Coupled relaxations in a blend of PMMA and a polycarbonate

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Proton lineshape and proton spin–lattice relaxation, $T_{1\rho}$, measurements were made on blends of bisphenol chloral polycarbonate and perdeutero poly(methyl methacrylate) (PMMA). The solution-cast blends are optically clear and display a single thermal glass transition temperature, T_g, as reported. The proton lineshape and proton relaxation data are used to follow the dynamics of the polycarbonate in the blend. The glass transition process is monitored by lineshape collapse as a function of temperature and the sub-glass transition process associated with π flips of the phenylene group is monitored by the proton $T_{1\rho}$ values as a function of temperature. The glass transition as viewed from the polycarbonate remains similar in character to the behaviour observed in pure polycarbonate. Below T_g, the lineshape consists of a broadened Pake doublet and above T_g a narrow Lorentzian grows in on top of the Pake pattern. The bimodal behaviour and the growth of the narrow line with temperature can be described by the Vogel–Tamman–Fulcher equation with T_0 values which decrease with PMMA concentration. The proton $T_{1\rho}$ data show antiplasticization in the form of suppression of the π flip process as PMMA is added. In addition, a new minimum associated with the motion of the polycarbonate is observed at the temperature and time scale of the ester group rotation of the PMMA. This apparent coupling of the sub-T_g relaxation processes is related to the behaviour of polycarbonate upon addition of low-molecular-weight ester diluents. The level of antiplasticization and the amount of coupling is underestimated by a lattice model and an assumption of random mixing. On the very local scale of the π flip motion and at the higher concentrations of PMMA, there are apparently fewer PMMA–polycarbonate contacts than a random mixing assumption indicates.

(Keywords: n.m.r.; blend; dynamics)

INTRODUCTION

The influence of blending on the dynamics of the constituent polymer chains in a miscible polymer blend system appears to be variable. Almost by definition, a single glass transition intermediate between those of the constituents is expected although there is strong evidence of residual heterogeneity in the dynamics at the glass transition, i.e. differences in the rates of motion, associated with local concentration fluctuations[1]. Recent theoretical and experimental advances have sparked renewed interest in this area[1–3]. The extent of the heterogeneity is far short of that associated with phase separation and also depends on the particular blend system under consideration. For sub-glass transition relaxations, cases are observed where there is little change in the low-temperature process as the second component is added[4] and in other systems there is an apparent antiplasticization or suppression of the motion[5]. With this general situation in mind, an n.m.r. study of the dynamics of a polycarbonate of 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene (Chloral-PC) blended with poly(methyl methacrylate) (PMMA) was undertaken to characterize both the glass transition and the low-temperature relaxation as seen through the local motions of the polycarbonate.

The dynamics of polycarbonates including Chloral-PC have been well studied[6–11] already, allowing for a comparison of motions in the pure polymer with those in the blend. The glass transition and the low-temperature loss peak in Chloral-PC are very similar to bisphenol A polycarbonate, prompting frequent comparisons between the two[6]. Chloral-PC has been selected for many n.m.r. studies because it contains only phenylene protons and the predominant dipolar interaction between the protons is parallel to the phenylene backbone units as shown in *Figure 1*. This allowed for the first indications[7] that the

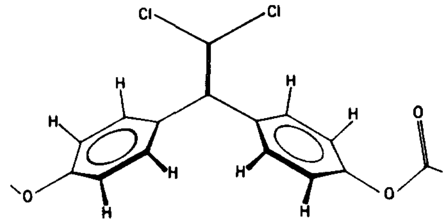

Figure 1 Chloral-PC repeat unit structure

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low-temperature motion involving the phenylene units must be some kind of rotation about the 1,4-axis, later determined to be π flips[12,13]. Using a stretched exponential correlation function, the π flip motion observed in the proton $T_{1\rho}$ minimum was linked to the low-temperature dynamic mechanical loss peak[8]. The apparent activation energy is about 50 to 60 kJ mol^{-1} and the fractional exponent is about 0.15 to 0.2. The glass transition in Chloral-PC occurs at 160°C. In dilute solution, the barrier to phenylene group rotation is found to be 10 kJ mol^{-1} when the effects of solvent viscosity are subtracted, and the motion can be described by a single exponential correlation time. Thus about 40 kJ mol^{-1} of the barrier to rotation comes from intermolecular interactions and the very broad distribution of correlation times associated with a fractional exponent of 0.20 must also arise from local differences in intermolecular interactions or packing.

From room temperature up to the glass transition temperature, T_g, the proton spectrum of pure Chloral-PC consists of a broadened Pake doublet which shows little collapse over this temperature range[7]. This is direct evidence that there is minimal reorientation of the phenylene backbone units other than by 1,4-rotation. From the glass transition up to about 200°C, the proton lineshape is bimodal, consisting of the broadened Pake pattern with a narrow Lorentzian superimposed on top[10,11]. The narrow component grows at the expense of the broad component as the temperature increases and the growth can be described by the Vogel–Tamman–Fulcher (VTF) equation. The narrow component of the proton lineshape is identified with mobile domains in the glass which grow in size as the temperature is increased.

The T_g of PMMA is about 115°C[14], which is significantly lower than that for Chloral-PC. On the other hand, the principal sub-glass transition motion occurs at a much higher temperature. At a frequency of 1 Hz, the large low-temperature loss[6] peak of Chloral-PC is at −100°C. For PMMA, under comparable circumstances the loss peak[14] is at 30°C and corresponds to rotation of the ester side-group. To further contrast the two, the Chloral-PC sub-T_g process involves rotation of a backbone unit and the PMMA process involves rotation of a side group. The apparent activation energy of the PMMA side-group motion is about 80 kJ mol^{-1} which is significantly higher than the value for Chloral-PC. Thus, although PMMA has the lower T_g, it is a more rigid material below the temperature at which ester group rotation occurs.

