Investigation of Compatibility in Syndiotactic Poly(methyl methacrylate)/Poly(vinyl chloride) Blends

Brigitte Albert, Robert Jérôme, and Philippe Teyssié

Laboratory of Macromolecular Chemistry and Organic Catalysis, University of Liège, Sart-Tilman, B-4000, Liège, Belgium

Gerard Smyth, Noel G. Boyle, and Vincent J. McBrierty*

Department of Pure and Applied Physics, Trinity College, University of Dublin, Dublin 2, Ireland. *Received June 11, 1984*

ABSTRACT: Pulsed NMR and nonradiative energy transfer (NRET) measurements on blends of s-PMMA and PVC are described. Sources of the small-scale heterogeneity evident in all blends are discussed. Although it was not possible to arrive at a definitive model of this small-scale heterogeneity, consideration was given to factors which had important bearing on the miscibility achieved: (i) the method of mixing used and the relative sensitivity of the investigative techniques used, (ii) the effects of tacticity, molecular weight, and polydispersity on polymer–polymer miscibility, and (iii) the difference in the solubilization power of PVC for PMMA and PMMA for PVC.

Introduction

Considerable ingenuity has been brought to bear in the study of miscibility in polymer blends on scales ranging from molecular, near-neighbor distances to macroscopic dimensions, of the order of microns or greater, typical of some phase-separated domains. The dimensional scale probed and the sensitivity achieved are dictated by the experimental technique used, a fact which undoubtedly contributes to differences in interpretation occasionally encountered in the literature. That different interpretations have emanated even from the same experiment involving ostensibly similar polymer blends also underpins the need for continued vigilence regarding the preparative and thermal history of the blends under examination.

Consider the polymer pair poly(vinyl chloride) (PVC) and syndiotactic poly(methyl methacrylate) (s-PMMA). DSC and dynamic mechanical data of Schurer and co-workers[1] indicated compatibility for s-PMMA/PVC compositions up to 60/40 wt %, corresponding to a monomer unit ratio of about 1:1. Phase separation occurred when s-PMMA exceeded 60 wt %, the first phase representing the 1:1 compatible composite and the second, the excess s-PMMA. The glass transition temperature, T_g, for the blend, determined from DSC measurements, was observed to increase reasonably linearly (from ~70 to 90 °C) with increasing s-PMMA content up to 60 wt %. Above this concentration T_g was independent of composition and, in addition, a higher T_g (120 °C) corresponding to pure s-PMMA was detected. Schurer et al. surmised that 1:1 material dissolved in excess PVC but remained insoluble in excess s-PMMA. They noted further that the ester group in PMMA was a proton-accepting group while PVC was weakly proton-donating via the α-hydrogen. In this sense the two polymers were considered to be complementary. The fact that such hydrogen-bond-like interactions, aside from potential dipole–dipole interactions, were favored in s-PMMA, and not in isotactic PMMA (i-PMMA), was invoked to explain the compatibility of s-PMMA and incompatibility of i-PMMA with PVC. Blends were prepared according to three different procedures: (i) by evaporation of 3 wt % mixed PVC/PMMA solutions in DMF, (ii) by precipitation from 3 wt % mixed PVC/PMMA solutions in an excess of 10:1 water–methanol mixture, and (iii) by melt blending on a two roll mill at 180 °C. Unfortunately, Schurer et al. did not mention the source of samples characterized by the different techniques reported in their paper.

The significantly shorter range of compatibility observed in PVC/PMMA blends by Razinskaya and co-workers[2] was rationalized by Schurer et al. in terms of molecular weight differences of PVC in the two studies. There was insufficient information to compare tacticities.

Vanderschueren and co-workers[3-5] also studied PMMA/PVC blends using DSC and the thermally stimulated depolarization current method (TSDC). Their central motivation was to illustrate the sensitivity of TSDC in the characterization of multiphase polyblends: as such, they were less concerned with the ultimate state of mixing of the blends. In their sample preparation, solid PVC and PMMA were mixed in a grinder at room temperature followed by molding at 160 °C. Mindful of the different preparative histories of the blends investigated, the conclusions of Vanderschueren et al.[3-5] differed in two important respects from those of Schurer and co-workers.[1] While a single T_g was again observed in DSC measurements for compositions from 0 to 60 wt % s-PMMA, its magnitude was essentially independent of composition within this concentration range and remained close to T_g for pure PVC (73 °C). Secondly, the maximum range of compatibility was judged to be significantly smaller (0–10 wt % s-PMMA) than that proposed by Schurer et al.[1] (0–60 wt % s-PMMA). Evidence cited in support of the latter observation included the detection of a Maxwell–Wagner–Sillars (MWS) peak in the TSDC data for blends with greater than 10 wt % s-PMMA. It is recalled that the MWS effect is considered to arise from trapping of charge carriers at phase boundaries which, in turn, implies at least some degree of phase separation.[6-8]

In an effort to rationalize the two viewpoints or at least to understand them more fully, a number of s-PMMA/PVC blends of different composition were carefully prepared by controlled evaporation of 2 wt % methyl ethyl ketone (MEK) solutions for examination by nuclear magnetic resonance (NMR)[9-11] and by the nonradiative energy transfer (NRET) technique developed recently by Morawetz and co-workers.[12-15] Compatibility in polymer blends has been studied by NMR on a dimensional scale of about 2–20 nm through exploitation of the short-range nature of the contributing nuclear spin interactions and the way in which nuclear spins can communicate through the mechanism of spin diffusion. In the NRET method, which also responds to events on a molecular dimensional scale, a fluorescent chromophore is anchored onto each component polymer. In a binary blend (A + B), the emission spectrum of the chromophore (the "donor") attached to polymer A must, at least partly, overlap the absorption spectrum of the chromophore (the "acceptor") carried by polymer B for nonradiative energy transfer to

