Compatibility in polymer blends of poly(vinyl acetate) and poly(methyl methacrylate) studied by nuclear magnetic relaxation

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The nuclear magnetic relaxation times T_1 and $T_{1\rho}$ were measured as a function of temperature and composition in blends of poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVAc) prepared from benzene solutions. For temperatures in the solid state at which the reorientations of the α-methyl groups in PMMA cause minima in T_1 and $T_{1\rho}$, the multicomponent relaxation behaviour was discussed in terms of spin diffusion. The diffusion lengths were estimated using a simple multiphase model and correspond to dimensions of domains of the order of 20 nm. After annealing, an irreversible phase separation was observed. The results discussed are supported by additional studies.

INTRODUCTION

The compatibility of different polymers on a molecular level is usually defined by taking into account that the macromolecular chains are mutually interpenetrating. Bohn[1] termed such systems 'one-phase molecular homogeneous mixtures'. Generally the decision about compatibility depends on the experimental methods applied. For investigations of polymer blends, structural methods (wide angle X-ray scattering, small-angle X-ray scattering, neutron scattering, light scattering, electron microscopy, dynamical methods (mechanical, dielectric, nuclear magnetic resonance) or thermodynamic methods are preferentially used[2,3]. The detection of heterogeneous areas (generally termed 'domains') depends on many facts, caused by the peculiarities of the methods applied, the measuring conditions and the preparation of the blends. Therefore, the results of different experiments on the same blended systems are frequently contradictory.

Especially for our case, where the polymer blends contain the chemically similar polymers poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVAc), the results published up to now show no clear statements concerning compatibility. Singh and coworkers[4] presented results of ultrasonic studies in PMMA–PVAc blends prepared from toluene solutions. They concluded from the linear behaviour of the ultrasonic velocity that, for a wide composition range, compatibility exists in their blends; but only for PMMA contents higher than 70 wt% is a favoured aggregation of PMMA domains supposed, leading to a heterogeneous blend structure.

However, their discussions are limited to domains of dimensions larger than 100 nm. They supported their

results by electron microscopy. In contrast to this reference, Sobliovschi and coworkers[5] indicated no compatibility in the same polymer blend system prepared from tetrahydrofuran (THF) for contents of PVAc lower than 40 wt%. From their thermogravimetric studies they concluded a so-called 'chain pseudo-compatibility' for PVAc concentrations greater than 40 wt%, which shows a maximum at a composition 80/20 PVAc/PMMA.

A very interesting effect was found by Ichihara and coworkers[6], who prepared transparent PMMA–PVAc blends by a freeze-drying technique. In differential scanning calorimetry (d.s.c.) experiments these blends showed only one glass transition, a characteristic indication of compatible polymer blends. However, after annealing of the blends at 400 K, two glass transitions were detected corresponding to the glass transitions of the homopolymers. The authors explained this by demixing of the frozen non-equilibrium state at temperatures higher than the glass transition temperatures of PMMA and PVAc. As a supplement to dynamic mechanical experiments, Jenckel and coworkers[7] carried out refractometric studies. They prepared transparent foils from chloroform solutions with compositions of 70/30 and 50/50 PMMA/PVAc. In spite of good transparency for both kinds of investigation, two separate glass transitions near the glass transition temperatures of PMMA and PVAc were observed.

In view of the conflicting data, the present studies are intended to give some insight into compatibility in solid blend systems of PMMA and PVAc prepared from solutions of benzene using methods of nuclear magnetic resonance. We obtained no successful results in solid ^{13}C cross-polarization n.m.r. and in free induction decay (FID) studies. Therefore we preferred studies of ^{1}H

relaxation in the laboratory frame (T_1) and in the rotating frame $(T_{1\rho})$, including the effect of spin diffusion. In particular, the dominant activity of the ^1H nuclei of α-methyl groups of PMMA (α-CH$_3$) in low-temperature relaxation opens the possibility to use spin diffusion more quantitatively. In this way it is also possible under favourable circumstances to estimate characteristic lengths corresponding to structural dimensions.

BASIC PRINCIPLES

Numerous papers have dealt with investigations of heterogeneous structures in polymers using different n.m.r. methods. In our special case of polymer blends the usefulness of n.m.r. relaxation experiments for the indication of domain structures was demonstrated for the first time by Kwei and Nishi[8,9] in blends of poly-(vinyl methyl ether)–poly(styrene) and by McBrierty[10] in blends of poly(methyl methacrylate)–poly(styrene-*co*-acrylonitrile).

Two fundamental aspects of these relaxation experiments are important[11–13]:

(i) the short-range nature of the dipole–dipole interaction between magnetic moments of spins; and
(ii) the efficiency of spin diffusion in solid polymers at low temperatures, which causes the transport of spin energy (magnetization) over lengths of some nanometres $(T_{1\rho})$ up to some tens of nanometres (T_1).