Miscible blends of PMMA and Chloral-PC can be prepared by casting from tetrahydrofuran over the entire concentration range[15,16]. A single glass transition is observed in differential scanning calorimetry (d.s.c.) with the apparent T_g slightly depressed from that estimated from simple proportionality based on concentration and the pure component T_gs.

To follow the dynamics of Chloral-PC as PMMA is added, proton lineshape and proton $T_{1\rho}$ experiments were performed on blends of this polycarbonate with perdeutero PMMA. Thus, the same experiments originally used to establish the geometry and time scale of the low-temperature process and the glass transition in Chloral-PC can be used for the same purposes in the blend. Similar experiments have been used to follow the motion of d_6-BPA-PC upon addition of the diluent, di-*n*-butyl phthalate (DBP). Only phenylene protons are present in d_6-BPA-PC, just as in Chloral-PC, and perdeutero DBP was used so that simple proton experiments could be used to monitor the polycarbonate dynamics[17]. The $T_{1\rho}$ data for BPA-PC showed a suppression of the π flip process, antiplasticization, at low concentrations of DBP and then the appearance of a new low-temperature minimum at higher concentrations of DBP. A lattice model to calculate nearest neighbour contacts[18] was used to account for the suppression by assuming that one nearest neighbour DBP improved local packing, thereby preventing the π flip process. The appearance of a lower-temperature minimum at higher concentrations of DBP was associated with contacts between BPA-PC repeat units and clusters of diluent molecules (a 'soft' environment). The diluent and polymer were placed on the lattice in a random fashion and clusters in this context are just random diluent–diluent contacts not related to phase separation. In these kinds of systems, overall rotational diffusion of the diluent occurs in the clusters, allowing for rapid phenylene group motion in the neighbouring polycarbonate units[19].

With this background in mind, the polymeric ester (PMMA) can be compared to the low-molecular-weight ester (DBP) in terms of any changes observed in the motion of the Chloral-PC. However, in the case of the polymeric ester the inherent dynamics are quite different from DBP and this may be reflected in the blend dynamics. The dynamic mechanical response of the blends is also measured for comparison with the n.m.r. data.

EXPERIMENTAL

The Chloral-PC was supplied by General Electric Research and Development and is part of the same lot used in earlier studies[6–11,16,20]. The intrinsic viscosity is 0.5 dl g^{-1}. The perdeutero PMMA was obtained from Bruker Instruments and has been characterized in a previous n.m.r. study by Landry and Henrichs[5].

Films of the blends were prepared by solution casting from tetrahydrofuran following the procedure of Chiou and Paul[15]. D.s.c. thermograms of the perdeutero PMMA/Chloral-PC blends displayed single T_gs within experimental error of those reported for protonated PMMA[15].

Proton lineshapes were acquired on a Bruker MSL 300 as f.i.d.s following a single $\pi/2$ pulse of 1 μs and a cycle time of 50 s. The sweep width was 200 kHz. Proton $T_{1\rho}$ data were acquired at a locking field of 1 mT corresponding to a frequency of 44 kHz. The proton $T_{1\rho}$ data are well characterized by a linear least-squares analysis of ln A_τ *versus* τ where τ is the spin-lock time.

Multiple layers of film were compression moulded to form specimens for dynamic mechanical analysis. A Polymer Laboratories DMTA was used for these measurements.

RESULTS

Figure 2 presents lineshapes of Chloral-PC as a function of temperature and blend composition. These spectra were corrected by spectral subtraction to remove the small contribution from the few protons present in the perdeutero PMMA. This correction was made by subtracting pure perdeutero PMMA proton spectra from

