Miscibility in PMMA/PVF$_2$ Blends, Studied by ^{19}F–^{13}C CPMAS NMR

C. H. Klein Douwel, W. E. J. R. Maas, and W. S. Veeman*

Department of Molecular Spectroscopy, Faculty of Science, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

G. H. Werumeus Buning and J. M. J. Vankan

Philips Research Laboratories, P.O. Box 80.000, 5600 JA Eindhoven, The Netherlands.

Received February 28, 1989; Revised Manuscript Received March 30, 1989

ABSTRACT: Blends of poly(methyl methacrylate) (PMMA) with poly(vinylidene fluoride) (PVF$_2$) are studied by fluorine-enhanced ^{13}C solid-state nuclear magnetic resonance, while spinning at the magic angle (^{19}F–^{13}C CPMAS NMR). Data were acquired under simultaneous proton and fluorine dipolar decoupling. From these experiments it can be concluded that PMMA/PVF$_2$ blends with weight ratios 80/20, 60/40, 40/60, and 20/80 are mixed at the molecular level. The average distance between PMMA C=O and OCH$_3$ carbons and PVF$_2$ fluorines in all blends is found to be between 2.6 and 3.1 Å.

Introduction

Mixing of different polymers has revealed a new realm of technically important materials, whose properties can be altered by varying the composition of the polymer blends. Although a large number of combinations of polymers are possible, there are relatively few that lead to a totally miscible system. A blend of two components 1 and 2 is classified miscible thermodynamically if the Gibbs free energy of mixing $\Delta G < 0$ and $[\delta^2 G/\delta\Phi_2{}^2]_{T,P} > 0$ (Φ_2 is the volume fraction of component 2). Experimental evidence of miscibility is often found when a single and sharp glass transition temperature is observed at a temperature in between the T_g's of the individual components. Differential scanning calorimetry (DSC), dynamic mechanical relaxation, dilatometry, and dielectric relaxation measurements are common techniques used for the determination of T_g.[1]

The calorimetric techniques, however, do not give information about mixing on the molecular scale. When the domain sizes are 150 Å or smaller, it is believed that a single glass transition temperature[2] will be observed. The gap between domain sizes on the order of 150 Å and truly intimate mixing on the molecular scale is quite large. Fluorescence spectroscopy and solid-state NMR are techniques with which this gap can be bridged. For some polymer blends known to be "miscible" and showing one single T_g, fluorescence spectroscopy and solid-state NMR have detected differences in miscibility on a molecular scale.

The fluorescence technique, nonradiative energy transfer (NRET),[3] has been applied to polymer blends by Albert et al.[4] In this method the two polymers composing the blend are labeled with a donor and an acceptor. The efficiency of the energy transfer from donor to acceptor depends on the distance r^{-6}. Mixing appeared to be more intimate in the poly(methyl methacrylate) (PMMA)/poly(vinyl chloride) (PVC) blend than in the PVC/styrene–acrylonitrile (SAN) blend[4] although both blends show one single T_g. The energy transfer in the NRET technique is believed to be efficient at distances up to 2 nm.

Various solid-state NMR techniques have been applied to probe the domain size and intimacy of mixing in polymer–polymer systems. Proton $T_{1\rho}$'s of a multicomponent system are strongly dependent on the short-range spatial proximity of the various components.[5] Averaging of proton $T_{1\rho}$'s in a blend by spin diffusion therefore indicates intimate mixing of the components. For this technique no specific labeling of the blend components is required. For the above mentioned PMMA/PVC blend $T_{1\rho}$ measurements showed that heterogeneity exists on a scale of 2.5 nm,[6] in agreement with the NRET data. Stejskal et al. found the same ^{1}H $T_{1\rho}$'s for poly(phenylene oxide) (PPO) homopolymer as in the PPO/poly(p-chlorostyrene) blend, indicative of the absence of any significant interchain mixing.[5] For the 75/25 PPO/poly(styrene) (PS) blend $T_{1\rho}$'s lying in between the values of the homopolymers are strong evidence for intimate mixing, although a very small fraction of isolated PS was also found for this blend composition. Methyl substitution of polystyrene in this blend influences miscibility markedly.[7] The poly(4-methylstyrene)/PPO blend shows homogeneity for the blends having a low PPO content. Two different $T_{1\rho}$'s, indicating phase separation of component macromolecules at scales in excess of 3 nm, are found for the PPO-rich blends as well as for all the poly(2-methylstyrene)/PPO blends. Heterogeneity on a scale of 2 nm was found for the PMMA/SAN blend.[8]

Spin diffusion measurements have been used to investigate miscibility in the range 0.5–10 nm.[9–13] The spin diffusion technique used by Caravatti et al. in their study of the poly(vinyl methyl ether) (PVME)/PS blend revealed quantitative information about the mixing process.[11,12] This blend is known to be immiscible when it is obtained from a chloroform solution and miscible when cast from a toluene solution. For the latter blend (PS/PVME 59/41) a mixed phase containing 79% of the total polymer mass was found, consisting of 64 wt % PS and 36 wt % PVME. Linder et al. used carbon–carbon interchain spin diffusion to study a ^{13}C-enriched bisphenol A polycarbonate/poly(ethylene terephthalate) (PET) blend.[13] The interchain distance can be distilled from the rate of this process, and distances as small as 5 Å were found for this blend.

Recently NMR studies of blends in concentrated solution, using 2D NOE, revealed that the ultimate miscibility behavior of a blend starts to develop in concentrated solutions of these blends.[14,15]

Another solid-state NMR technique, polarization transfer from protons of one component to carbons of another, deuterated component in a blend, has proved useful, since

0024-9297/90/2223-0406$02.50/0

this polarization transfer has an r^{-6} dependence, which limits effective polarization transfer to distances up to 5 Å. Again for the PVME/deuterated-PS blend effective cross-polarization was observed, whereas no[16] or very little[17] polarization transfer was found for the PMMA/deuterated-PS blend.

