is entirely consistent with the rapid recovery in the rigid phase signal despite the reduced D. This semiquantitative estimate for the plasticizer domain size clearly indicates that in fact we do not have domains of plasticizer since the size of the putative domain is only that of a molecule. A corollary of the absence of plasticizer domains is that it is more realistic to consider the rate-limiting process to be the transfer of magnetization from the mobile to rigid phase at the interface. If this is the case then the recovery in the rigid phase magnetization should be compatible with a simple CP picture[31] in which the mobile phase plays the part of the low temperature spin system while the rigid matrix is the high temperature system; polarization transfer will then occur until thermal equilibrium is achieved, corresponding to the normal ^{1}H f.i.d. A long rise time constant would be expected given the much reduced dipolar coupling while the decay time would be the spin-lattice relaxation time. Good agreement is seen between the observed increase in rigid phase magnetization and that calculated using the coupled differential equations (equation (4.67a) in reference 32], used to describe the CP process (*Figure 6*). Thus the Goldman-Shen results are consistent with a picture of a molecular level dispersion of plasticizer throughout the PVC matrix. Owing to the rate-limiting nature of the

Figure 5 Recovery of the magnetization for the PVC resonance, $R(t)$, in a Goldman-Shen experiment after a preparation period of 100 μs as a function of the spin diffusion time t

spin transfer from the mobile to rigid phase in combination with the small size of any domains of unplasticized PVC it is not possible to determine the size of such regions.

It is difficult to compare these results with those found at lower plasticizer levels because in these systems unplasticized PVC could be resolved from plasticized PVC in the ^1H f.i.d. by working at 85°C. Here we could only see a small contribution from the short T_2 component associated with the ordered regions at temperatures above 60°C.

^{13}C n.m.r. results

The ^{13}C n.m.r. spectra were obtained using two types of acquisition procedure. In the first, known as single pulse excitation (SPE), the intrinsic carbon polarization is used while in the second method, CP, the carbon polarization is enhanced by transfer from protons. If a fast pulse recycle time is used in the SPE experiment we can think of the SPE experiment as selecting the mobile species while the CP experiment will favour the more rigid components. Overall we know from the ^1H n.m.r. results that the PVC matrix is rigid while the plasticizer molecules are mobile. Consequently we would expect the ^{13}C SPE n.m.r. spectrum to be dominated by the plasticizer resonances. This is indeed the case, as can be seen in Figure 7a. In the CP ^{13}C n.m.r. spectrum the reverse is true with the PVC resonances dominating (Figure 7b). When we come to examine the n.m.r. spectra for evidence of a specific interaction between the plasticizer molecule and the PVC matrix an important consideration is that, if the plasticizer molecule interacts strongly with the PVC matrix we would expect it to be enhanced in intensity with respect to the weakly interacting molecules in the ^{13}C CP n.m.r. spectrum. Yet
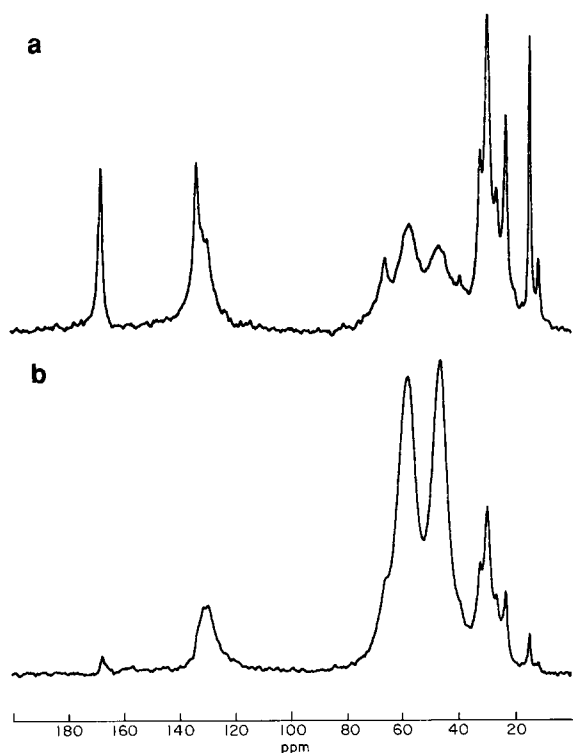