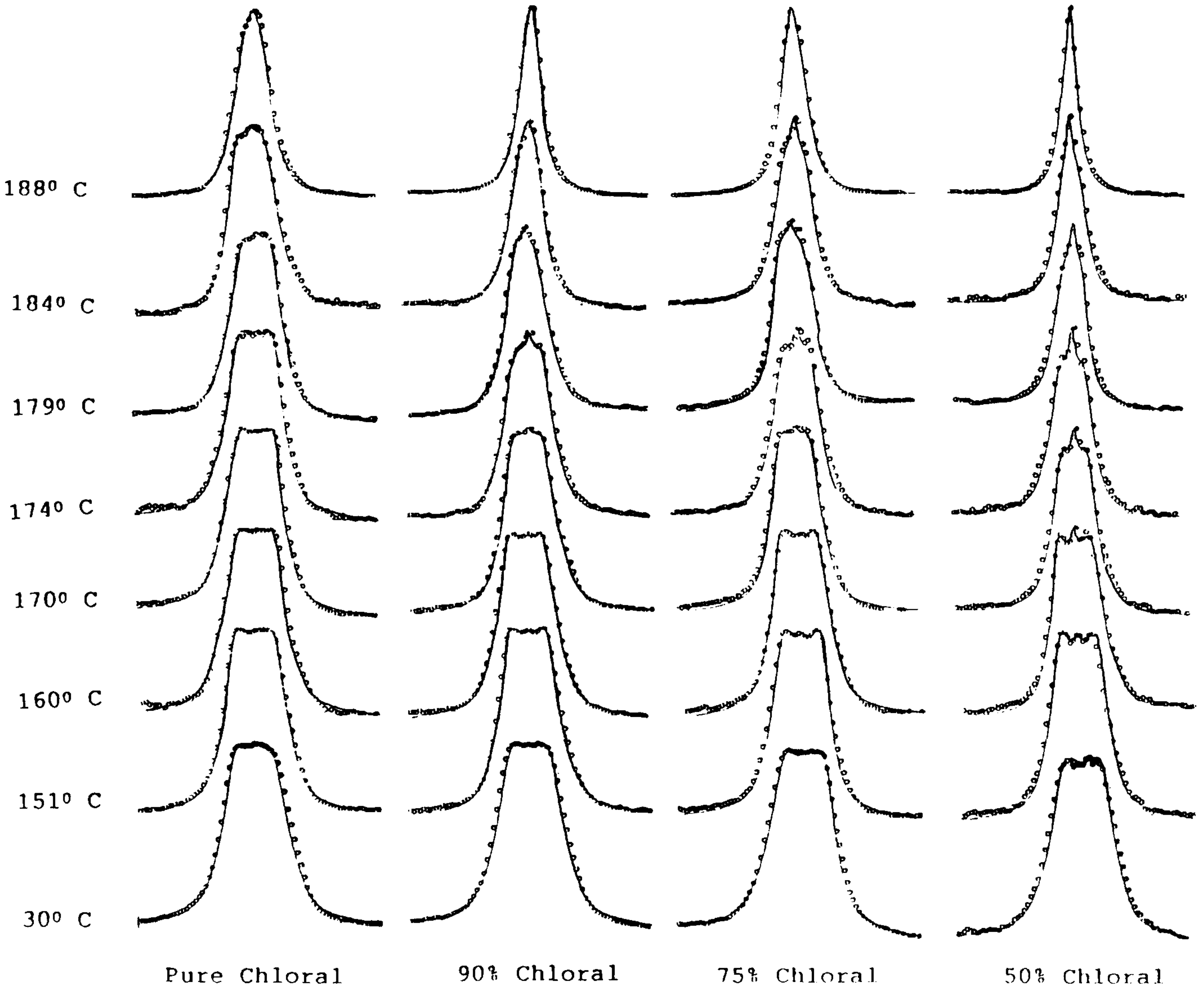

Figure 2 Proton lineshape of Chloral-PC/perdeutero PMMA blends *versus* temperature and concentration

the blend spectra weighted according to the composition of the blend.

Figure 3 displays proton $T_{1\rho}$ data as a function of temperature for pure Chloral-PC and three blend compositions.

Figure 4 shows the dynamical mechanical response as a function of temperature and at a frequency of 3 Hz for pure Chloral-PC, three blends and pure PMMA.

INTERPRETATION

The proton lineshapes of the blends in *Figure 2* are qualitatively similar to that of the pure Chloral-PC which was fit in a bimodal fashion in an earlier study of the glass transition[10]. A similar strategy will be followed here so that the lineshape is divided into broad and narrow components which are centred at the same position. The broad component is modelled as a Pake doublet which arises from adjacent phenylene protons and is broadened by intermolecular dipole–dipole interactions. This component is associated with phenylene groups which are unable to undergo segmental motion on a time scale comparable to the Pake splitting in frequency. The narrow component, on the other hand, is depicted as a Lorentzian line corresponding to highly mobile phenylene groups undergoing rapid, nearly isotropic segmental motion. Thus, four parameters are required to simulate the proton lineshapes: the Pake doublet splitting, the line broadening of the Pake pattern, the linewidth of the narrow Lorentzian component and the fractional population of the broad component. Lorentzian broadening of the Pake doublet was employed although largely comparable results could be obtained from Gaussian broadening. The simulations are compared with the experimental lineshapes in *Figure 2* and the simulation parameters are summarized graphically in *Figures 5–8*.

As has been noted before[7,10], the Pake splitting in pure Chloral-PC persists at 3 Gauss up to the T_g (160°C), and then it begins to fall. This was interpreted as evidence for little phenylene group reorientation in glassy Chloral-PC. The same general behaviour is exhibited in the blends so that the Pake splitting starts to fall at about 150, 142 and 132°C for 90, 75 and 50 wt% Chloral-PC, respectively. Thus, in these blends the backbone units of the Chloral-PC do not begin significant reorientation other than rotations about the 1,4-axis until the glass transition is reached.