It is now well established that PMMA and poly(vinylidene fluoride) (PVF_2) are completely miscible[18,19] over the entire composition range in the molten state below the lower critical solution temperature (LCST) at $\simeq$350 °C.[20] The Flory–Huggins interaction parameter χ has been reported to be about −0.3,[19,21,22] which is one of the most negative values reported in literature. This indicates strong interactions between the components of the blend, which leads to the observed miscibility. In an FT-IR study of this blend a shift of the ester carbonyl absorption of PMMA was observed.[23] Furthermore, evidence has been presented that strong hydrogen bonding exists between the carbonyl and the two α-protons of PVF_2.

PVF_2 is partially crystalline; it can exist in a variety of crystalline forms, which are referred to as α, β, γ, and α_p modifications.[24] This crystallization interferes at higher PVF_2 content with the formation of a miscible, single, amorphous phase. Depending on the method of blend preparation, the amount, and also the crystal form, of the crystallites can be influenced. X-ray investigations and dielectric relaxation studies by Hahn et al.[25] revealed that, in the case PVF_2 crystallizes in the blend, a three-phase system is formed, consisting of PVF_2 crystallites, an amorphous PVF_2 interphase, and a miscible amorphous PMMA/PVF_2 phase.

The PMMA/PVF_2 blend has also been studied in the past by using various solid-state NMR techniques.[26-30] The results obtained in these studies are very dependent on blend preparation. Douglass and McBrierty[26] measured cross-relaxation effects between ^1H and ^{19}F by transient Overhauser effects on blends that contained a crystalline PVF_2 phase. They concluded that at least 20% of the amorphous PVF_2 in the PMMA/PVF_2 40/60 blend "sees" PMMA molecules at nearest-neighbor distances. Lin and Ward observed intensity attenuations of the PMMA carbon signals due to strong intermolecular dipolar interactions between the fluorines in PVF_2 and the carbons in PMMA,[27,28] which indicates intimate mixing. Grinsted and Koenig recently used ^1H–^{13}C cross-polarization with variable contact times to show the importance of aging for this blend.[30]

In this study on blends of poly(methyl methacrylate) (PMMA) with poly(vinylidene fluoride) (PVF_2) we investigated the polarization transfer from fluorine nuclei of PVF_2 to the carbons of PMMA. Carbon spectra were recorded under simultaneous proton and fluorine high-power decoupling. The use of fluorine–carbon cross-polarization NMR to study polymer blends has an advantage over proton–carbon cross-polarization NMR[16,17] in that no deuterated blends have to be used, whose thermodynamical behavior is different from that of protonated ones.[1] We also avoid problems arising from incomplete deuteration of a component. Furthermore the interpretation is straightforward in the sense that only ^{13}C signal from the PMMA can be observed if a sufficient number of PVF_2 chains are in the neighborhood of PMMA chains.

Experimental Section

Experiments were performed on a Bruker CXP-300 spectrometer, operating at 300.1, 282.2, and 75.4 MHz for ^1H, ^{19}F, and ^{13}C NMR, respectively. The pulse scheme is depicted in Figure 1. A $\pi/2$ pulse at the ^{19}F frequency is applied prior to a spin lock on ^{19}F and ^{13}C of variable duration τ. The free induction decay of the carbon magnetization was then monitored under simultaneous high-power proton and fluorine decoupling. The experiment was performed with spin temperature alteration[31] to cancel the signal that is not due to ^{19}F–^{13}C cross-polarization.

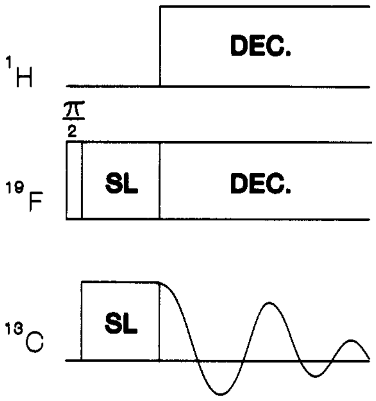

Figure 1. ^{19}F–^{13}C cross-polarization sequence with ^1H and ^{19}F dipolar decoupling during data acquisition.

Table I
Glass Transition Temperatures (T_g) Determined for the Weight Ratios Studied by DSC

PMMA/PVF_2	T_g, K	PMMA/PVF_2	T_g, K
100/0	379	40/60	323.5
80/20	362.5	20/80	321[a]
60/40	341	0/100	243

[a] A weak transition was found at 241.5 K due to an amorphous PVF_2 phase.

We used a standard Bruker double-bearing MAS probe. Spinning rates were between 4.5 and 5 kHz. In order to triple tune the coil we followed an approach quite similar to that described by Kendrick and Yannoni.[32] First we tuned the probe at 290 MHz. Between the ^1H input of the probe and the transmitter cable we connected a stripline filter, also tuned at 290 MHz.[33] By intentionally overcoupling the resonant circuits of the filter and the probe, the initial resonance is split in two and one obtains a circuit that can be tuned and matched to coincide with both the fluorine and the proton frequencies. A proton high-power rf (radio frequency) was generated by the standard Bruker high-power CXP amplifier, while for the fluorine power an additional MSL 300 amplifier was used. Both frequencies were routed to the probe by means of an ENI PMD80-2 combiner, resulting in a 3 dB attenuation of both rf powers. With this setup we were able to achieve rf fields of 40 kHz on protons and 65 kHz on fluorines.

The PMMA used was PMMA 6N from Röhm GMBH (Darmstadt, FRG). This polymer contains 10% methyl acrylate groups. Its average molecular weight $\bar{M}_w$, determined with GPC relative to polystyrene standards, was 100 000 g/mol. The T_g of the material was 379 K (DSC, heating rate 20 °C/min). The PVF_2 used was Kynar homopolymer grade 401 with an average molecular weight $\bar{M}_w$ of 530 000 g/mol and a T_g of 243 K. Blends were prepared via coprecipitation and subsequent compression molding, as described by Roerdink and Challa.[22] A certain composition ratio of the blend, 7.5 g, was dissolved in 250 g of DMF (Merck). The solution was added dropwise to 3 L of water. The precipitated mixture was filtered off and dried at high vacuum for 6 days at 50 °C and for several hours at 160 °C to remove the last traces of solvent. The dried mixture was then molded in a press at 200 °C prior to quenching from the melt in liquid nitrogen.