Recently, numerous papers have been published on the problem of n.m.r. studies for clarifying structural aspects in heterogeneous polymer systems including fundamental issues of spin diffusion; see for instance Packer[14,15], Stejskal[16], Cheung[17,18], Linder[19], Tanaka[20–22] and Caravatti[23]. In the present work the results are analysed following the concepts in ref. 10. The dominant influence of spin diffusion on the relaxation times T_1 and $T_{1\rho}$ makes it possible to estimate dimensions of molecular heterogeneities. In particular, in blend systems consisting of PMMA and PVAc, the α-CH$_3$ groups of PMMA act as relaxation sinks at low temperatures, and can also influence the relaxation of all protons in PVAc via spin-diffusion coupling.

In nuclear relaxation in solids by spin diffusion, two limits can be distinguished, which play an important role for quantitative descriptions[24,25]: diffusion-limited relaxation and rapid spin diffusion. In the case of a two-phase spin system (A, B), the following conditions must be fulfilled:

rapid spin diffusion

$$T_k^A \gg T_k^B \gg t_s^A \qquad (1)$$

diffusion-limited relaxation

$$T_k^A \approx t_s^A \qquad T_k^B \approx t_s^B \qquad (2)$$

Here the spin-diffusion times are $t_s^{A,B} \approx L_{A,B}^2/D_s^{A,B}$; $(T_k^{A,B})^{-1}$ are the relaxation rates in A and B, and index k refers to 1 or 1ρ; $D_s^{A,B}$ are the spin-diffusion coefficients; $L_{A,B}$ are the spin-diffusion path lengths; and A, B are the relaxation regions.

In n.m.r. relaxation experiments a multicomponent relaxation function $S(t)$ can be observed in the latter case:

$$S(t) = S_0[p^A \exp(-t/T_k^A) + p^B \exp(-t/T_k^B)]$$

where the relative signal intensities p^A and p^B correspond to the numbers of nuclei in the relaxation areas.

Only an averaged single-exponential relaxation function is observed in the former case:

$$S(t) = S_0 \exp(-t/T_k^{av})$$

where the averaged relaxation time T_k^{av} is a function of intrinsic relaxation times T_k^A and T_k^B and of the relative proton intensities:

$$(T_k^{av})^{-1} = p^A/T_k^A + p^B/T_k^B \qquad (3)$$

If the conditions of equations (1) and (2) are not strictly fulfilled, then the parameters of the relaxation functions have more complicated relationships and well defined conclusions are problematic.

Because the efficiency or inefficiency of spin diffusion is affected strongly by the relation of relaxation times to spin-diffusion times, the morphology of spin-diffusion regions (including sizes and spatial dimensions) is an important aspect in this field. If it is possible to follow the relaxation time–spin-diffusion times–diffusion path length–domain size relations, the dimensions of heterogeneous morphological units can be estimated.

In our case we find obviously an intermediate case between 'rapid spin diffusion' and 'diffusion-limited relaxation', i.e. the relation between T_k and t_s does not satisfy equations (1) or (2). Because of lack of other exact relations we assume $t_s \approx T_k$ and use it for estimating the mean-square diffusion path length $\langle L^2 \rangle = 6t_s D_s$, where the spin-diffusion coefficient D_s is correlated to $D_s \approx \langle l_0^2 \rangle / T_2$ (ref. 26). The mean distance $\langle l_0^2 \rangle^{1/2}$ and the time rate T_2^{-1} correspond to the jump length between neighbouring spins (approximately C–C distance in polymers) and to the flip-flop rate of spin energy exchange, respectively. With typical values for T_2 in solid PMMA and PVAc ($T_2(^1H) = 12\,\mu s$, $l_0 = 0.11$ nm), the value of D_s is about $10^{-15}\,m^2\,s^{-1}$.

Additionally, the spin-diffusion coefficient is also influenced by interfaces and other diffusion barriers. Only in special cases can the different effects be separated, for example in well defined block copolymers[21].

The following discussion of our experimental results is more qualitative, because no very regular morphologies exist and information about characteristic scales of inhomogeneities is missing. Nevertheless, if the microscopic spatial dimensions are of the order of 1–10 nm, the $T_{1\rho}$ and T_1 measurements can reflect some characteristics.

EXPERIMENTAL

The proton relaxation times T_1 and $T_{1\rho}$ were measured on a Bruker SXP 4-100 spectrometer operating at 88 MHz. The spin–lattice relaxation times T_1 in the laboratory frame and $T_{1\rho}$ in the rotating frame were determined by the common pulse sequences $(\pi)_x$–τ–$(\pi/2)_x$ and $(\pi/2)_x$–$(B_1(\tau))_y$, respectively. The strength of the spin-locking field B_1 was 1 mT, corresponding to an effective frequency $f_1 = 42$ kHz. The signal-to-noise ratio was estimated to be better than 100 for all experiments. The relaxation times and relative intensities of the individual components of the total multicomponent relaxation function were calculated by a least-squares fit program realized on a MC-80 microcomputer. Errors of the experimental data are less than 10% for the longest component and less than 25% for the shortest one. The blends were prepared from commercial polymers:

Table 1 Characteristic data of the homopolymers PMMA-SP90 and PVAc-SP60

	α_{synd}^{a}	ρ (g cm^{-3})	M_w (g mol^{-1})	M_n (g mol^{-1})	T_g (K)
PMMA	0.80	1.18	58 000	42 000	378
PVAc	0.45	1.18	317 000	95 000	306

^{a} The degree of syndiotacticity was determined by ^{13}C and ^{1}H high-resolution n.m.r.
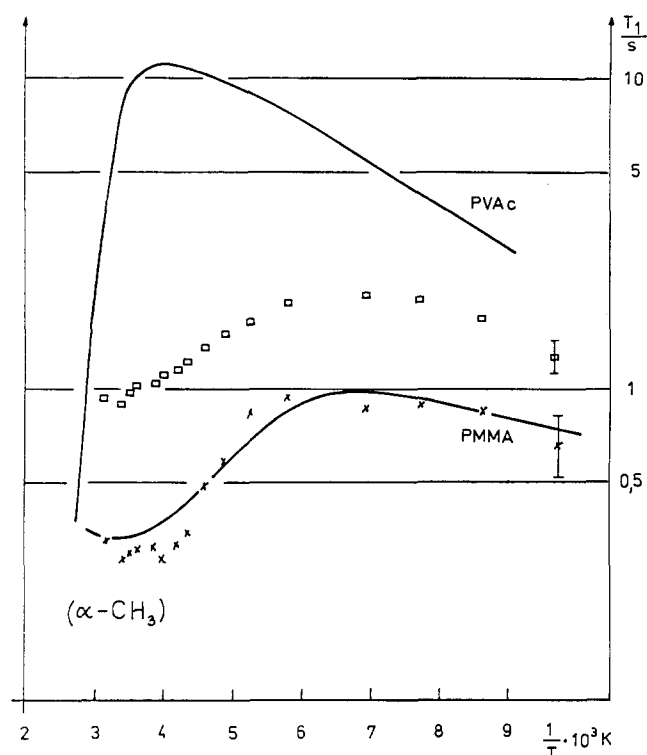
Figure 1 Temperature dependence of spin–lattice relaxation time T_1 for PMMA, PVAc and blend 50/50 PMMA/PVAc: (□) long component and (×) short component of biexponential relaxation in the blend

PMMA-SP90 (VEB Stickstoffwerk Piesteritz) and PVAc-SP60 (VEB Chemische Werke BUNA). Some characteristic data of these polymers are shown in *Table 1*.

Blend foils were obtained from 2 wt% solutions in benzene by drying at 330 K under low vacuum. After that, the transparent foils of about 300 μm thickness were sealed in glass tubes for n.m.r. measurements under high-vacuum treatment for 24 h. The residual content of solvent was smaller than 2%, as indicated by ^{13}C high-resolution n.m.r. The two homopolymers were prepared in the same manner to avoid preparation effects. Note that the compositions of blends is given in proton per cent (p%) for a more direct comparison with the signal intensities of the individual relaxation components. The mass ratio of the two components was determined from the ratio of protons by:

$$\frac{m^A}{m^B} = \frac{p^A}{p^B} \frac{k^B}{k^A} \frac{M^A}{M^B}$$

where $M^{A,B}$ are the relative molecular masses and $k^{A,B}$ the proton numbers of a single monomer unit in the components A or B, respectively. This yields:

$$\frac{m^{\text{PMMA}}}{m^{\text{PVAc}}} = 0.872 \frac{p^{\text{PMMA}}}{p^{\text{PVAc}}}$$