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Table I
Spectroscopic Data for the Donor and Acceptor Molecules

compd	λ_{ex}, nm	λ_{em} nm	$\epsilon_{ex} \times 10^{-3}$, M^{-1} cm^{-1}	$J \times 10^{15}$, [b] cm^6 mol^{-1}	ϕ_D^0 [b]	R_0, nm
donor						
α-methylnaphthalene	282	338	6.7	4.52	0.25	2.1
acceptor						
9-methylanthracene	282	417	0.63			

[a] λ_{ex}, excitation wavelength; λ_{em}, emission wavelength; ϵ_{ex}, molar extinction coefficient; J, R_0, and ϕ_D^0, see text. [b] Reference 15.

be effected. Any electronic excitation energy of the donor can then be transferred by a nonradiative mechanism to the acceptor, which can reemit this energy independently of a direct excitation.[12] The efficiency of energy transfer, E, is dependent on the distance between donor and acceptor according to the equation

$$E = R_0^6/(R_0^6 + r^6) \quad (1)$$

r is the distance between donor and acceptor R_0 the critical transfer distance for which half of the excitation energy is transferred. R_0 is described by the relation

$$R_0^6 = \frac{9000 \ln (10K_2J\phi_D^0)}{128\pi^5Nn^4} \quad (2)$$

ϕ_D^0 is the quantum yield of the donor in the absence of transfer, n is the refractive index of the medium, N is the Avogadro number, K^2 is a dimensionless factor depending on the mutual spatial orientation of the transition dipole moments of the donor and acceptor, and J is the overlap integral between the emission spectrum of the donor and the absorption spectrum of the acceptor.

The sensitivity of the fluorescence technique used in the study of polymer miscibility is related to the R_0 value. The donor/acceptor pair is selected in such a way that nonradiative energy transfer is efficient over distances of about 2 nm. Decreasing miscibility means an increase in the average distance between donor and acceptor and a consequent reduction in energy-transfer efficiency. Of course, the opposite effect results from the intimate interpenetration of polymers A and B.

Experimental Section

Materials. The commercial PVC material, supplied by Solvay, Belgium (PVC RD 258), was purified by a twofold precipitation from tetrahydrofuran into methanol and finally dried under vacuum to constant weight. In this way PVC was expected to be free from stabilizer and plasticizer in contrast to the procedures used by Schurer et al.[1] and Vanderschueren et al.[3] where a further amount of stabilizer was added to the commercial PVC. Molecular weights ($\bar{M}_n$ = 43 000, $\bar{M}_w$ = 80 000) were determined in tetrahydrofuran at 25 °C by gel permeation chromatography (GPC).

Methyl methacrylate was anionically polymerized under anhydrous conditions in tetrahydrofuran at −78 °C using (diphenylmethyl)lithium as initiator. Polymerization was stopped by the addition of hydrochloric acid. The polymer was precipitated successively into methanol and hexane and dried under vacuum. Molecular weights ($\bar{M}_n$ = 150 000 and $\bar{M}_w$ = 190 000) were again measured in tetrahydrofuran at 25 °C by GPC. The tacticity of PMMA (89% syndiotactic, 11% heterotactic) was determined by 250-MHz NMR spectroscopy; a 5% solution in *o*-dichlorobenzene was analyzed at 130 °C with a CAMECA RMN 250 instrument.[16]

Attachment of Fluorescent Chromophores.[17] Naphthalene and anthracene were selected as donor and acceptor, respectively, in the investigation of PVC/s-PMMA blends. (9-Anthrylmethyl)lithium was used to attach the anthracene moiety onto PVC by nucleophilic substitution of secondary chlorine atoms. The reaction proceeded under anhydrous conditions in tetrahydrofuran at 0 °C. (9-Anthrylmethyl)lithium itself was prepared by metalation of 1,2-di(9-anthryl)ethane by lithium in tetrahydrofuran under anhydrous conditions.[18] Its formation was checked by UV spectroscopy (λ_{max} = 694, 675, and 635 nm). The 1,2-di(9-anthryl)ethane was prepared by reducing 9-anthraldehyde with lithium aluminum hydride in refluxing tetrahydrofuran.[19]

The naphthalene moiety was similarly attached to PVC by reaction of (α-naphthylmethyl)lithium with PVC in tetrahydrofuran at 0 °C. (α-Naphthylmethyl)lithium, synthesized by metalation of 1,2-di(α-naphthyl)ethane by lithium[20] and characterized by UV spectroscopy (λ_{max} = 498 nm), was also used to attach the naphthalene moiety onto PMMA by reaction with ester side groups. The reaction was performed under anhydrous conditions in tetrahydrofuran at room temperature and stopped by addition of aqueous hydrochloric acid. 1,2-Di(α-naphthyl)-ethane was prepared according to procedures devised by Copeland, Dean, and McNeil.[21]