Table I summarizes the T_g's for different weight ratios of the blend and their starting materials. One single T_g was found for all compositions, except for the PMMA/PVF_2 20/80 blend, which is in agreement with literature data. ATR FTIR revealed that the PMMA/PVF_2 20/80 blend contained some PVF_2 crystals, the α as well as the β modification. As mentioned in the

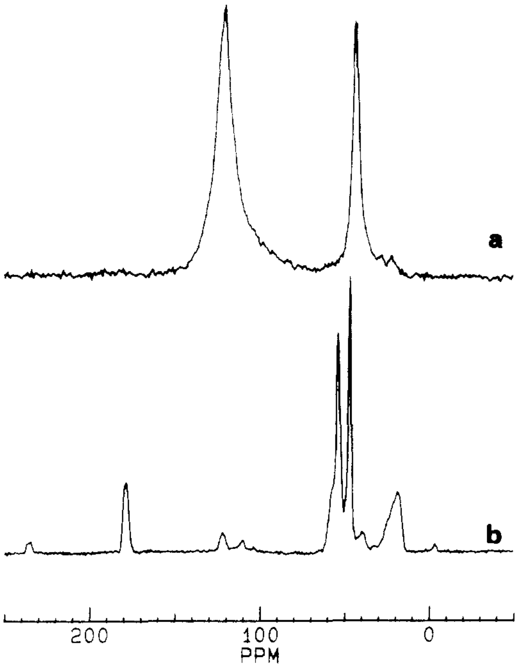

Figure 2. Magic angle ^{13}C NMR spectra of (a) PVF_2, cross-polarized from ^{19}F with ^1H and ^{19}F high-power decoupling, and (b) PMMA, cross-polarized from ^1H with ^1H dipolar decoupling. The resonances are assigned as follows. For PVF_2: 120 ppm, CF_2; 43 ppm, CH_2. For PMMA: 176 ppm, C═O; 50 ppm, OCH_3; 43 ppm, quaternary C; 15 ppm, CH_3; the CH_2 resonance appears as a shoulder on the left side of the OCH_3 resonance.

Introduction, PVF_2 crystals are surrounded by an amorphous PVF_2 interphase, with a thickness of about 2 nm.[25]

Results

Figure 2 shows the ^{13}C NMR spectra of PMMA and PVF_2. As can be seen from these spectra, the carbonyl and methoxy resonances of PMMA will be suitable to monitor in the blends, since they do not overlap with PVF_2 carbon lines. In Figure 3 the $^{19}F-^{13}C$ CP spectra of the PMMA/PVF_2 blends are depicted, for different ratios of PMMA and PVF_2, under conditions of both ^1H and ^{19}F decoupling (the resonance marked with an asterisk is due to the Kel-F cap of the spinner). Figure 5 shows the peak areas of the C═O and OCH_3 resonances of PMMA for the 60/40 blend as a function of the contact time, obtained from the spectra shown in Figure 4. Following Mehring,[34] we applied the following equation to fit the data of Figure 5:

$$S(t) = \frac{S_0}{a_+ - a_-}\left[\exp\left(\frac{-a_- t}{T_{IS}}\right) - \exp\left(\frac{-a_+ t}{T_{IS}}\right)\right] \qquad (1)$$

in which

$$a_\pm = a_0[1 \pm (1 - b/a_0^{\,2})^{1/2}]$$

$$a_0 = (1/2)(1 + \epsilon + T_{IS}/T_{1\rho}^{\,I} + T_{IS}/T_{1\rho}^{\,S})$$

$$b = \frac{T_{IS}}{T_{1\rho}^{\,I}}\left(1 + \frac{T_{IS}}{T_{1\rho}^{\,S}}\right) + \epsilon\frac{T_{IS}}{T_{1\rho}^{\,S}}$$

$$\epsilon = \frac{N_S S(S + 1)}{N_I I(I + 1)}$$

and where S_0 is the maximum carbon magnetization available in a cross-polarization experiment without dissipative processes, $T_{1\rho}^{\,I}$ and $T_{1\rho}^{\,S}$ are the rotating frame spin-lattice relaxation times for the I and S spins, respectively, and T_{IS} is the cross-polarization time. Since T_{IS} and $T_{1\rho}^{\,S}$ are of the same order, we are no longer allowed to neglect the carbon rotating frame relaxation, as is usually done. The ^{19}F $T_{1\rho}$'s and ^{13}C $T_{1\rho}$'s were measured in separate experiments. The ^{19}F $T_{1\rho}$'s were determined in two different ways: directly via ^{19}F NMR and via a $^{19}F-^{13}C$ cross-polarization experiment in which the fluorine magnetization is transferred to the carbons at the end of a variable-time ^{19}F spin-lock experiment.[5] The $^{19}F-T_{1\rho}$ values from these two experiments and from each carbon resonance agree well. The cross-relaxation times for the carbonyl resonances as well as for the methoxy resonances, found by fitting the data shown in Figure 5 with eq 1, are summarized in Table II, together with the carbon and fluorine rotating frame relaxation times.