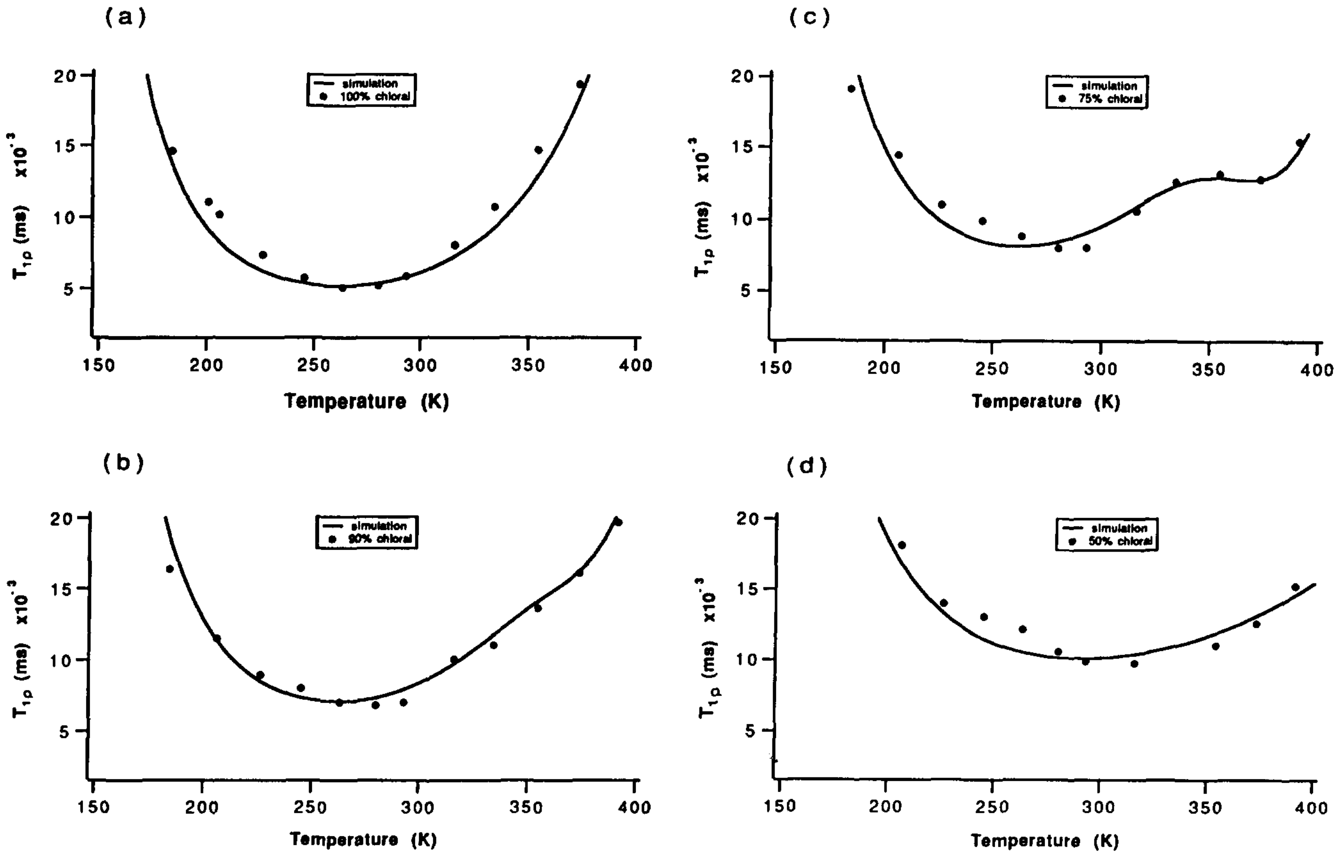

Figure 3 $T_{1\rho}$ *versus* temperature for: (a) pure Chloral-PC; (b) 90% Chloral-PC; (c) 75% Chloral-PC; (d) 50% Chloral-PC. (The points represent the experimental data, and the lines, the theoretical fit as described in the text)

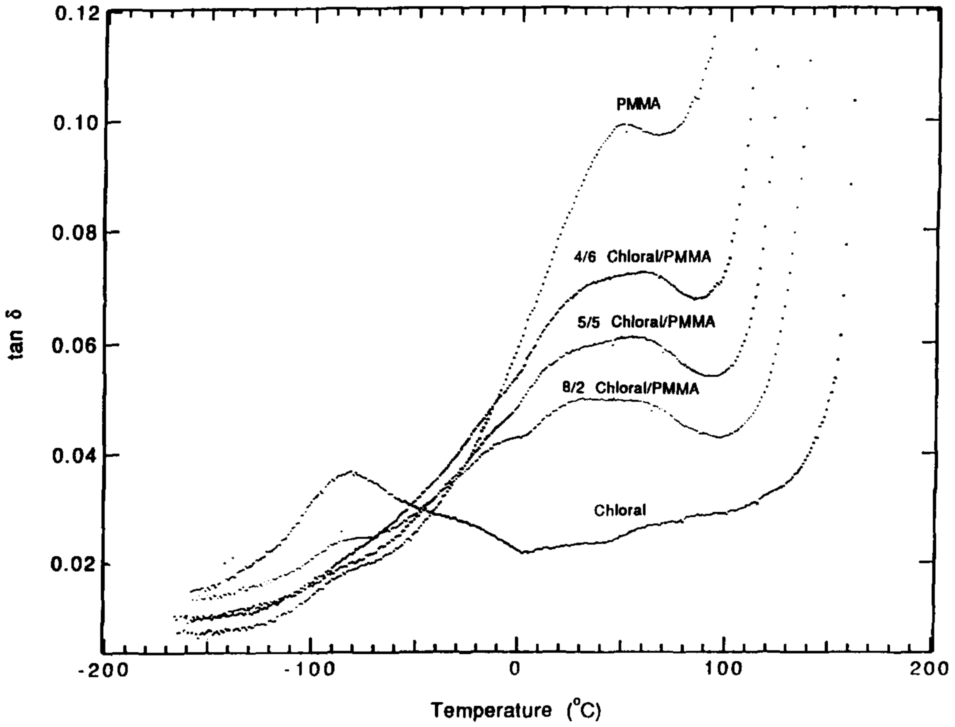

Figure 4 Mechanical loss at 3 Hz for Chloral-PC blends with PMMA

The fractional population of the narrow component also follows a pattern similar to the behaviour reported[10] for pure Chloral-PC. In the sub-T_g glass the broad component has a constant population approaching 100% of the observed intensity. The narrow component does not begin to grow until the T_g is reached. The fractional population of the narrow component, δ, was previously described by the VTF equation which can be applied to the blends in the same manner that it was applied to the pure Chloral-PC. In a simple two-parameter fit form, the