The crudely labeled polymers obtained in this fashion were purified by repeated dissolution in tetrahydrofuran and precipitation twice into methanol and twice into hexane. In that way, the percentage of chromophores remained constant and any trace of grease was removed. The absorption spectra of 9-methylanthracene and α-methylnaphthalene were identical with those of the parent moieties anchored onto polymers. The content of naphthalene and anthracene moieties in the labeled polymers was determined by UV spectroscopy. PMMA was labeled with 1.54 mol % anthracene, whereas PVC contained 0.99 mol % naphthalene and 1.20 mol % anthracene, respectively. The blend of PVC labeled with naphthalene and anthracene was used as a reference in the measurement of nonradiative energy transfer. The spectroscopic characteristics of the labeled polymers were assumed to be the same as those of the corresponding model systems, 9-methylanthracene and α-methylnaphthalene (Table I). R_0 was estimated from Berlman's data[22] using n_{PMMA} = 1.50, n_{PVC} = 1.55, and K^2 = 0.476 for a random orientation of donor and acceptor in a rigid medium.[23]

NRET Measurements. The labeled polymers were diluted with corresponding unlabeled polymers in order to prepare films containing 10^{-2} mol L^{-1} of donor and acceptor, respectively. Films were cast from 2% methyl ethyl ketone solutions onto quartz plates. The solvent was allowed to evaporate slowly for 2 days at room temperature under a nitrogen atmosphere and the films were finally dried under vacuum at 50 °C for 48 h. They were kept under nitrogen before measurement. Film thickness was ~25 μm.

Emission spectra were recorded with a Hitachi Perkin-Elmer MPF-ZA spectrofluorimeter. Following the procedures of Amrani et al.,[14] the exciting beam was directed at 60° to the surface of the sample sandwiched between quartz plates, emission was observed at 30° to the surface. Energy-transfer efficiency was characterized by the ratio of the emission intensity of the naphthyl and anthryl labels (I_N/I_A), measured at 338 nm for the donor and 417 nm for the acceptor. The donor was selectively excited at 282 nm. The ratio I_N/I_A was plotted as a function of blend composition.

NMR Measurements. Three s-PMMA/PVC blends of respective composition 25/75, 40/60, and 60/40 by weight were prepared as thin films by controlled evaporation of dilute solutions at room temperature. The solvent methyl ethyl ketone was selected according to the conditions defined by Zeman and Patterson with a view to obtaining PVC/PMMA blends largely unaffected by the presence of the solvent.[24,25] Each polymer was separately dissolved in methyl ethyl ketone, and the resulting solutions (3 wt %) were mixed together by stirring overnight. After mixing, the solutions were filtered, poured into Petri dishes, and allowed to evaporate slowly (for at least 1 week) under a slight nitrogen

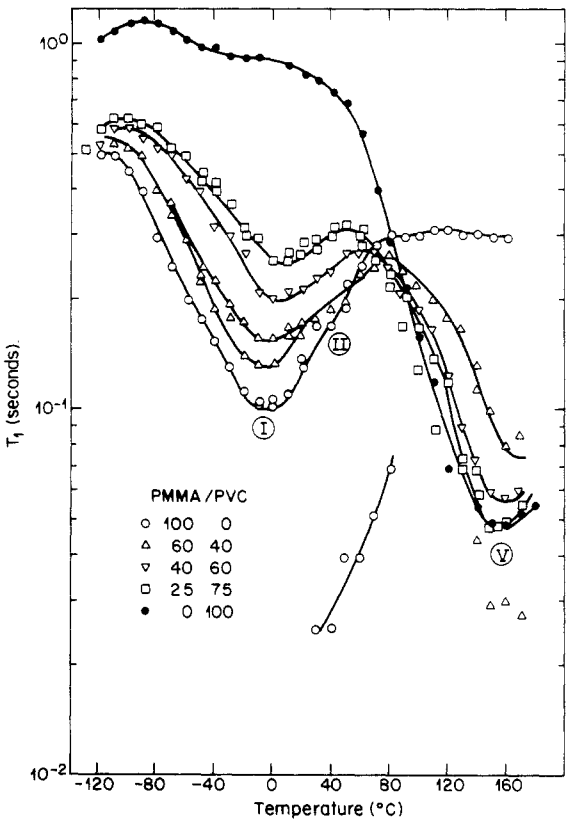

Figure 1. T_1 data (40 MHz) for s-PMMA, PVC, and s-PMMA/PVC blends. Relaxations labeled I, II, and V are explained in the text.

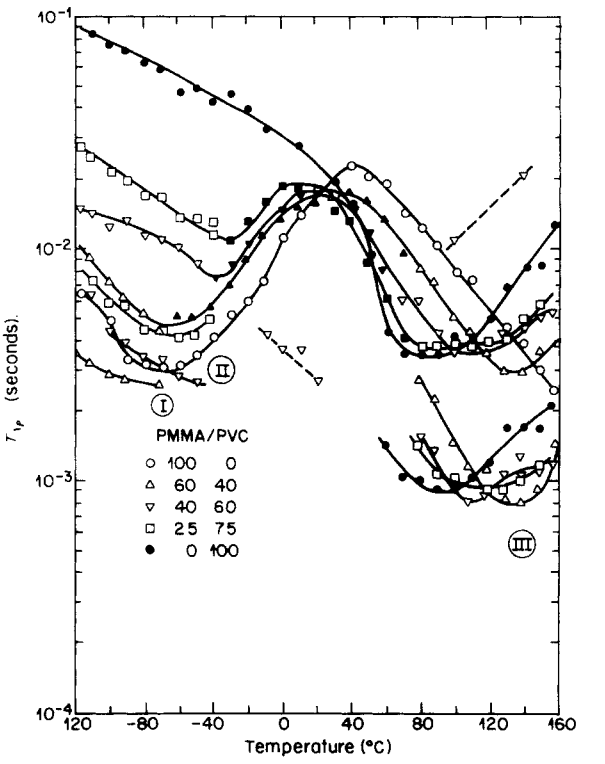

Figure 2. $T_{1\rho}$ (H_1 = 10 G) for s-PMMA, PVC, and s-PMMA/PVC blends. Relaxations I, II, and III are explained in the text.

stream. The resulting films were further dried under vacuum at 50 °C to constant weight, then cut into small pieces, and packed in NMR tubes of 10-mm diameter. A 60/40 physical mixture of PVC and s-PMMA, for comparison with the 60/40 blend, was prepared by mixing finely chopped pieces of homopolymer film in proportions of 60/40 wt % in an NMR tube. All sample tubes were sealed under vacuum.