RESULTS

Temperature dependence of relaxation times T_1 and $T_{1\rho}$

The temperature dependences of T_1 and $T_{1\rho}$ for the two homopolymers PMMA and PVAc and the blend 50/50 PMMA/PVAc are shown in *Figures 1* and *2*. The broad minima observed for PMMA in T_1 relaxation at 280 K and $T_{1\rho}$ relaxation at 160 K correspond to molecular reorientations of α-methyl groups. For a more detailed study of the α-CH$_3$ relaxation in PMMA we have realized T_1 measurements at different frequencies. In *Figure 3* a transition map is presented incorporating our own results and also results from the literature[27]. We calculated the activation energy for the methyl group reorientations using an Arrhenius equation and obtained a value of 25 kJ mol^{-1}, which agrees with values from the literature[28]. The wide temperature regions of the minima are mainly caused by differences in mobility of α-CH$_3$ groups in syndiotactic and isotactic sequences in the macromolecules. The influence of this configurational effect on the position and width of the minima was detected by means of ^{1}H and ^{13}C solid-state n.m.r. pulse experiments on special PMMA samples[29,30]. In *Figure 1* T_1 relaxation time *versus* reciprocal absolute temperature is presented for the 50/50 blend. Whereas the short component analysed from the biexponential relaxation behaviour corresponds to the dependence of pure PMMA, the slowly relaxing component shows substantial deviation from that of PVAc. Furthermore, the experimental relative intensities of the short p_s (~ 0.20) and long p_l (~ 0.80) components presented in *Figure 4* disagree with the values of composition over the whole temperature range. Both effects manifest the influence of spin diffusion on spin–lattice relaxation, as can be seen in more detail
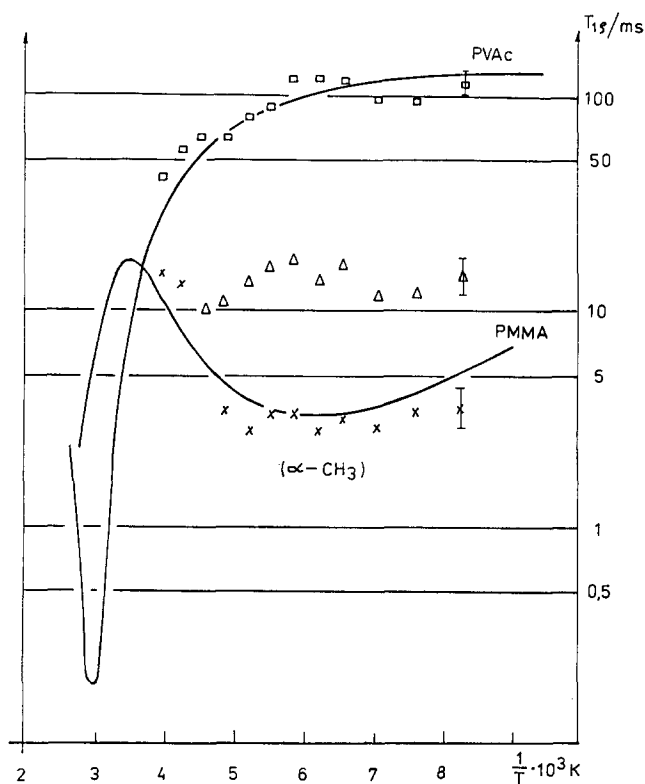
Figure 2 Temperature dependence of $T_{1\rho}$ for PMMA, PVAc and blend 50/50 PMMA/PVAc: (□) long, (△) medium and (×) short components analysed from the three-exponential relaxation function in the blend
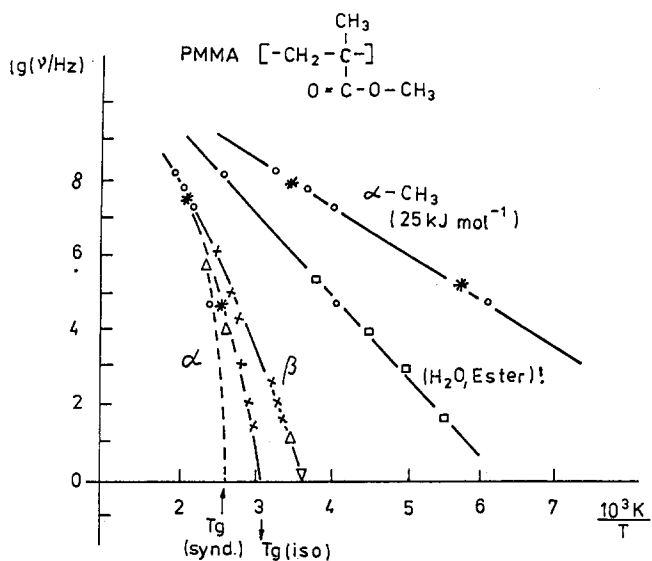
Figure 3 Arrhenius plot of PMMA: (O) our n.m.r. studies and (↑, ↓) d.s.c. measurements; along with results from the literature[27] ((*) n.m.r., (×) dielectric, (△) mechanical relaxation, (▽) T_g and (□) mechanical studies)
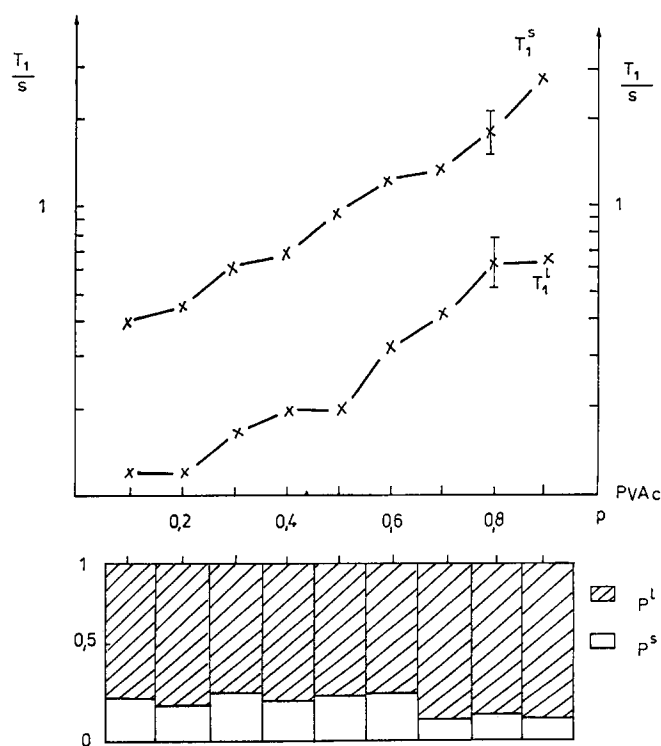