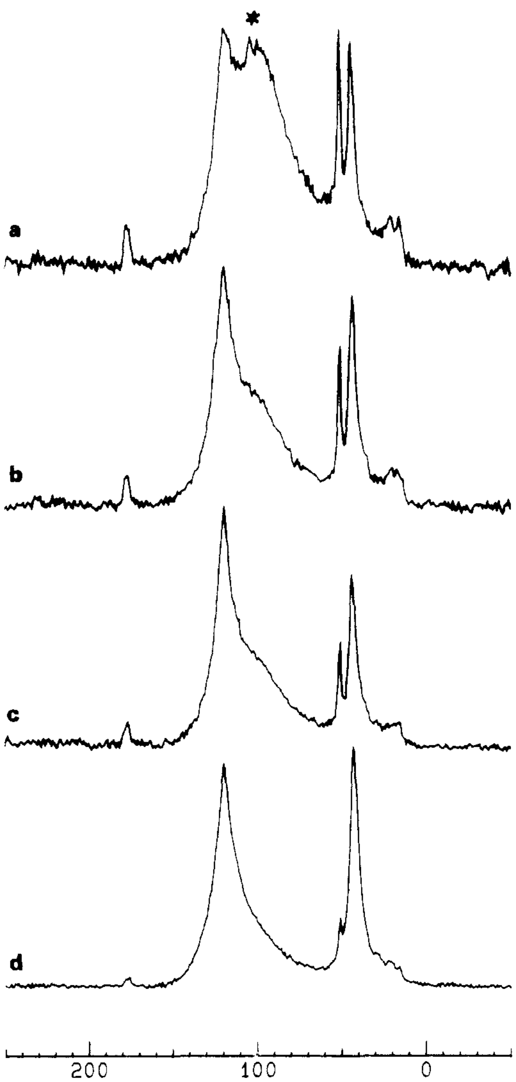

Figure 3. $^{19}F-^{13}C$ cross-polarization spectra (MAS 5 kHz) of PMMA/PVF_2 blends with weight ratios 80/20 (a), 60/40 (b), 40/60 (c), and 20/80 (d). The resonance marked with an asterisk is due to the KEL-F cap of the spinner.

In addition, a "physical" mixture of a PMMA/PVF_2 60/40 blend was investigated. This blend was mixed in a mortar after dissolution and precipitation of the separate components. Parmer et al.[17] showed that in a phase-separated blend one could still observe cross-polarization from one component to the other at the interfacial areas of the separate domains. In our physical mixture we did not observe any PMMA signal when cross-polarizing from the fluorines of PVF_2, not even for long contact times (see Figure 6).

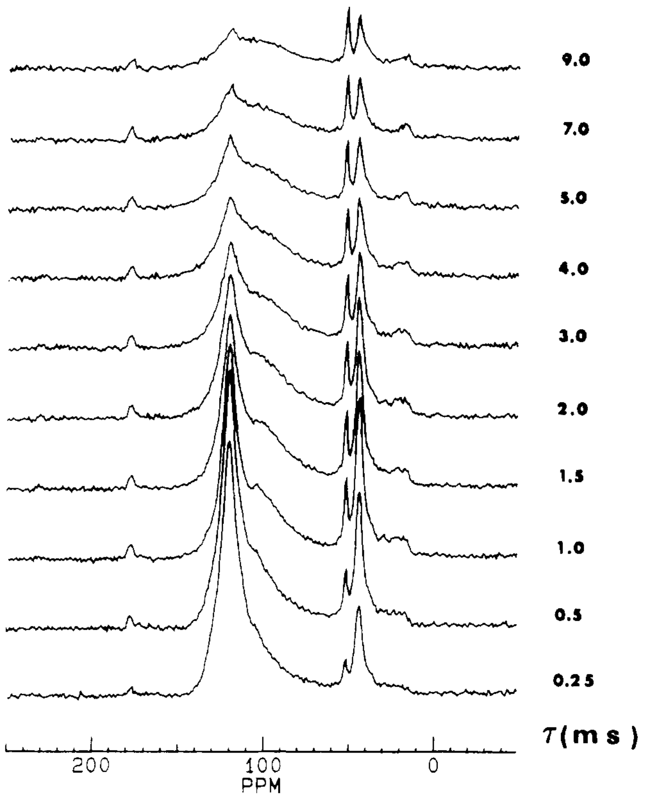

Figure 4. ^{19}F–^{13}C CPMAS spectra of PMMA/PVF$_2$ 60/40, for various contact times τ.

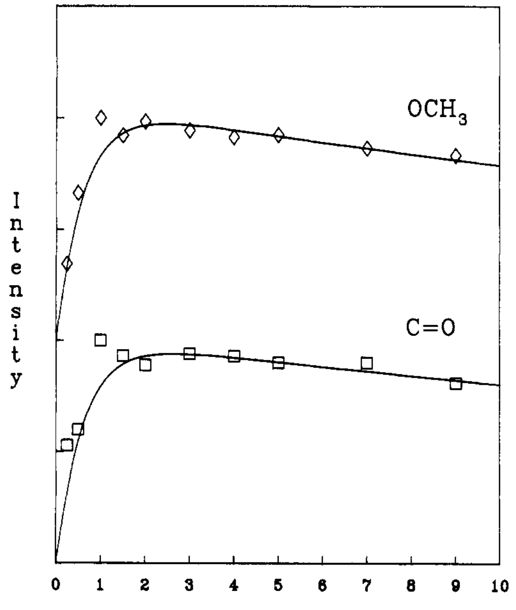

Figure 5. Intensities of the PMMA carbonyl and methoxy ^{13}C resonances as a function of contact time, obtained from the spectra shown in Figure 4. Intensities are in arbitrary units and the methoxy data are shifted upward with respect to the carbonyl intensities. The solid lines are data fits with eq 1; the parameters are listed in Table II.

Estimation of Domain Sizes from T_{IS}. Because of the r^{-6} dependence of the cross-relaxation rate, the experimentally found T_{IS} value can be used to make a prediction on domain sizes and nearest-neighbor ^{19}F–^{13}C distances in PMMA/PVF$_2$ blends. As derived by Demco et al.[35] for the high-effective-field spin-lock experiment, the cross-relaxation rate can be approximated as

$$T_{IS}^{-1} = (1/2)\sin^2\theta_I \sin^2\theta_S M_{2,SI} J_x(\Delta\omega_{\rm eff}) \qquad (2)$$

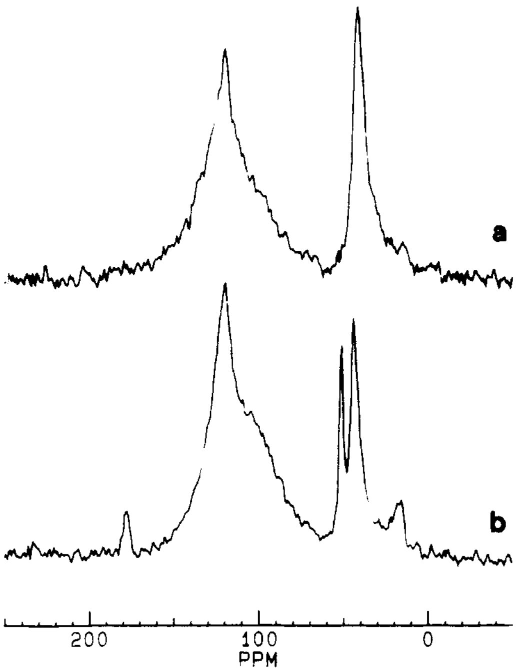

Figure 6. Comparison of ^{19}F–^{13}C CPMAS spectra of a PMMA/PVF$_2$ 60/40 physical mixture (a) and blend obtained from coprecipitation (b), for a contact time of 5 ms.