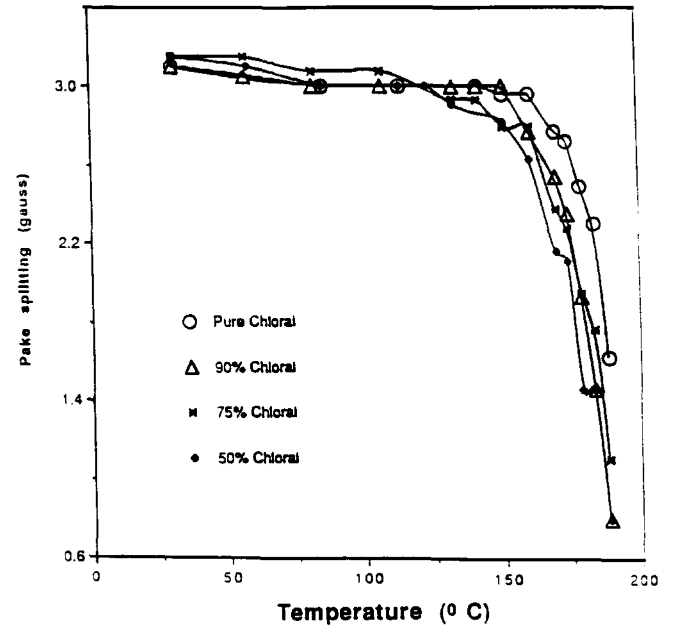

Figure 5 Pake splitting *versus* temperature based on simulation of the proton line shapes

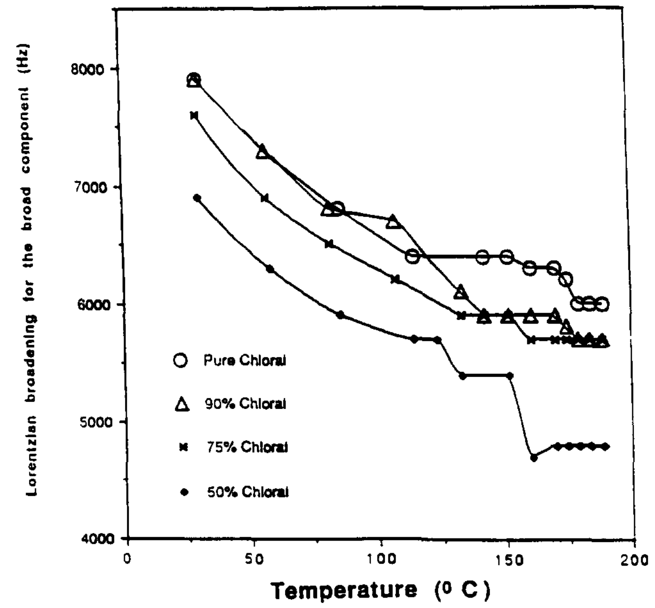

Figure 6 Lorentzian line broadening for the broad component *versus* temperature based on simulation of the proton lineshapes

VTF equation can be written as

$$\delta=\exp[-B'/(T-T'_0)] \qquad (1)$$

Fits of the data to this equation are shown in *Figure 9* and the corresponding parameters are shown in *Table 1*.

The proton $T_{1\rho}$ data *versus* temperature in pure Chloral-PC were fit to the stretched exponential correlation function

$$\phi(t)=\exp[-(t/\tau)^{\alpha}] \qquad (2)$$

In the actual fitting process, the stretched exponential is written as a sum of exponentials:

$$\phi(t)=\sum_{k=1}^{n} P_k \exp(-t/\tau_k) \qquad (3)$$

The spectral density corresponding to this form is a sum of Lorentzians which can be directly entered into the equation for $T_{1\rho}$

$$1/T_{1\rho}=(2/3)\gamma^2 S(1.5J_e(2\omega_e)+2.5J_1(\omega_H)+J_2(\omega_H)) \qquad (4)$$

where ω_e is the effective rotating field frequency, γ is the

Table 1 Parameters for the VTF simulation of the fractional population of the narrow components

Sample	B'	T'_0 (°C)
Pure Chloral-PC	178.0	142
90% Chloral-PC	140.0	138
75% Chloral-PC	133.1	132
50% Chloral-PC	114.1	123

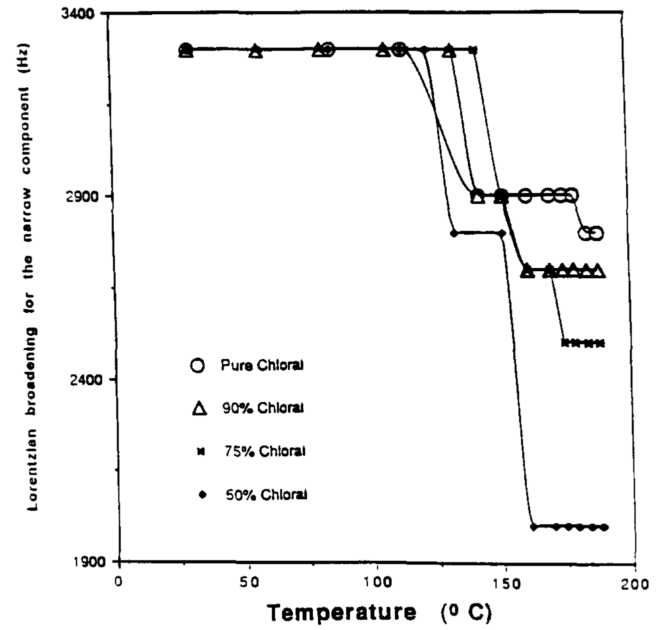

Figure 7 Lorentzian line broadening for the narrow component *versus* temperature based on simulation of the proton lineshapes