Proton resonances at 40 MHz were recorded with a Bruker SXP pulsed NMR spectrometer interfaced to a Commodore PET computer via a Biomation transient recorder. 180°–τ–90°[26] and 90°–90° (phase shift) spin-locking[27] pulse sequences yielded T_1 and $T_{1\rho}$ (H_1 = 10 G), respectively. Short, intermediate, and long T_2 decays required the 90°–τ–90°$_{90°}$ solid echo sequence,[28] a 90° pulse, and the 90°–τ–180° spin-echo sequence,[26] respectively. Sample temperature was controlled to ±1 °C. Details of data analysis have been described elsewhere.[29]

Results and Discussion

NMR. T_1, $T_{1\rho}$, and T_2 for the five samples are presented in Figures 1–3. Considering first the data for neat s-PMMA, it is recalled that T_1 and $T_{1\rho}$ minima at about 0 °C and −80 °C, respectively, herald the onset of α-methyl motion (labeled relaxation I).[30] The corresponding transition in T_2 is small and is usually unresolved. There is a barely detectable shoulder on the higher temperature side of the T_1 and $T_{1\rho}$ minima, more clearly evident in earlier data,[31] which has been attributed previously to local main-chain torsional motion (relaxation II).[30,31] This assignment has been queried in the light of more recent experiments.[32,33] The increase in T_{2_s} beginning about 130 °C manifests the onset of the glass transition (relaxation III). Again recalling earlier data for PMMA,[31] we expect the corresponding $T_{1\rho}$ minimum to begin to form at 160 °C, the upper limit of our available temperature range. Of added interest is the appearance of a longer, albeit weak (~10–15%), T_{2_L} component for temperatures above ambient and the very weak (≤10% intensity) second T_1 component (relaxation IV). These components, which

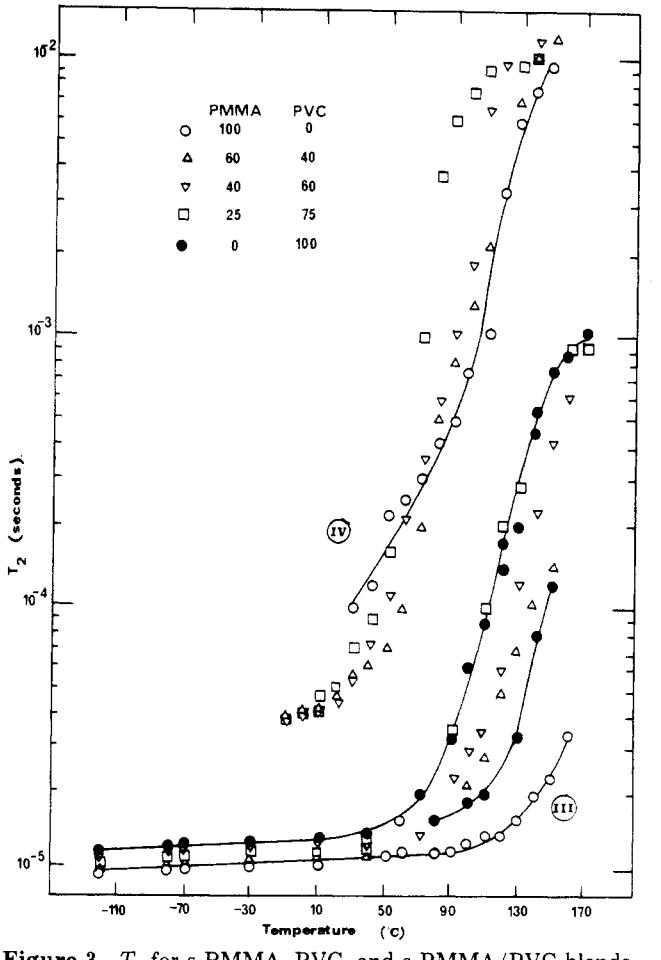

Figure 3. T_2 for s-PMMA, PVC, and s-PMMA/PVC blends. Some of the data points are omitted for clarity. Relaxations III and IV are explained in the text.

manifest mobile material, survived annealing to 120 °C under vacuum for 6 h. While the possibility of residual

solvent is the most likely candidate, one may also speculate that low-molecular-weight polymer or a small amount of i-PMMA, which has a much lower T_g than s-PMMA, can give rise to a long T_2 and, in certain cases, a short T_1 component. In our case, however, the polydispersity of PMMA is small and no isotactic triads could be detected by NMR. It has been shown too that the presence of small amounts of water can plasticize PMMA to produce a characteristic relaxation in this general temperature region.[30] A definitive interpretation must await further study.