in which $\theta_i = \tan^{-1}[\omega_{1i}/(\omega_{0i} - \omega_i)]$; $i = I, S$; $\omega_{0i} - \omega_i$ is the offset from resonance; ω_{1i} is the strength of the applied spin-lock field; $M_{2,SI}$ is the second moment of the S spin resonance line determined by coupling with the I spins; J_x is the cross-polarization spectral density function of the I spins; and $\Delta\omega_{\rm eff}$ is the mismatch from the Hartmann–Hahn condition.

We used the following expression[36] to describe the second moment:

$$M_{2,SI} = (1/3)\gamma_I^2\gamma_S^2\hbar^2 I(I+1)1/N\sum_{\rm I,S}(1 - 3\cos^2\theta_{IS})^2 r^{-6} \qquad (3)$$

In our approximation we considered an average distance between ^{19}F and ^{13}C, which allowed us to place the r^{-6} in front of the summation sign. If we assume a random distribution of the direction of the internuclear vector for a given distance between a fluorine and a carbon nucleus, this summation can be replaced by its powder average. In agreement with Maricq and Waugh,[37] we find for the second moment an expression, which is independent of magic angle spinning

$$M_{2,SI} = (1/5)\gamma_I^2\gamma_S^2\hbar^2 r^{-6} \qquad (4)$$

The next step is to find an approximation for the spectral density function J_X. Since we neglect the deviation from the Hartmann–Hahn condition ($\Delta\omega_{\rm eff} = 0$), we do not expect to introduce a large error by assuming a Gaussian shape for the correlation function,[35] which leads to the following expression for the spectral density function:

$$J_X(\Delta\omega_{\rm eff}) = (1/2)\pi^{1/2}\tau_c \exp\left[\frac{\Delta\omega_{\rm eff}^2\tau_c^2}{4}\right] \qquad (5)$$

Substitution of (4) and (5) in (2) and taking $\Delta\omega_{\rm eff} = 0$ yields

$$T_{IS}^{-1} = 7.17 \times 10^{-53}\sin^2\theta_I \sin^2\theta_S\, \tau_c r_{IS}^{-6} \qquad (6)$$

The correlation time τ_c was estimated from the fluorine

Table II
The Relaxation Times T_{IS}, $T_{1\rho}^{I}$, and $T_{1\rho}^{S}$ [a]

PMMA/PVF$_2$		T_{IS}, ms	$T_{1\rho}^{I}$, ms	$T_{1\rho}^{S}$, ms	r, Å
80/20	C=O	30 ± 5	0.8 ± 0.2	70 ± 5	2.7 ± 0.2
	OCH$_3$	30 ± 5	0.8 ± 0.2	50 ± 5	2.7 ± 0.2
60/40	C=O	60 ± 10	0.8 ± 0.2	150 ± 20	3.1 ± 0.2
	OCH$_3$	50 ± 10	0.8 ± 0.2	80 ± 10	3.0 ± 0.2
40/60	C=O	45 ± 5	0.8 ± 0.2	80 ± 5	3.0 ± 0.2
	OCH$_3$	40 ± 5	0.8 ± 0.2	80 ± 7	2.9 ± 0.2
20/80	C=O	25 ± 5	0.8 ± 0.2	70 ± 10	2.6 ± 0.2
	OCH$_3$	30 ± 5	0.8 ± 0.2	70 ± 10	2.7 ± 0.2

[a] The spin–lattice relaxation times were measured in separate experiments and T_{IS} has been determined with the help of eq 1. The average ^{19}F–^{13}C distance r was calculated from T_{IS} with eq 7.

NMR line width of the blend to be 2 × 10^{-4} s. For $\theta_C = \theta_F = \pi/2$ we are left with the following expression for the cross-polarization time:

$$T_{IS}^{-1} = 1.4 \times 10^{-56} r_{IS}^{-6} \quad (T_{IS} \text{ in s}, r_{IS} \text{ in m}) \qquad (7)$$

From this expression an average distance between a carbon nucleus of PMMA and a fluorine nucleus on PVF$_2$ for the composition range studied has been calculated and the values are listed in Table II.

This radius represents an average ^{19}F–^{13}C distance, for all nuclei involved in the cross-polarization process. Fluorines at larger distances from the PMMA carbons will have a smaller heteronuclear dipolar interaction and therefore will not effectively transfer their magnetization. Also for this reason, we expect magic angle spinning to interfer with cross-polarization at large C–F distances by averaging out the dipolar interactions. In fact, as noticed by Lin and Ward,[28] in order to observe ^{13}C–^{19}F dipolar couplings under MAS conditions, the carbon–fluorine distance should be smaller than approximately 4 Å. This agrees well with our values for r.

We note that, although we made a number of simplifying approximations in deriving the average carbon–fluorine distance, the outcome will still be a good estimate, since to find the average ^{19}F–^{13}C distance we had to take the inverse sixth power of the cross-relaxation time. An error in T_{IS} has only a small effect on the value of r. However, the oscillations in Figure 5 make it clear that the ^{19}F–^{13}C cross-polarization process is more complicated than assumed here.

Discussion

Considerations on Miscibility. We have shown that a reasonable number of PMMA molecules are in close proximity to PVF$_2$ molecules. In this section we will consider the miscibility of PMMA/PVF$_2$ blends, using a simple theoretical model, prior to trying to quantify the degree of mixing in the next section.