Figure 7 ^{13}C MAS n.m.r. spectra of PVC and DIDP processed at 170°C: (a) single pulse excitation spectrum with a relaxation delay of 10 s; (b) CP spectrum after a contact time of 1 ms
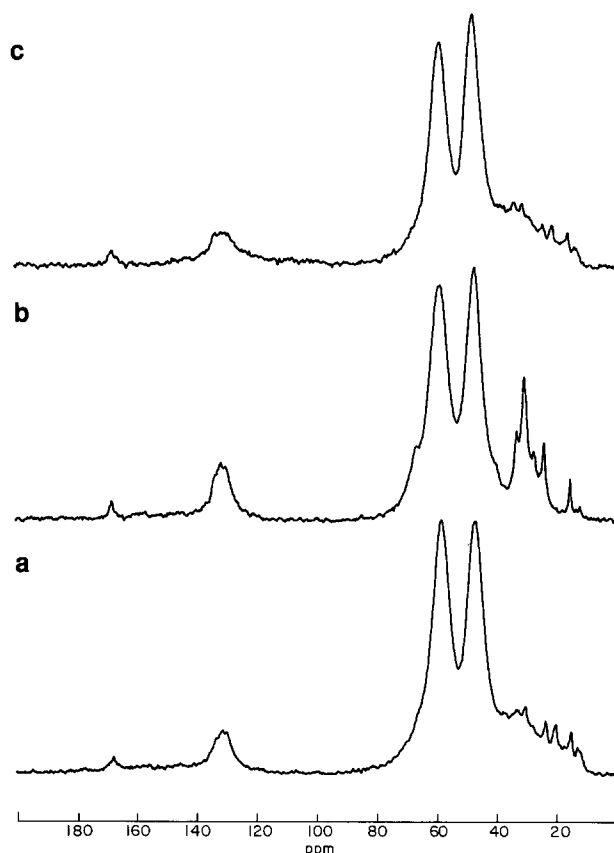

Figure 8 ^{13}C CP MAS n.m.r. spectra of PVC and DIDP processed at: (a) 130°C; (b) 170°C; (c) 200°C. A contact time of 1 ms and recycle time of 3 s were used

despite the differences in intensity the ^{13}C n.m.r. spectra of the plasticizer molecules acquired by the SPE and CP method are rather similar, suggesting that there are not two types of plasticizer molecule corresponding to a freer molecule and one tightly bound to the PVC chains. Thus the overall impression is that there are no specific interactions between the ester molecule and the PVC matrix.

In previous studies using vibrational spectroscopy it has been proposed that the carbonyl group of the phthalate ester interacts with the C–Cl dipole of the PVC chain. However, the ^{13}C n.m.r. chemical shift of the phthalate carbonyl group in the plasticized PVC gives no evidence for an interaction since the observed chemical shift is very similar to that observed in the free ester. One point of difference is that the vibrational studies were carried out on systems with a lower plasticizer content and it is possible that specific interactions are favoured at low plasticizer levels. The other alternative, that the carbonyl chemical shift is not sensitive to the proposed interaction, is also plausible given that only minor changes in chemical shift can be seen[33] when the carbonyl oxygen acts as a Lewis base in complexes with $MgCl_2$. No significant differences are seen in the ^{13}C chemical shifts of the phthalate end of the plasticizer when the processing temperature is changed. In contrast to this, large changes are seen in the aliphatic region, corresponding to the alcohol moiety of the ester, as is evident from Figure 8. This feature may well be related to the dependence of plasticization properties on the aliphatic chains. Thus the plasticizing efficiency of the linear C_{10} n-decyl phthalate is superior to the branched isodecyl phthalate as shown by the cold

flex temperature and softness[34]. Effective plasticization involving long aliphatic chain phthalates could well be dependent upon attaining an optimum chain extended conformation to maximize the electrostatic interactions[35]. The explanation for the changes in the n.m.r. spectra is not at all clear-cut; the conformation of the aliphatic chain depends on the processing temperature but the reason for this is not yet understood. One way of looking at the changes in the chemical shifts would be in terms of how the aliphatic group is extended in between the polymer chains. The [13]C n.m.r. spectra of the samples processed at 130 and 200°C are similar while the intermediate temperature processed sample gives a different spectrum. The reasons for the similarity between the ^{13}C MAS n.m.r. spectrum of the samples processed at 200 and 130°C are unclear at present, especially in view of the steady improvement in physical properties as the processing temperature is increased from 130 to 170°C, but no significant improvement as the processing temperature is raised from 170 to 200°C.

CONCLUSIONS

Overall the picture presented by the n.m.r. measurements is that highly plasticized PVC has a rather homogeneous morphology involving a molecular level distribution of plasticizer molecules without any significant domains of plasticizer and only small domains of ordered PVC which remains free of plasticizer. Little evidence was found for n.m.r. differences between the PVC samples processed at different temperatures which could be readily interpreted in terms of the sample morphology. That is not to say that differences were not found, for example the proportion of the various exponentials in the $T_{1\rho}$ relaxation decay curve changed from sample to sample. However, as pointed out, this measurement is subject to the complications of spin diffusion averaging the magnetization information. Similarly in the [13]C n.m.r. experiments marked differences were seen in the pattern of the aliphatic resonances between the samples processed at 130 and 170°C. Only in this case the sample processed at 200°C gave a [13]C n.m.r. spectrum more like that of the sample processed at 130°C than that of the sample processed at 170°C to which it was expected to · be comparable. Quite why the n.m.r. measurements were not more sensitive to the effect of processing is unclear, particularly as the relaxation properties are affected by microscopic structural changes involving domains of the order of 100 Å or less. In part, the explanation must lie in an actual similarity in the morphology of the samples despite obvious variations in other properties, such as the tensile strength. Although n.m.r. is sensitive to changes occurring on a very local basis it must be borne in mind that n.m.r. is a bulk measurement with all the local

arrangements integrated into a sum so that any property difference which relies on a localized phenomenon will clearly not be well described.

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