NMR data for the carefully purified PVC studied here are generally consistent with previous measurements where the T_1 minimum at 160 °C and the broad $T_{1\rho}$ minima in the vicinity of 100 °C manifest the glass transition (relaxation V).[30,34-36] In earlier experiments on plasticized PVC, DSC[37] and NMR[35,36] measurements pointed toward two glass transitions, corresponding to identifiably different phases in PVC. It was observed that plasticizer affected one of the phases to a much greater extent than the other. The observation of two resolved $T_{1\rho}$ minima of skewed shape (Figure 2) clearly reflects the complexity of events in the vicinity of the glass transition, despite the absence of plasticizer or stabilizer. The β-relaxation in PVC is weak and, in earlier measurements by McCall and Falcone,[34] appeared only as a shoulder near room temperature in $T_{1\rho}$ vs. temperature. This relaxation is less well-defined in our data. The tendency for T_1 to level off below ~40 °C was also a feature of the earlier results and almost certainly reflects weak relaxation by impurities.

Regarding the NMR response of the blends, first consider the temperature region where the α-methyl protons are relaxing efficiently (relaxation I). As in previous work on PMMA/PSAN,[38] a single T_1 is observed in all cases in this temperature region, implying compatibility on a dimensional scale defined by $\langle r^2\rangle^{1/2} \approx (6D\tau)^{1/2}$, where $\langle r^2\rangle^{1/2}$ is the root mean square diffusive path length, $D \approx 10^{-12}$ cm^2 s^{-1} is the diffusion coefficient, and $\tau \approx T_1$ is the time over which diffusion takes place. For $T_1 \approx 0.25$ s, $\langle r^2\rangle^{1/2} \approx 12$ nm, indicating that there can be no detectable number of protons in s-PMMA or PVC at distances greater than about 12 nm from the relaxing α-CH_3 groups. This is illustrated particularly clearly in Figure 4, where T_1 for the 60/40 physical mixture of s-PMMA/PVC is compared with T_1 for the 60/40 blend. In the former case the observed decay represents a superposition of signals for the component homopolymers while in the latter, a single-exponential decay is observed as expected for an intimate mixture of the two homopolymers on the dimensional scale of 12 nm.

On the basis of strong spin diffusion coupling

$$K = K_1\frac{N_1}{N_T} + K_2\frac{N_2}{N_T} \qquad (3)$$

where K is the observed relaxation rate, K_1 is the intrinsic relaxation rate of the N_1 α-CH_3 protons, and K_2 allows a contribution to relaxation of the N_2 PVC protons. N_T is the total number of protons in the spin system. Equation 3 may be rewritten

$$(w + 1.5)K = w(0.94K_1 - 1.5K_2) + 1.5K_2 \qquad (4)$$

where w is the weight fraction of s-PMMA. Equation 4 provides a satisfactory description of the T_1 data (Figure 5) in support of the notion of intimate mixing on the scale specified.

In contrast, $T_{1\rho}$ decay for α-CH_3 relaxation in the blends is nonexponential. This is consistent with the view that the α-CH_3 groups are unable to relax fully the remaining

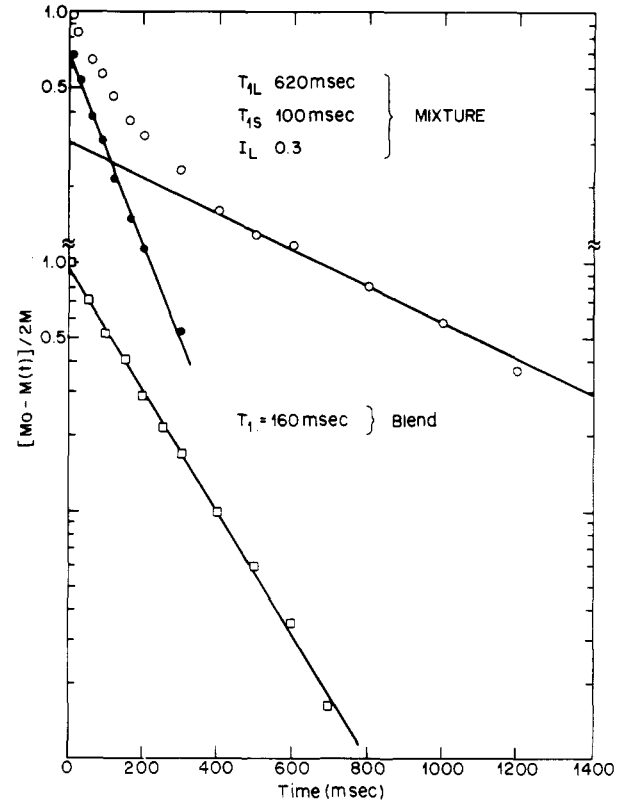

Figure 4. Comparison of T_1 for a 60/40 physical mixture of s-PMMA and PVC (○, ●) with T_1 for the 60/40 blend (□) at 0 °C. Note that the fraction of PVC protons in the 60/40 blend is 0.29.

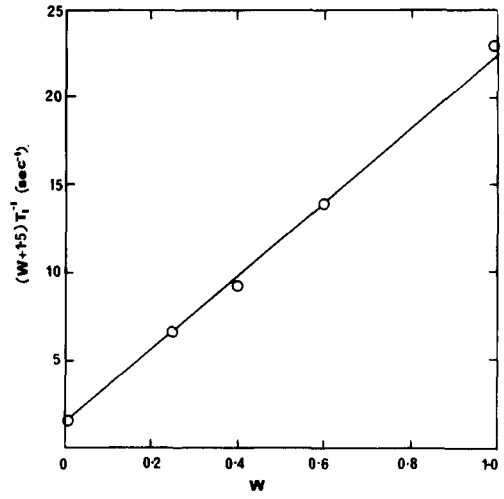

Figure 5. Plot of $(w + 1.5)K$ vs. w for s-PMMA/PVC blends. w is the weight fraction of s-PMMA in the blend and $K = T_1^{-1}$ for relaxation I due to α-CH_3 groups.

protons on the shorter time scale of ~10^{-2} s and the correspondingly shorter diffusive path length of ~2.5 nm. The blends are considered to be heterogeneous on this scale.