For blend compositions rich in PVF$_2$, all the PMMA carbons can in principle be surrounded by fluorine atoms such that ^{19}F–^{13}C cross-polarization intensities represent all the carbons of the PMMA. At low PVF$_2$ concentration, however, it can easily be understood that even for ideally mixed blends not all the PMMA carbons can have a fluorine nucleus at nearest-neighbor distance, which is necessary for efficient cross-polarization. Below a critical PVF$_2$ concentration C^*, not every PMMA carbon will have a fluorine nucleus to cross-polarize from, because there is not enough PVF$_2$ present. In trying to estimate the value of C^* to be expected for the PMMA/PVF$_2$ blend, we will prove below that if one is considering such short distances, a decrease in magnetization transfer can be expected at the edges of the composition range only due to a dilution effect, which has nothing to do with miscibility at the molecular scale.

An estimate for the number of PMMA/PVF$_2$ contacts can be obtained from contact statistics considerations, originating from lattice model computations.[38] In lattice theories it is common practice to subdivide the macromolecules into segments, each occupying a lattice site. In this discussion we have chosen the size of a segment to be the repeating unit of PMMA. As the van der Waals volume of a repeating unit of PVF$_2$ is about half of the value of PMMA,[39] one lattice site is occupied by two PVF$_2$ repeating units. If we consider a central PMMA segment containing one carbonyl, this segment will be surrounded by 12 other segments if we assume the closest packing of spheres. In order to observe a carbonyl carbon in a ^{19}F–^{13}C cross-polarization experiment, at least one fluorine nucleus should be at nearest-neighbor distance from this carbonyl carbon. This means that at least one of the surrounding segments has to be a PVF$_2$ segment. So, adapting a mean-field approximation, we must at the limiting composition have 1 PVF$_2$ segment and 12 PMMA segments. Via the differences in volumes this gives us 12 repeating units of PMMA to 2 repeating units of PVF$_2$, a molar ratio of 6:1. Via the molecular weights of the PMMA units (100) and PVF$_2$ (64) the critical concentration C^* corresponds to a PMMA/PVF$_2$ weight ratio of 90/10.

In this contemplation one important simplification was used. We considered the segments to be independent of each other, and the connectivity of the segments, due to the fact that they are part of a polymer, was neglected. Furthermore, the effect of end groups, folding back, and local excluded volume was ignored. Concentration fluctuations are also observed for the PMMA/PVF$_2$ blend.[21] These fluctuations are correlated over distances that extend up to 10 Å. However, they are not included in a mean-field approximation, as is used here. In addition, the Flory–Huggins interaction parameter shows a strong composition dependence for this blend.[21,40] At higher PMMA concentrations, this parameter becomes less negative, which may mean that interactions are less strong in this composition range.

All these effects will direct the critical concentration C^* to higher PVF$_2$ levels. The 90/10 ratio calculated here is derived for the most favorable way of distributing the PVF$_2$ segments.

Distance-sensitive techniques such as cross-polarization solid-state NMR and excitation-transfer fluorescence spectroscopy can give information about nuclei or groups at an average distance of a few angstroms. An important conclusion of the contemplation given here is that if one is considering such short distances, a decrease in energy transfer can be expected at the edges of the composition range only due to a dilution effect, which has nothing to do with miscibility on a molecular scale. With all the simplifications in this model mentioned above in mind, it may be expected that for the blend studied here, the PMMA/PVF$_2$ 80/20 composition will be very near, or even in, the dilution range.

Quantitative Aspects of the Mixing. Until now, almost all solid-state NMR studies on polymer blends described in literature concentrated on the distance aspect of mixing. The distance between nuclei of the different components (as described above), or the scale of heterogeneities present in a blend, was investigated. Only once[12] the quantitative aspects of mixing, i.e., how much of the components are intimately mixed, were described. As this is one of the most intriguing and challenging aspects in the miscibility behavior of polymer blends, we have attempted below to get some insight into it for the PMMA/PVF$_2$ blend.

The cross-relaxation data enable us to quantify the degree of mixing. First we remark that, although the carbonyl peaks are very small, they still represent a large number of PMMA molecules. Because of the short $T_{1\rho}$ of the fluorines, as compared to the cross-relaxation time T_{IS}, the buildup of carbon magnetization is restrained.

From eq 1 we can find S_0, the maximum carbon signal due to magnetization transfer from the fluorines of PVF$_2$ if there were no dissipative processes. Comparison of S_0 for the carbonyl resonance of PMMA with S_0 for the CF$_2$ resonance of PVF$_2$ directly yields the number of PMMA molecules in close proximity to PVF$_2$ molecules and the degree of mixing:

$$f_{\mathrm{mix}} = \frac{S_0(\mathrm{C{=}O})}{S_0(\mathrm{CF_2})}\left(\frac{\mathrm{PVF_2}}{\mathrm{PMMA}}\right) \qquad (8)$$

where f_{mix} is the fraction of PMMA carbonyl carbons cross-polarized from fluorines of PVF$_2$ and (PVF$_2$/PMMA) is the molar ratio of the blend.

For the PMMA/PVF$_2$ 80/20 blend we found f_{mix} to be 0.35, meaning that about 35% of the carbonyls of PMMA "see" a fluorine of PVF$_2$ at nearest-neighbor distance. For the other compositions, however, percentages of 100% or more were found, meaning that our model, as expressed by eq 1, is not adequate to accurately obtain S_0. Variation of, for instance, T_{IS} within the confidence limits listed in Table II can easily cause large deviations in S_0, while still yielding good data fits. Furthermore, the question arises as to what percentage of mixing can be found, in an ideally mixed blend, by comparing the number of cross-polarized carbonyl carbons with the number of CF$_2$ carbons in the blend. Polymer tacticity and, related to this, the polymer conformations have a large influence on the specific interactions possible between the different components of a blend. Léonard et al.[4] showed, using simple molecular models, that the PVF$_2$ all-trans conformation allows efficient interactions with the PMMA ester groups. However, the presence of gauche bonds leads to a fairly large mismatch between the repeat distance, characteristic of the PVF$_2$ chains, and the spacing between the ester groups in PMMA. Detailed conformational information on the mixed phase of the PMMA/PVF$_2$ blend, which is not available at the moment, will be needed to determine to extent of mixing.