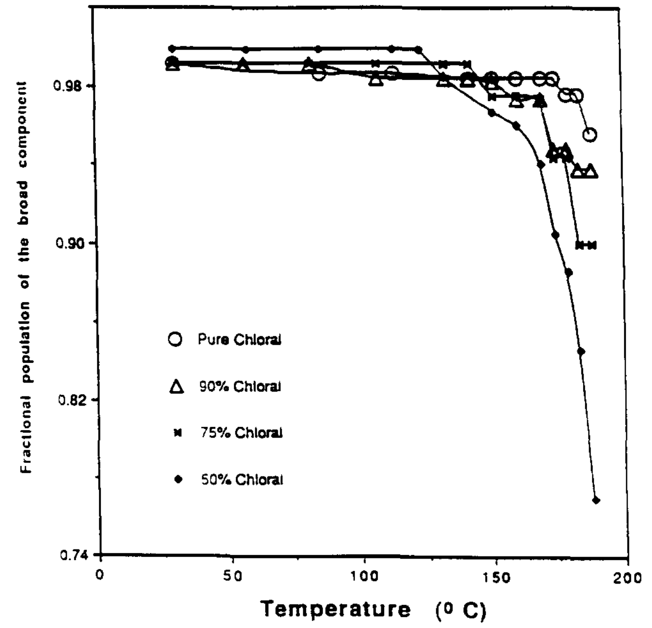

Figure 8 Fractional population of the broad component *versus* temperature based on simulation of the proton lineshapes

gyromagnetic ratio, ω_H is the Larmor frequency, and J is the spectral density. The second moment, S, for pure Chloral-PC[8] is $1.8 \times 10^{-2}\,\mathrm{mT}^2$. A fit of the data in *Figure 3* can be obtained by adjusting the value of the fractional exponent, the apparent activation energy, E_a, and the Arrhenius prefactor of the correlation time τ. In this fit no librational motion was included to simplify the analysis. The parameters of the fit are given in *Table 2*, which are similar though not identical to those given in earlier reports[8].

If an analysis of the $T_{1\rho}$ data for Chloral-PC is to be carried out as PMMA is added in an analogous fashion to the case of adding an ester diluent to d_6-BPA–PC, a lattice description of the polymer blend must be developed. Using the densities of the two polymers[15] and the mass of the repeat unit, a relative volume of the Chloral-PC unit to the PMMA unit can be estimated to be 2.6. If the lattice is constructed to contain one Chloral-PC repeat unit per site, then a site will contain 2.6 PMMA repeat units. The lattice can be visualized in terms of integral numbers of repeat units by defining a lattice site as either two Chloral-PC units or five PMMA units. The weight fraction of the blends can be converted to a fraction of sites occupied by a given type of repeat unit.

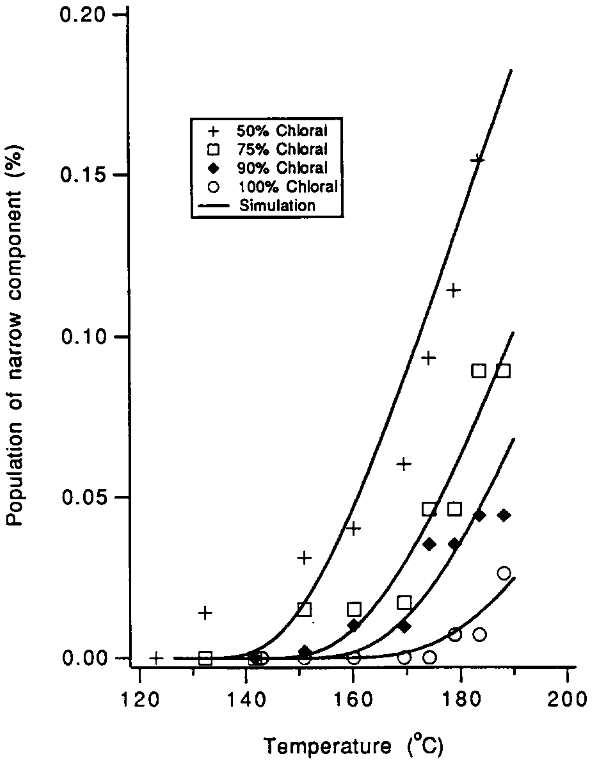

Figure 9 Vogel–Tamman–Fulcher (VTF) fits to the growth of the narrow component of the proton lineshapes with temperature

Let p = fraction of sites occupied by Chloral-PC and d = fraction of sites occupied by PMMA. The fraction of Chloral-PC units, F_i, with i nearest neighbour sites occupied by PMMA can now be calculated for $i = 0$–4:

$$
\begin{aligned}
F_0 &= p^4 \\
F_1 &= 4p^3d \\
F_2 &= 6p^2d^2 \\
F_3 &= 4pd^3 \\
F_4 &= d^4
\end{aligned}
\qquad (5)
$$

To relate these lattice populations to relaxation, the concepts developed for the low-molecular-weight diluent case will be applied. If the Chloral-PC is surrounded by other Chloral-PC units, the relaxation of the unit will be assumed to be unchanged and the associated population is F_0. Antiplasticization of the Chloral-PC will be assumed to occur if one neighbouring lattice site is occupied by PMMA, as was done for the low-molecular-weight system. Antiplasticization is clearly present in the dynamic mechanical response shown in *Figure 4* since the amplitude of the low-temperature loss peak obviously drops faster than the dilution effect as PMMA is added. Also, antiplasticization was identified in deuterium lineshape studies of PMMA/BPA-PC blend[5]. According to the earlier lattice model for low-molecular-weight diluents, the fraction which is antiplasticized is F_1, except this will be reduced by the factor p^3, which accounts for a PMMA site in contact with PMMA sites other than those resulting from chain connectivity.