Now consider $T_{1\rho}$ for relaxation II (−40 °C), where the decay is exponential in all but the 25/75 sample. Distinct minima are observed for the 25/75 and 40/60 blends. At least in a qualitative sense, it would appear that the molecular mechanism responsible for relaxation II in s-PMMA can relax the complete proton spin system somewhat more efficiently than α-CH_3 groups even on the shorter dimensional scale defined by $T_{1\rho}$. Since it has been demonstrated earlier that α-CH_3 groups were unable to relax the whole spin system, it is unlikely that main-chain

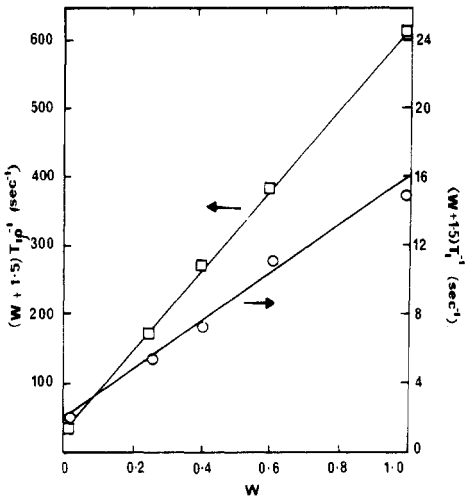

Figure 6. Plots of $(w + 1.5K)K$ vs. w for s-PMMA/PVC blends. w is the weight fraction of s-PMMA in the blend and $K = T_1^{-1}$ and $T_{1\rho}^{-1}$ for relaxation II.

Table II
Temperatures (°C) of T_2 Transitions and T_1 and $T_{1\rho}$ Minima in the High-Temperature Region

			$T_{1\rho}$	
PMMA/PVC	T_{2_s}	T_1	$T_{1\rho_s}$	$T_{1\rho_L}$
100/0	155		>160	>160
60/40	115	>170	135	135
40/60	105	160	105–(125)	100–130
25/75	90	150	90–130	80–120
0/100	90	155	~90	~90

torsional motion, presumed earlier to be the source of relaxation II,[30,31] would be any more successful. Taking this observation together with the conclusions of Shibayama et al.[32] and Naito et al.,[33] who question the assignment of ester side group motion to the β-relaxation in PMMA, it is plausible that relaxation II may in fact arise from the motion of ester side groups. One would expect ester side groups in s-PMMA to be in better contact with PVC in the blends and therefore to constitute more efficient relaxation centers. Of course, one cannot rule out impurity water as the source of relaxation.[30] Equation 4 is also applicable in the case of ester group relaxation since methyl groups are again the source of relaxation. Reasonably linear plots of $w + 1.5K$ vs. w are indeed observed for both T_1 and $T_{1\rho}$ data (Figure 6), thereby lending at least semiquantitative support to the scenario that motion of ester side groups is responsible for relaxation II in s-PMMA and that these groups are in reasonable contact with PVC in the blends. In the plot shown in Figure 6, the magnitude of the longer $T_{1\rho}$ component for the 25/75 blend was used, the shorter component reflecting internal equilibration of the spin system.[39]

The salient features of the NMR data at high temperatures are summarized in Table II. Transition temperatures for T_1 and T_{2_s} tend to increase with increasing s-PMMA content. Details of the small-scale heterogeneity discussed above are not resolved at all in T_1 and marginally so in T_2. $T_{1\rho}$, on the other hand, displays the familiar complexity associated with PVC and its blends and obviously reflects a heterogeneous system. The mobile material responsible for T_{2_L} is barely detectable in $T_{1\rho}$; the sparce set of data points for the 40/60 blend linked by the dashed line in Figure 2 are assigned to this source. Minima in $T_{1\rho}$ for neat PVC occur at ~90 °C with additional relaxation of comparable magnitude manifested at higher temperatures. The 60/40 blend, which, it is recalled, corresponds to a monomer ratio of about 1:1 is characterized by minima at 135 °C in the two $T_{1\rho}$ components. Greatest complexity attaches to the intermediate, 40/60 and 25/75, blends, for which $T_{1\rho}$ minima are particularly broad. The extremes of these minima however fall within the temperature span defined by $T_{1\rho}$ for neat PVC on the low-temperature side and by $T_{1\rho}$ for the 60/40 blend on the high-temperature side. Note that the $T_{1\rho}$ relaxation times for the 25/75 and 40/60 blends are significantly shorter than $T_{1\rho}$ for neat PVC in the vicinity of 135 °C, indicating that relaxation in the blends cannot be due to relaxation mechanisms in PVC in this temperature region. In no case is there a response typical of neat s-PMMA, for which a $T_{1\rho}$ minimum is expected somewhat above 160 °C.[31] $T_{1\rho}$ component data indicate some remanent spin diffusion coupling between the heterogeneous regions.