In addition, the fit of eq 1 to the experimental intensities versus contact time for the blend compositions studied is not completely satisfactory. This may be due to various reasons. First, as shown by Grant et al.[42] in their investigations on cross-polarization dynamics in organic molecules of low or remote protonation, the r^{-6} dependence does not necessarily discriminate between different fluorines involved in the magnetization transfer. In the case of directly bonded protons or fluorines, these nuclei will dominate the cross-polarization process, since their dipolar coupling with the bonded carbon atom will be much larger than the dipolar interaction of a remote proton or fluorine with the same carbon atom. In the PMMA/PVF$_2$ case, however, we can expect a distribution in carbon–fluorine distances with comparable ^{13}C–^{19}F interactions. The plot of carbon intensity versus contact time will therefore be a superposition of curves with different T_{IS} values.

Second, the cross-polarization data from all experiments seem to show an oscillatory behavior. This behavior will be subject to future investigation but illustrates that the cross-polarization process is more complicated than described by eq 1. The ^{19}F–^{13}C distances we evaluated from the T_{IS} data are all about 3 Å. No significant differences were found between ^{19}F–carbonyl distances and ^{19}F–methoxy distances. As mentioned in the Introduction, Léonard et al.,[23] using FTIR, found evidence for strong hydrogen bonding between the carbonyl oxygen of PMMA and the α-hydrogens of PVF$_2$. The ^{13}C–^{19}F distances we found do certainly agree with these findings. However, we do not observe a shift of the carbonyl resonances, as compared to pure PMMA, something we would expect in the case of strong hydrogen bonding. This may be due to limits in resolution; shifts of the order of 0.1–0.2 ppm will not be detected within the accuracy of our experiments.

Conclusions

The miscibility behavior of the PMMA/PVF$_2$ blend has been investigated with ^{19}F–^{13}C CPMAS and simultaneous proton and fluorine high-power dipolar decoupling. For all the blends studied a large number of PMMA and PVF$_2$ units are in close proximity to each other. For these neighboring units the distance between carbons in PMMA OCH$_3$ and C=O groups and PVF$_2$ fluorines is found to be only about 3 Å. Although the degree of mixing cannot accurately be determined for most blends, our results do seem to indicate that in the 80/20 blend (PMMA/PVF$_2$) less PMMA units are in close contact with PVF$_2$ units than in the other compositions. A simple model has been introduced, which shows that below a critical PVF$_2$ concentration on the order of 20% a decrease of magnetization transfer from PVF$_2$ fluorines to PMMA carbons can be expected, even for an ideally mixed blend, because of a dilution effect.

Acknowledgment. This work was supported by the Dutch Research Foundation (NWO/SON). We thank J. W. M. van Os, A. A. G. van Oijen, and J. J. M. Joordens for technical assistance at the Dutch National NMR facility at Nijmegen. Dr. E. Nies (Polymer Institute, Eindhoven) is thanked for many helpful discussions.

References and Notes

(1) Olabisi, O; Robeson, L. M.; Shaw, M. T. *Polymer–Polymer Miscibility*; Academic: New York, 1979.
(2) Kaplan, S. *J. Appl. Polym. Sci.* **1976**, *20*, 2615.
(3) Morawetz, H.; Amrani, F. *Macromolecules* **1978**, *21*, 29224.
(4) Albert, B.; Jérôme, R.; Teyssié, Ph. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 551.
(5) Stejskal, E. O.; Schaefer, J.; Sefcik, M. D.; McKay, R. A. *Macromolecules* **1981**, *14*, 275.
(6) Albert, B.; Jérôme, R.; Teyssié, Ph; Smyth, G.; Boyle, N. G.; McBrierty, V. J. *Macromolecules* **1985**, *18*, 388.
(7) Dickinson, L. C.; Yang, H.; Chu, C.-W.; Stein, R. S.; Chien, J. C. W. *Macromolecules* **1987**, *20*, 1757.
(8) MacBrierty, V. J.; Douglass, T. C.; Kwei, T. K. *Macromolecules* **1978**, *11*, 1265.
(9) VanderHart, D. L. *J. Magn. Reson.* **1987**, *72*, 13.
(10) Henrichs, P. M. *Macromolecules* **1988**, *20*, 2099.
(11) Caravatti, P.; Neuschwander, P.; Ernst, R. R. *Macromolecules* **1985**, *18*, 119.
(12) Caravatti, P.; Neuschwander, P.; Ernst, R. R. *Macromolecules* **1986**, *19*, 1889.
(13) Linder, M.; Henrichs, P. M.; Hewitt, J. M.; Massa, D. J. *J. Chem. Phys.* **1985**, *82*, 1585.
(14) Crowther, M. W.; Cabasso, I.; Levy, G. C. *Macromolecules* **1988**, *21*, 2924.
(15) Mirau, P. A.; Tanaka, H.; Bovey, F. A. *Macromolecules* **1988**, *21*, 2929.
(16) Gobbi, G. C.; Silvestri, R.; Russel, T. P.; Lyerla, J. R.; Fleming, W. W.; Nishi, T. *J. Polym. Sci., Polym. Lett. Ed.* **1987**, *25*, 61.
(17) Parmer, J. F.; Dickinson, L. C.; Chien, J. C. W.; Porter, R. S. *Macromolecules* **1987**, *20*, 2308.