In the BPA-PC plus diluent case, a new relaxation minimum occurred at a temperature below the position of the minimum associated with π flips. This minimum was identified with BPA-PC units in contact with diluent clusters, i.e. two or more neighbouring diluent units. In such diluent clusters, rotational diffusion of the diluent

Table 2 $T_{1\rho}$ simulation parameters for pure Chloral-PC and Chloral-PC/perdeutero PMMA blends using the lattice model and the stretched exponential correlation function

	Concentration of Chloral-PC			
	100%	90%	75%	50%
Low-temp site				
E_a (kJ mol^{-1})	66.8	66.8	66.8	
τ_∞ (s)	5.2×10^{-20}	5.2×10^{-20}	5.2×10^{-20}	
α	0.14	0.14	0.14	
F_0	1.00	0.73	0.63	$E_a = 79.0$ $\tau_\infty = 7.0 \times 10^{-21}$ $\alpha = 0.09$
High-temp site				
E_a (kJ mol^{-1})	–	80.0	80.0	
τ_∞ (s)	–	1.6×10^{-17}	1.6×10^{-17}	
α	–	0.60	0.60	
F_C	0.00	0.03	0.06	

has been observed[18] and this produces increased mobility in the neighbouring polymer units. In the present system, the polymeric PMMA units do not undergo isotropic rotational diffusion but locally the ester side-group does undergo anisotropic rotational diffusion, producing a mechanical loss peak at around 30°C, well below the T_g. In regions of PMMA clusters, we will assume that the ester group rotation occurs much as it does in bulk PMMA. Consequently, Chloral-PC units near these clusters could be influenced by the PMMA side-group motion at temperatures below the T_g. In fact, at a concentration of 25 wt% PMMA, a minimum appears on the high-temperature side of the usual minimum for π flips, approximately at the temperature where the ester group motion would be at the frequency of the $T_{1\rho}$ experiment, 44 kHz. Thus, the analogy with the low-molecular-weight diluent appears reasonable since the $T_{1\rho}$ data are consistent with the presence of intermolecular cooperativity between the sub-glass transition relaxation processes of the two polymers. The population of Chloral-PC in contact with diluent clusters (in this case, PMMA units) would be $F_2+F_3+F_4$ to which must be added the term $F_1(1-p^3)$, which represents the remaining polymer units in contact with one PMMA unit which happens to be in contact with other PMMA units. The antiplasticized population F_1p^3 is assumed to have no sub-glass transition relaxation. The pertinent lattice populations of various types are shown in *Table 3* for the blend concentrations under consideration.

The second moment in equation (4) arises from intermolecular dipole–dipole interactions so when the nearest neighbour is changed from a protonated Chloral-PC unit to a deuterated PMMA, the second moment should be reduced. The deuterated PMMA units will be treated as having no contribution to the intermolecular dipole–dipole interactions and the value of the intermolecular second moment in Chloral-PC will be assumed to be divided between the four nearest neighbours which are not covalently connected to the reference unit.

All factors for a fit of the $T_{1\rho}$ data have been presented and the resulting simulations are shown in *Figure 3*. Briefly again the Chloral-PC units which are surrounded by other Chloral-PC units are assumed to have the same central correlation time, the same correlation time distribution, and the same activation energy as is observed for the pure polymer. The population of this component is F_0. The antiplasticized component, F_1p^3, is assumed not to appear as a sub-T_g relaxation process. The Chloral-PC units in contact with PMMA clusters, $F_c=F_2+F_3+F_4+F_1(1-p^3)$, are assumed to relax cooperatively with the PMMA side-group motion. The activation energy is set at 80 kJ mol^{-1}, the fractional exponent at 0.6, and the Arrhenius prefactor at 1.6×10^{-17} s, in approximate agreement with the literature[14]. The second moment associated with this process is adjusted for the effects of deuteration. The actual numerical values of the parameters are given in *Table 2*, where F_0 and F_c have been adjusted to produce the fit.

Table 3 The fractional population according to the lattice model

F_i	90% Chloral-PC $p=0.882$ $d=0.118$	75% Chloral-PC $p=0.706$ $d=0.294$	50% Chloral-PC $p=0.444$ $d=0.556$
$F_0=p^4$	0.605	0.248	0.039
$F_1=4p^3d$	0.324	0.414	0.195
$F_2=6p^2d^2$	0.065	0.258	0.366
$F_3=4pd^3$	0.006	0.072	0.305
$F_4=d^4$	0.000	0.007	0.096
$F_1(1-p^3)$	0.102	0.201	0.178

This procedure allows for simulation of the 100, 90 and 75% Chloral-PC data with common dynamic parameters. However, the 50% data cannot be fit by this approach but can be fit as one broad relaxation process with a single activation energy, prefactor and exponent. The activation energy and prefactor are intermediate between the individual component values and the fractional exponent is quite small, indicative of the breadth of the distribution of correlation times.

DISCUSSION

The dynamics of the Chloral-PC in blends with PMMA is fairly closely related to the dynamics in the pure polymer. In both the pure polymer and the blends, the broadened Pake lineshape persists until the glass transition is reached. Above T_g the lineshape is bimodal and the growth of the more mobile narrow component follows the VTF equation, much as it does in the pure polymer, except the onset of the growth of the narrow component commences at lower temperatures.

The sub-T_g relaxation process of the Chloral-PC units also remains quite similar. Since the broadened Pake lineshape persists in the blends, no motion other than some form of phenylene group rotation can occur. The $T_{1\rho}$ minimum associated with the phenylene group is reduced faster than the dilution effect since it is fit with a value of F_0, which is smaller than the weight or volume fraction of Chloral-PC. On the other hand, the value of F_0 used to fit the data is larger than that estimated from the lattice model and random mixing, especially at higher PMMA concentrations. Our explanation for the discrepancy between the lattice model estimates and fitting results is that there are fewer Chloral-PC contacts with PMMA than random mixing predicts at higher concentrations of PMMA. The probe of contacts is very local, the flipping of the phenylene groups, and mixing at this scale is not random at concentrations higher than about 10% PMMA. This may reflect the connectivity of the PMMA chain which was not included in the lattice model or there may simply be less than random mixing on a very local distance scale. At low concentrations of PMMA, contacts with Chloral-PC appear to be reasonably well estimated, which is in agreement with the results of ^{13}C spin-diffusion studies in another blend system[17]. Modelling of dynamics at the glass transition with the lattice model in blends has been successful at higher concentrations[21] but the distance scale may be larger for segmental motion at the glass transition than for π flips.