Figure 4 T_1 relaxation times as a function of composition in PMMA–PVAc blends measured at 280 K (α-methyl minimum); and a histogram of relative intensities of the short (p^s) and long (p^l) components

in the following subsection. In *Figure 2* the temperature dependence of $T_{1\rho}$ is shown for the same samples as in *Figure 1*. Because of the smaller effective frequency in $T_{1\rho}$ experiments (42 kHz) compared to T_1 experiments (88 MHz), the active relaxation processes are shifted to lower temperatures. Therefore the characteristic α-methyl minimum appears at 160 K and the minimum at 335 K reflects the dynamic glass transition of PVAc[31]. In contrast to the T_1 relaxation function, we analysed a three-component relaxation with long, medium and short components for T_1. Apparently this behaviour is generated

by domains of PVAc and PMMA that are relatively unaffected by spin diffusion (see relaxation times in *Table 2*). Compared to the short and long components of the relaxation function, the medium one can be caused either by boundary phases between PVAc and PMMA domains containing both kinds of macromolecules or by the effect of spin diffusion between neighbouring domains. In the former case the changed relaxation time $T_{1\rho}^m$ of the medium component has to be attributed to changed molecular mobility in this mixing phase, but in the latter case spin-diffusion coupling at the boundaries of domains would cause an averaged relaxation behaviour dependent on the parameters of spin diffusion presented above under 'Basic principles'. This problem will be discussed later.

Dependence of relaxation times T_1 and $T_{1\rho}$ on blend composition

In *Figure 4* the dependence of T_1 on the content of PVAc in the blend is shown. The composition varies from 90/10 to 10/90 PMMA/PVAc in steps of 10 p%. Note that the relaxation times of both components (T_1^s, T_1^l) increase over the whole range with increasing content of PVAc, but even for the highest concentration of PVAc in the blend the time of the long component is far below T_1 of homo-PVAc (~ 12 s). The biexponential T_1 relaxation for all compositions indicates relaxation regions averaged incompletely by spin diffusion, otherwise only a single exponential relaxation according to equation (3) would be observed. We explain this behaviour by a simplified diffusion model (*Figure 5*). It is demonstrated that some of the PMMA protons interact with the PVAc protons and the relaxation behaviour of the whole blend is strongly influenced by the action of spin diffusion. For details, see below and Appendix. Similarly in *Figure 6* the dependence of $T_{1\rho}$ relaxation times on the content of PVAc in the blends is shown.

For nearly the whole composition range except 90/10 PMMA/PVAc the relaxation function was analysed by a

Table 2 Relaxation times of the homopolymers compared to those determined from the multicomponent relaxation functions in the blend 50/50 PMMA/PVAc at temperatures of the minima for α-methyl relaxation in PMMA (the composition 50/50 and the relative intensities of components given in parenthesis are presented in proton per cent)

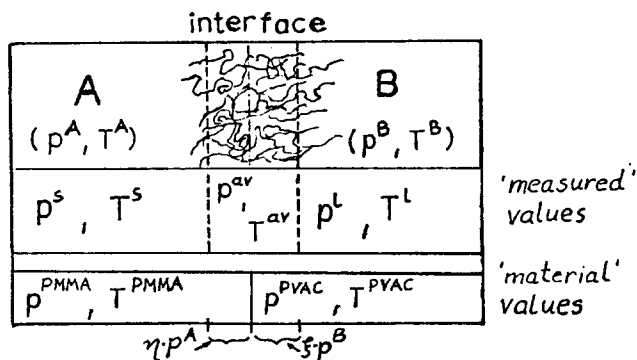|	PMMA	PVAc	Blend 50/50 PMMA/PVAc
T_1 (s)	0.32	11.3	0.20 (20), 0.68 (80)
$T_{1\rho}$ (ms)	3.2	102	2.3 (25), 13 (33), 98 (42)

Figure 5 Schematic three-region model for n.m.r. relaxation influenced by spin diffusion in PMMA–PVAc blends
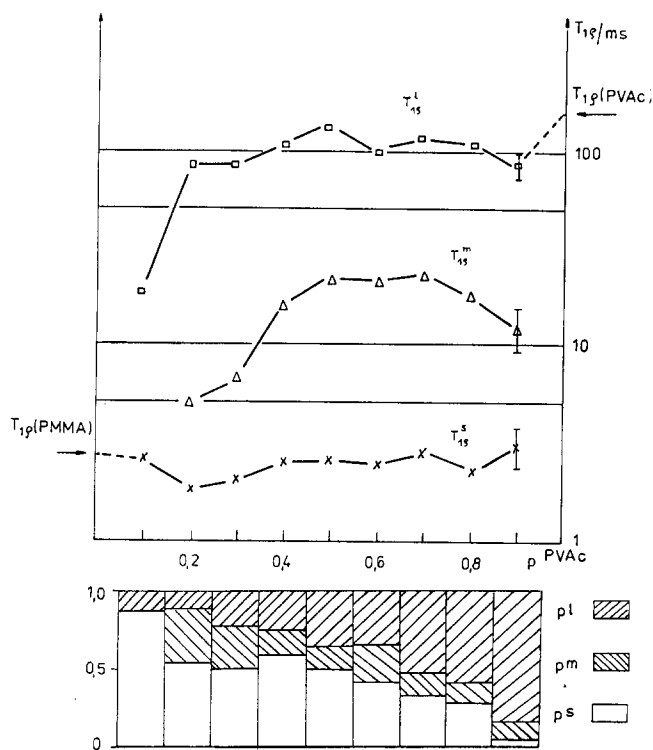
Figure 6 $T_{1\rho}$ relaxation times as a function of composition in PMMA–PVAc blends at 160 K (α-methyl minimum); and a histogram of relative intensities of the short (p^s), medium (p^m) and long (p^l) components analysed from the three-exponential relaxation function