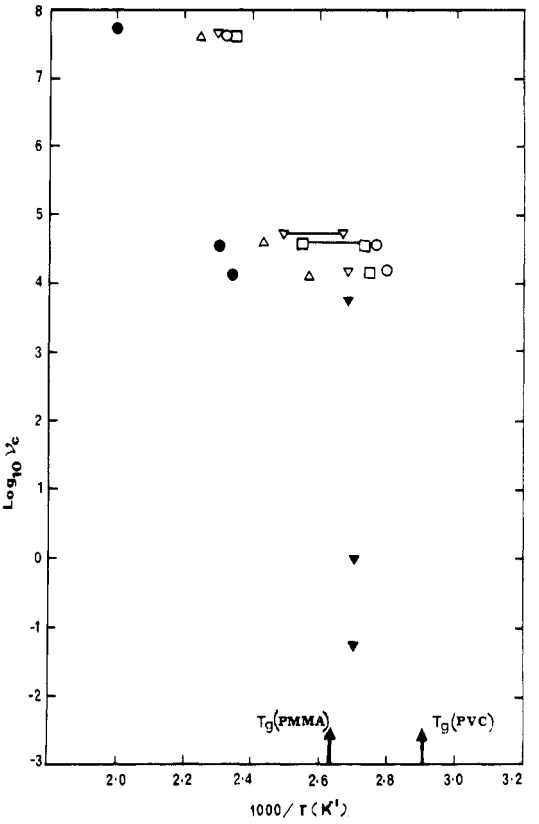

Figure 7. Transition map of log ν_c vs. $10^3/T$ for s-PMMA (●), PVC (○), and s-PMMA/PVC blends with compositions of 25/75 (□), 40/60 (▽), and 60/40 (△). All data relate to NMR measurements with the exception of the points denoted by (▼) for the 40/60 blend which are taken from ref 1 and 4.

This general pattern is perhaps more evident in the transition map of Figure 7 which portrays the relaxation behavior of the component homopolymers and their blends. It is recalled that the correlation frequency ν_c measured at various temperatures T provides an approximate description of molecular motions responsible for the observed relaxation.[29,30] All systems show the characteristic behavior described by Williams, Landel, and Ferry[40] but experimental data are too sparce to attempt meaningful fits to the WLF expression.

Before drawing general conclusions from these data, let us first consider the effects of nonradiative energy transfer.

NRET. The emission intensity ratio I_N/I_A is recorded as a function of blend composition in Figure 8. These data may be compared with the ratio $I_N/I_A \simeq 0.18$ for a PVC reference material labeled with both donor and acceptor moieties, constituting a reasonably homogeneous reference blend. The observation that the emission intensity ratios for the blends ($0.35 < I_N/I_A < 1.0$) are significantly higher

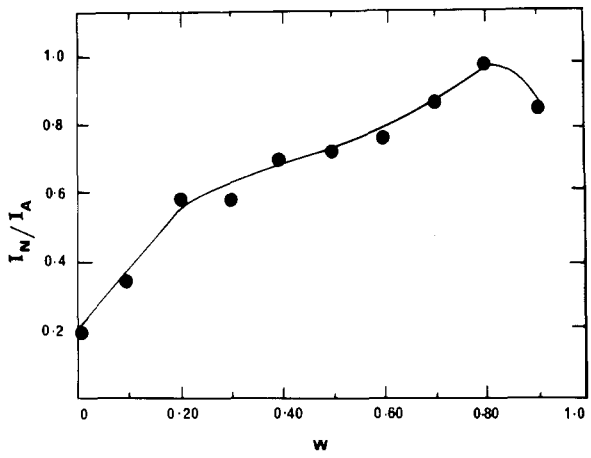

Figure 8. Emission intensity ratio I_N/I_A vs. w for s-PMMA/PVC blends. w is the weight fraction of s-PMMA.

than 0.18 indicates that the PVC/s-PMMA blends are inhomogeneous on the 2-nm scale. The significance of the I_N/I_A magnitudes involved is clarified in the following rough calculation. For solutions of 9-methylanthracene and α-methylnaphthalene of equal absorbancy irradiated at 282 nm, the emission intensity ratio at 338 and 417 nm is 1.24. As the ratio of the molar extinction coefficients of the chromophores is 10.7, an emission intensity ratio of 13.2 is expected for equimolar concentrations in acceptor and donor in the absence of energy transfer. The reported I_N/I_A values are more than 1 order of magnitude lower, indicating an efficient transfer between donor and acceptor. This supports the view that the heterogeneous domains in the blends must be extremely small, in general accord with the results of NMR.

In rationalizing these observations let us first consider the possible contributors to the NMR response. In support of the notion that PVC and s-PMMA are complementary polymer pairs[1] and guided by earlier observations on PVC/PMMA[1-3] and PVC/PCL,[41] one might anticipate that there is a tendency for the two components to form blended polymer in a 1:1 monomer ratio. Indeed a 1:1 PVC/s-PMMA associate looks like a well-defined compound and as such corresponds to the highest level of miscibility which can be attained in the complete composition range. This view finds support in the NMR data where the relative importance of immiscible PVC decreases and virtually disappears at 60 wt % s-PMMA. On this premise there will be excess PVC in the 25/75 and the 40/60 blend, which may itself contain further sources of microscopic heterogeneity in the form of small amounts of "paracrystalline phase".[35,36] The mobile material corresponding to T_{2_L} may well assume the role of plasticizer at high temperatures even for the otherwise pure PVC. There is no evidence in the NMR data to indicate the presence of neat s-PMMA.