(18) Noland, J. S.; Hsu, N. N.-C.; Saxon, R.; Schmitt, J. M. *Adv. Chem. Ser.* **1971,** *99,* 15.
(19) Nishi, T.; Wang, T. T. *Macromolecules* **1975,** *8,* 909.
(20) Bernstein, R. E.; Cruz, C. A.; Paul, D. R.; Barlow, J. W. *Macromolecules* **1977,** *10,* 681.
(21) Wendorff, J. H. *J. Polym. Sci., Polym. Lett. Ed.* **1980,** *18,* 439.
(22) Roerdink, E.; Challa, G. *Polymer* **1978,** *19,* 173.
(23) Léonard, C.; Halary, J. L.; Monnerie, L. *Polymer* **1985,** *26,* 1507.
(24) Léonard, C.; Halary, J. L.; Monnerie, L. *Macromolecules* **1988,** *21,* 1265.
(25) Hahn, B. R.; Herrmann-Schonherr, O.; Wendorff, J. H. *Polymer* **1987,** *28,* 201.
(26) Douglass, D. C.; McBrierty, V. J. *Macromolecules* **1978,** *11,* 766.
(27) Ward, T. C.; Lin, T. S. In *Polymer Blends and Composites in Multiphase Systems*; han, C. D., Ed.; Advances in Chemistry 206; American Chemical Society: Washington, DC, 1984, p 59.
(28) Ward, T. C.; Lin, T. S. *Polym. Prepr.* **1983,** *24,* 136.
(29) Tékély, P.; Laupretre, F.; Monnerie, L. *Polymer* **1985,** *26,* 1081.
(30) Grinsted, R. A.; Koenig, J. L. *Polym. Prepr.* **1988,** *29*(1), 15.
(31) Stejskal, E. O.; Schaefer, J. *J. Magn. Reson.* **1975,** *18,* 560.
(32) Kendrick, R. D.; Yannoni, C. S. *J. Magn. Reson.* **1987,** *75,* 506.
(33) *The Radio Amateur's Handbook*; Myers, R., Ed.; The American Radio Relay League: Newington, CT, 1974.
(34) Mehring, M. Principles of High Resolution NMR in Solids. In *NMR—Basic Principles and Progress*, 2nd ed.; Springer-Verlag: New York, 1983; Vol. 12, p 282.
(35) Demco, D. E.; Tegenfeldt, J.; Waugh, J. S. *Phys. Rev. B* **1975,** *11,* 4133.
(36) Slichter, C. P. Principles of Magnetic Resonance. In *Springer Series in Solid-State Sciences*, 2nd ed.; Springer: New York, 1980, Vol. 1.
(37) Maricq, M. M.; Waugh, J. S. *J. Chem. Phys.* **1979,** *70,* 3300.
(38) Staverman, A. J. In *Integration of Fundamental Polymer Science and Technology*; Kleintjens, L. A.; Lemstra, P. J., Eds.; Elsevier: London, 1986, p 19.
(39) CHEMX, developed and distributed by Chemical Design Ltd., Oxford. The van der Waals volume of a repeating unit of PVF_2 and PMMA was calculated by using CHEMX. Values found were 40.4 and 77.3 Å, respectively.
(40) DiPaola-Baranyi, G.; Fletcher, S. J.; Degré, P. *Macromolecules* **1982,** *15,* 885.
(41) Léonard, C.; Halary, J. L.; Monnerie, L. *Macromolecules* **1988,** *21,* 2988.
(42) Alemany, L. B.; Grant, D. M.; Pugmire, R. J.; Alger, T. D.; Zilm, K. W. *J. Am. Chem. Soc.* **1983,** *105,* 2142.

Registry No. PMMA, 9011-14-7; PVF_2, 24937-79-9.

Intermolecular Cross-Polarization Studies of the Miscibility Enhancement of PS/PMMA Blends through Ionic Interactions

Xinsheng Zhang,[†] Almeria Natansohn,[‡] and Adi Eisenberg[*,†]

Departments of Chemistry, McGill University, Montreal, Quebec, Canada H3A 2K6, and Queen's University, Kingston, Ontario, Canada K7L 3N6. Received December 27, 1988; Revised Manuscript Received May 11, 1989

ABSTRACT: The CP/MAS ^{13}C NMR technique is employed in this study to probe the bulk structures of deuteriated PS/protonated PMMA blends containing ionically interacting groups. Deuteriated PS does not show a ^{13}C NMR signal in CP/MAS experiments since the magnetization of ^{13}C is primarily polarized by protons. However, if protons of the PMMA chains can be found within a few angstroms of the deuteriated PS, then the ^{13}C NMR signals of PS can be observed, with the intensity of PS signals depending upon the proximity of deuteriated PS to the PMMA. The present results show that the PS/PMMA pair is immiscible. However, when PS is lightly sulfonated (3.3 mol % of $-SO_3H$) and PMMA is copolymerized with 2.3 mol % 4-vinylpyridine (4VP), the miscibility of the blend is enhanced, due to proton transfer from the $-SO_3H$ to the 4VP with the formation of ionically interacting sites on the deuteriated PS and the PMMA. By the introduction of about 9.5 mol % of interacting groups ($-SO_3H$ and 4VP), the blend shows much greater enhancement in miscibility. When the $-SO_3H$ on the deuteriated PS is neutralized with $N(CH_3)_4OH$ and the 4VP is quaternized with CH_3I, the blends exhibit similar or even better miscibility compared with the proton-transfer blends. This is attributed to the direct ion–ion interactions in the blends. Blend recovery methods affect the chain proximity in the blend.

Introduction

In recent years, polymer blends have been the subject of extensive investigations.[1-3] In many instances, the properties of the blends are superior to those of the individual components. Since most polymer pairs are not miscible, one of the important features of polymer research is the investigation of miscibility enhancement techniques since control of miscibility allows one to control the final properties.

Many miscibility enhancement strategies have been explored in the past. These include copolymerization, either in the form of random copolymers or preferably in the form of blocks used as emulsifiers,[4] utilization of hydrogen bonding between the dissimilar chains,[5,6] formation of donor–acceptor complexes,[7] and, in addition, dipole–dopole,[8] ion–dipole,[9] and ion–ion interactions.[10]

Miscibility enhancement by ionic interactions has been the subject of extensive studies in this laboratory. For example, the immiscible polymer pair poly(ethyl acrylate) (PEA)/polystyrene (PS) can be made miscible by the incorporations of ca. 5 mol % 4-vinylpyridine into the PEA and a comparable amount of sulfonic acid in the PS.[10] In the process of mixing, proton transfer occurs from the sulfonic acid to the pyridine, which results in the formation of opposite charges on the different chains and leads to strong coulombic interactions which hold the chains together. A wide range of other systems has been treated in a similar manner, including the pair poly(tetrafluoroethylene)/poly(ethyl acrylate).[11] Ion–dipole interactions are another way for improving misci-

---

[*] To whom correspondence should be addressed.
[†] McGill University.
[‡] Queen's University.

0024-9297/90/2223-0412$02.50/0