three-component superposition. Already in the previous subsection the three-component relaxation was explained on the assumption that three different relaxation regions correspond to domains of PMMA and PVAc and to interfacial regions. The relative intensities of the components depend on the composition in a characteristic manner as shown by the histogram in *Figure 6*. The intensity of the long component p^l increases with higher PVAc content in blends whereas the intensity of the short component p^s, generated by unmixed PMMA macromolecules, decreases.

In contrast to this, the intensity of the medium component in $T_{1\rho}$ relaxation p^m is in the range of about 15–20p% for all concentrations. A detailed discussion of the $T_{1\rho}$ dependence of blend composition will follow later.

DISCUSSION

To obtain more insight into the character of the morphological arrays we examined the blends on a scanning electron microscope without special preparation of the blend samples. But because the electron density distributions in the two polymer components were very similar, no clear structural characteristics could be observed in the micrographs. Therefore, we have no direct information about the expected domains with regard to size and shape. Only small-angle X-ray scattering showed little effects of heterogeneous structures indicated by a slight step in the scattering curve (*Figure 7*). The examination of the dimensions corresponding to these heterogeneities gives values in the range from 20 to 40 nm.

Notwithstanding the absence of well defined structural data, we have established the spin-diffusion length quantitatively by using the ideas above under 'Basic

principles' to estimate domain dimensions. The basis of our considerations is the model shown in *Figure 5* and derived in the Appendix. The model was developed to describe the relaxation behaviour of two coupled spin systems whereby the spin diffusion under certain conditions masks the individual relaxation in the two initial systems.

In our case, for both T_1 and $T_{1\rho}$ relaxations, PMMA represents the fast-relaxing component with α-methyl groups acting as 'relaxation sinks' and that is why we expect the influence of spin diffusion at first on the relaxation in PVAc, i.e. a magnetization transfer from PVAc protons to the α-methyl protons in PMMA. As seen before in the case of T_1 the individual relaxation behaviour of PVAc is completely changed ($T_1^{PVAc} \neq T_1^l$, $p^{PVAc} \neq p^l$).

We assume that the whole PVAc spin system is influenced by spin diffusion, whereby the magnetization flow is directed to PMMA macromolecules that remain at the interfacial regions between the domains. Taking into consideration the ideas above, and the intrinsic relaxation time for PVAc of about 10 s, the domain size of PVAc can be estimated to be of the order of 100 nm. This value is an upper limit of domain dimensions since the relaxation time in non-blended PVAc is an upper time for spin diffusion. The final test of this model is demonstrated in *Figure 8* using equation (A.4). The left-hand side of equation (A.4) contains only values of the homopolymers and the blend composition (broken line), whereas the right-hand side (abbreviated by PLOT) also contains measured values of the blends (T_1^l, p_s). The good agreement for blends with predominant content of PMMA is apparent. The deviations between the calculated results (broken line) and the experimental points with increasing content of PVAc can be explained by increasing domain sizes. Obviously, the relaxation time is not long enough for the diffusion to transport all magnetization through the PVAc domains to the phase boundaries. In the same manner as for the spin–lattice relaxation component T_1^l the PLOT data were calculated for the short component T_1^s, but for all compositions great differences exist between calculated and experimental data. This is not surprising because the predominant α-methyl relaxation concurs with spin diffusion and a more complex relaxation behaviour including the interfacial structure must be considered.

In contrast to T_1 data the $T_{1\rho}$ relaxation shows two uninfluenced components corresponding to domains of PMMA and PVAc, following from the short-range nature of spin diffusion in $T_{1\rho}$ relaxation, and a third
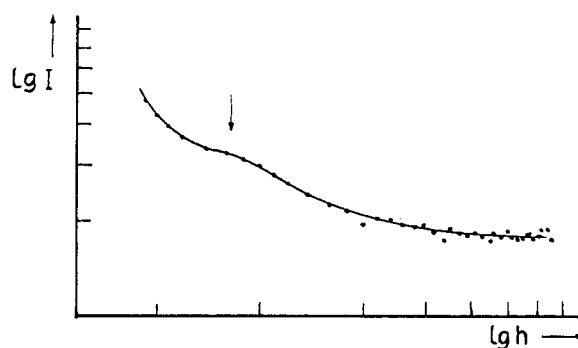