Those Chloral-PC units that are surrounded by other Chloral-PC units relax as they do in the pure polymer and account for most of the observed relaxation. A new relaxation process, most easily noted in the 75 wt% Chloral-PC data, appears at higher temperatures and can be correlated with the time scale and energetics of the PMMA ester side-group motion. The two minima used to fit the $T_{1\rho}$ data are shown separately in *Figure 10*. The motion of Chloral-PC units on the time scale of the PMMA ester group rotation is a clear

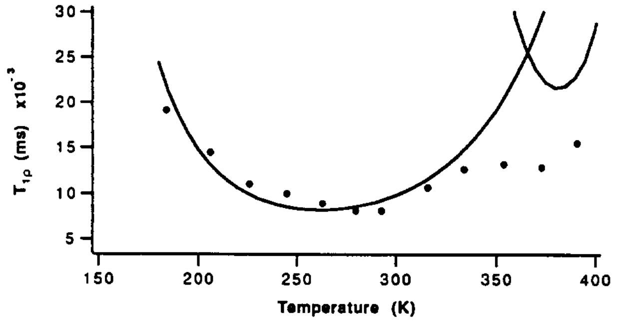

Figure 10 The two $T_{1\rho}$ minima used to simulate the 75% Chloral-PC data

identification of intermolecular cooperativity in sub-T_g relaxation behaviour which is generally difficult to identify though definitely absent in another related case[4]. The intermolecular cooperativity in this blend system is rather like that observed for BPA-PC and the low-molecular-weight diluent DBP and can be semiquantitatively analysed in a similar fashion. As mentioned earlier, the population of Chloral-PC contacts with PMMA is underestimated so that F_c is a smaller number than is produced by the lattice model assuming random mixing.

In the analysis of the $T_{1\rho}$ minimum in the BPA-PC plus the low-molecular-weight diluent, the activation energy of the BPA-PC minimum associated with repeat units surrounded by other BPA-PC units increased. This was interpreted as a selective suppression of the motion of the most mobile units in the inhomogeneous distribution of correlation times describing the π flip process. In the case of Chloral-PC antiplasticized by PMMA, there is no corresponding increase in the activation energy of the π flips of the units surrounded by other Chloral-PC units. Apparently during glass formation, PMMA is less effective at filling the high free-volume regions associated with the more mobile phenylene groups in the glass. This view is in general agreement with the lattice model interpretation being developed which repeatedly shows less effective mixing of the polymeric system relative to a low-molecular-weight diluent. The high free-volume regions associated with more mobile phenylene groups are probably very small, of the size of the phenylene unit; failure of PMMA to fill these regions may simply reflect the inability of the polymeric antiplasticizer, PMMA, to be preferentially positioned in those particular localized regions. The greater mobility of the low-molecular-weight diluent during the formation of the glassy film may allow it to fill more of the small, high free-volume regions usually associated with more mobile phenylene units.

Polymeric blends show reduced antiplasticization effects relative to the addition of low-molecular-weight diluents in a number of experiments. Significant densification is observed when low-molecular-weight diluents are added to polymeric glasses[22] while only slight negative deviations from volume additivity are observed in miscible polymer blends[16,23]. Similarly, gas permeability is greatly reduced upon the addition of low-molecular-weight diluent[22] and only small negative deviations are observed in the case of polymer blends[16,23]. Excess specific volume correlates with these differences while the suppression of low-temperature mechanical loss peaks associated with the motion of phenylene groups[24] correlates with a decrease in fractional free volume upon the addition of low-molecular-weight diluent. The n.m.r. data presented here are consistent with these macroscopic measurements in that both show less manifestations of antiplasticization in polymer blends relative to polymer diluent systems. The explanation suggested for all of these observations is the reduced ability of a polymeric additive to fill local high free-volume regions relative to low-molecular-weight diluents because of chain connectivity even if a favourable interaction between the components exists in both cases.

The concepts of plasticization and antiplasticization of the Chloral-PC dynamics upon addition of PMMA gives a satisfactory context for discussing the relaxation of the 90 and 75% Chloral-PC blends relative to pure Chloral-PC. However, the 50% blend is not well described by this approach but is better viewed as a single broad relaxation process. This seems reasonable since this system can no longer be viewed as particularly closely related to pure Chloral-PC because both components are present in equal amounts by weight and Chloral-PC is actually the minor component on a volume basis. A merging of the sub-T_g processes of the two components appears to be the best description although this view is developed by considering only the PC motion.

The factors that lead to a coupling of sub-T_g relaxations are not clear from this work; since cases where no coupling is observed have been reported, it would be helpful to understand more about the factors which produce the differences. In the system just studied, it would also be important to monitor the ester group motion of the PMMA in the blends to see if cooperative dynamics can be identified from this viewpoint. Of course, other blends where both components have low-temperature relaxation processes could also be informative. N.m.r. experiments are useful in the study of this problem since mechanical and dielectric data often cannot clearly separate the relaxation behaviour of each of the component polymers in the blend. One could argue for the presence of cooperativity in the mechanical response data on the Chloral-PC/PMMA system, but without the n.m.r. data and isotopic labelling, direct identification of motional contributions is difficult.

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