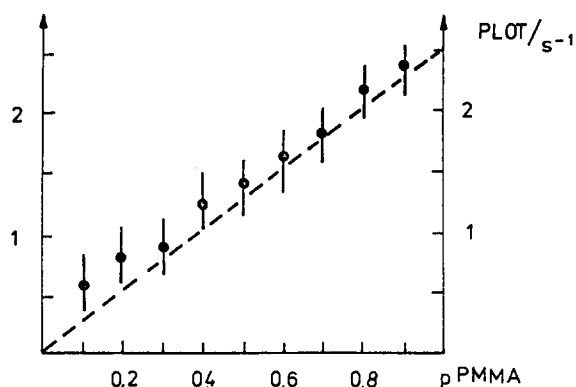**Figure 7** X-ray scattering curve for the blend 50/50 PMMA/PVAc

Figure 8 T_1 data for PMMA–PVAc blends; the broken line assumes strong coupled spin diffusion in the slowly relaxing component T_1^l (see text and Appendix)

component with an intermediate relaxation time. In the same manner as before for the long component of T_1 relaxation we estimated a lower limit for PVAc domains of about 10 nm. However, a test procedure based on equation (A.5) and the values of $T_{1\rho}^m$ failed, and it was not possible for this failure to be due to the effect of spin diffusion only. Therefore we assume that spin diffusion is not dominant and the difference between the experimental value $(T_{1\rho}^m)$ and the calculated value based on equation (A.5) may be due to the inadequacy of the theory formulated above under 'Basic principles' and in the Appendix. Presumably structural aspects in the sense of interpenetrating parts of macromolecules of PMMA and PVAc in interfacial regions must be considered too in the $T_{1\rho}$ relaxation theory.

If we consider the relative proton intensities of the compositions, analysed with superposition of three exponentials, we note that the medium component p^m only changes between about 15 and 20p% (*Figure 6*). From these data and the composition of blends, the relative content of PMMA and PVAc in this relaxing (mixing) phase was calculated and it was found that virtually only PVAc was involved in it. Consequently we support a blend morphology with separated domains of PVAc and PMMA with only isolated molecular contacts between them, which are responsible for the spin diffusion. The dimensions of the domains depend on the composition of the blends, and range from about 10 nm to more than 100 nm.

This picture is supported by differential scanning calorimetric studies. In general it is well accepted that the appearance of a single composition transition is adequate evidence of a single homogeneous amorphous phase. However, it does not imply a thermodynamic equilibrium state in every case, e.g. in rapidly freeze-dried PMMA–PVAc blend[6]. However, if two separated glass transitions near the transition of the homopolymers can be observed, separated domains on the scale of thermal fluctuations of a few nanometres exist. That is the case in our blends, as can be seen in *Figure 9* for the composition 50/50 PMMA/PVAc.

Recently we have performed some additional experiments with annealed blends prepared as described above, with blends prepared from toluene solutions and blends prepared by precipitation in cyclohexane from benzene solutions. After annealing for some hours at 150°C, effects of phase separation in the blends were detected. The analysis of spin–lattice relaxation separated into two components shows about the same values of the relaxation

times T_1 and of the relative intensities compared to the corresponding values for the pure polymers.

Analogous effects were observed with an annealing time of 24 h but at different temperatures. For annealing temperatures higher than 105°C the relaxation function is a superposition of the relaxation functions of the pure components, but separation begins already at 75°C. Similar results were obtained for $T_{1\rho}$ relaxation. Therefore we assume that the molecular contacts between PMMA and PVAc are caused only in interphase regions predominantly containing PVAc macromolecules. For temperatures higher than the glass transition temperature of PVAc (33°C) but lower than that of PMMA (105°C), phase separation (segregation) begins by macromolecules of PVAc slowly diffusing away from the interphases directed to PVAc domains. As tentative results obtained on precipitated blends and blends prepared from toluene solutions, the following results are consistent with these observations:

(a) In the precipitated blend foils, similar relaxation functions in T_1 and $T_{1\rho}$ experiments were measured, but the values of relaxation times and of the relative intensities were different from the values of the non-precipitated blends discussed in this paper. Especially the relative intensities of the short and long components as functions of the composition indicate a morphology where the contacts between domains of PVAc and PMMA are generated by macromolecules of PMMA, which are favoured in the interface regions. A first calculation assuming spin diffusion supports this picture.

(b) In contrast to the blends prepared from benzene solutions, the blends produced from toluene solutions by casting show a more averaged relaxation behaviour. The relaxation functions could be fitted by only one T_1 and two $T_{1\rho}$ components. This means that, on the scale of spin diffusion in T_1 of about 20 nm, fast spin diffusion between the domains of PVAc and PMMA is favoured based on a tight coupling between the two polymer spin systems.

Apparently in toluene solutions other specific interactions make possible smaller sizes of domains and a higher level of compatibility. This was also found in ultrasonic studies[4].

CONCLUSIONS

We have performed extended n.m.r. relaxation experiments to measure the spin–lattice relaxation time T_1 and the relaxation time $T_{1\rho}$ on blends of PMMA and PVAc prepared from benzene solutions by casting. The multicomponent relaxation functions indicate heterogeneous relaxation regions in T_1 and $T_{1\rho}$. Using a simple spin-diffusion model, diffusion path lengths could be
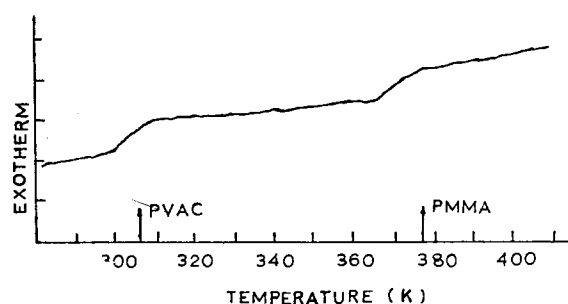

Figure 9 D.s.c. curve for blend 50/50 PMMA/PVAc measured by means of Perkin–Elmer apparatus DSC-2B

estimated corresponding to dimensions of domains of PVAc of the order of 10 nm and above.

The molecular contacts between the domains of PVAc and PMMA are caused by interfacial effects where macromolecules of PVAc are predominant in this interface. The incompatibility of our blends at the molecular level is confirmed by d.s.c. studies.

The interfacial molecular contacts that affect the spin diffusion between the different domains are unstable and dependent on thermal treatment. After annealing at temperatures higher than the glass transition temperature of PVAc, segregation of domains was detected by analysis of the relaxation functions in terms of the pure polymer components. Recent studies on blends prepared from toluene solutions show more compatible blends, and the question remains which specific molecular interactions are responsible for the changed morphology in blends of PMMA and PVAc.

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APPENDIX

Corresponding to equation (3) one can calculate a relaxation time averaged by spin diffusion:

$$(T^{av})^{-1} = (N^A/N^t)(T^A)^{-1} + (N^B/N^t)(T^B)^{-1} \quad (A.1)$$

with T^A, T^B the intrinsic relaxation times T_1 or $T_{1\rho}$ in the regions A and B, N^A, N^B, N^t the number of spins in the two regions influenced by spin diffusion and their total number, respectively, and T^{av} the averaged relaxation time by spin diffusion.

Now we assume the following schematic phase model as shown in *Figure 5*, where there are different intensities of the measured values (p^s, p^l, p^{av}) determined from the multiexponential relaxation function, and the 'material' values p^A and p^B depend on the two molecular phases A and B, with p^s, p^l, p^{av} the relative intensities of the short, long and averaged component analysed from the three-exponential relaxation function, and T^s, T^l, T^{av} the corresponding relaxation times of the components, respectively.

The relative numbers of spins in the regions A and B influenced by spin diffusion are related to the terms ηp^A and ξp^B. If we apply the relations:

$$N^A \sim \eta p^A \qquad N^B \sim \xi p^B \qquad N^A + N^B = N^t$$

$$p^A + p^B = 1 \qquad \eta p^A + \xi p^B = p^{av} \qquad p^s + p^l + p^{av} = 1 \quad (A.2)$$

then it follows from equation (A.1) that:

$$(\eta p^A + \xi p^B)(T^{av})^{-1} = \eta p^A (T^A)^{-1} + \xi p^B (T^B)^{-1}$$

and with relations from (A.2) that:

$$p^A(1/T^A - 1/T^B) = (1/T^{av} - 1/T^B) + p^s(1/T^A - 1/T^{av})$$
$$+ p^l(1/T^B - 1/T^{av}) \quad (A.3)$$

If the two experimental relative intensities p^l and p^s in equation (A.3) are zero, then only a single-exponential averaged relaxation analogous to equation (3) can be detected. However, if only $p^l = 0$ the relaxation behaviour of one component is masked completely by spin diffusion. This case is assumed for the T_1 relaxation in our blends with the following relations: PMMA = A, PVAc = B, $T^{av} = T_1^l$.

Consequently the final equation is:

$$p^{PMMA}(1/T_1^{PMMA} - 1/T_1^{PVAc}) = 1/T_1^l - 1/T_1^{PVAc}$$
$$+ p^s(1/T_1^{PMMA} - 1/T_1^l) \quad (A.4)$$

Note that the left-hand side of equation (A.4) contains only 'material' values, while on the right-hand side experimental values, analysed from the n.m.r. relaxation function of the blends, also occur.

Finally for $p^s \neq 0$ and $p^l \neq 0$ we find the case that only parts of the 'material' regions are influenced by spin diffusion. This is the case in $T_{1\rho}$ relaxation with the formula:

$$p^A(1/T_{1\rho}^{PMMA} - 1/T_{1\rho}^{PVAc}) = (1/T_{1\rho}^m - 1/T_{1\rho}^{PVAc})$$
$$+ p^s(1/T_{1\rho}^{PMMA} - 1/T_{1\rho}^m) + p^l(1/T_{1\rho}^{PVAc} - 1/T_{1\rho}^m) \quad (A.5)$$