At this point one might well propose a simple two-phase system comprising 1:1 blended polymer along with excess PVC. However, this somewhat simplistic view is at odds with the NRET data. The tendency for I_N/I_A to increase with increasing s-PMMA content implies a progressive decrease in the efficiency of nonradiative transfer and a concomitant increase in demixing in general accord with earlier observations. Aside from the marginal change in slope of I_N/I_A vs. w, however, there is no evidence of a sharp transition from homogeneous to demixed blends as detected in DSC and dynamic mechanical measurements at $w \sim 60$ wt %.[1,3] Recalling that NMR predicts highest miscibility for the 60/40 blend, one would expect a minimum in I_N/I_A for this composition. Obviously, this is not the case (Figure 8). While this may be due in part to the relative sensitivities of the NMR and NRET techniques and indeed it is common to detect small-scale demixing or local concentrations of homopolymer by nonradiative transfer in systems deemed to be wholly compatible by other techniques,[14,15] one must broaden the discussion to allow for other possibilities. Undoubtedly, molecular weight assumes an important role since it is well-known from entropy considerations that polymer–polymer miscibility decreases as the molecular weight increases. In the formation of an intimate blend, molecules above a certain molecular weight may well be excluded. It is recalled that the difference of molecular weights was invoked by Schurer et al.[1] to account for variations between their results and those of Razinskaya and co-workers.[2] It would be expected too that the discontinuity observed in T_g for 60 wt % s-PMMA should occur at a different composition upon a significant change in the molecular weight or polydispersity of PMMA and PVC.

It is noteworthy that all groups who have studied blends of PVC with s- or a-PMMA agree on the higher solubility of PMMA in PVC compared to that of PVC in PMMA. Thus, one can visualize a scenario where PMMA is dispersed in PVC as phases which are smaller than phases of PVC in a PMMA matrix. Accordingly, when PMMA is added to PVC, high-molecular-weight fractions of PMMA and PVC demix into particles or phases whose mean size and/or relative amount are too small, for example, to be detected by DSC (thus giving rise to a single T_g) but of sufficient size to induce a decrease in the efficiency of nonradiative energy transfer. As the weight percent of PMMA increases, the proportion of "immiscible" PMMA increases while that of PVC tends to decrease. As the mean size of the PMMA phases increases, there is a concomitant rise in the I_N/I_A ratio whereas T_g is expected to deviate from the values appropriate to a homogeneous blend, as observed by Schurer et al.[1]

At a composition depending on the molecular characteristics of PMMA and PVC, the nonblended PMMA forms the continuous phase (phase inversion) and PVC, dissolved in low-molecular-weight PMMA (the best solvent for PVC), forms dispersed, but rather large, particles, which could explain the observation of two T_g's as well as a more rapid increase of the I_N/I_A ratio. Such a pattern must depend on the morphological details, that is both on the preparation technique of the blends and on the molecular features (molecular weight and polydispersity) of the selected polymers. This is well illustrated by the discrepancy between our results and the conclusions of Vanderschueren et al.[3] In both cases, the selected polymers are quite similar (we use the *same* commercial PVC and practically the same synthesized s-PMMA) but they are blended by different pathways.

In addition to these general considerations there is the question of the small-scale heterogeneity in the PVC component. It may be presumed, for example, that the "paracrystalline" phase in PVC is less likely to form a compatible blend with s-PMMA and, as a result, its relative concentration in a PVC-rich component of the blend would be greater than in neat PVC. This may well induce, for example, an observable MWS peak in the TSDC spectrum for blends rich in PVC which is not evident in neat PVC.[3]

To conclude, both NMR and NRET data support the view that heterogeneities in the PVC/s-PMMA investigated are small. It was not possible to model definitively the small-scale heterogeneity present but consideration has

been given to those factors which exert an important influence on the degree of miscibility achieved: (i) the method of mixing used, (ii) the effects of tacticity, molecular weight, and polydispersity on polymer–polymer miscibility, and (iii) the difference in solubilization power of PVC for PMMA and PMMA for PVC, at least for the homopolymers selected thus far.

Acknowledgment. B.A. is indebted to SPPS (Services de la Programmation de la Politique Scientifique) for financial support in connection with her Ph.D. thesis work in Liège and to FNRS (Fonds National de la Recherche Scientifique) for funding to undertake advanced training in NMR at Trinity College, Dublin. We are grateful to Dr. C. David and Dr. D. Baeyens Volant (Universite Libre de Bruxelles) for their collaboration in the application of the nonradiative energy transfer method. Research support from the National Board for Science and Technology of Ireland is also gratefully acknowledged.

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On the Dynamics of Photostimulated Conformational Changes of Polystyrene with Pendant Azobenzene Groups in Solution

Masahiro Irie‡ and Wolfram Schnabel*†

Hahn-Meitner-Institut für Kernforschung Berlin, Bereich Strahlenchemie, D-1000 Berlin 39, Federal Republic of Germany, and Institute of Scientific and Industrial Research, Osaka University, Osaka, Japan. *Received April 23, 1984*

ABSTRACT: Copolymers of polystyrene and 4-(methacryloylamino)azobenzene containing between 2.2 to 6.5 mol % of the latter were irradiated with 15-ns flashes of 347-nm light in cyclohexane solution at 25 °C. It is inferred from optical absorption measurements that the trans → cis isomerization of pendant azo groups occurred during the flash, i.e., with $k \geq 10^8$ s^{-1}. Time-resolved light scattering intensity (LSI) measurement in the microsecond time range yielded evidence for polymer chain contraction (indicated by an increase of the LSI) with a rate constant of 10^3–10^4 s^{-1} as a consequence of the isomerization. At a later stage (several hundred milliseconds after the flash), another very strong light scattering intensity increase was observed, reflecting polymer aggregation and precipitation. The mechanism of conformational change and precipitation was discussed in terms of alterations of the balance of polymer–solvent and polymer–polymer interactions as a consequence of isomerization.

Introduction

Laser flash photolysis in conjunction with the light scattering (LS) detection method is an appropriate tool for investigating the dynamics of macromolecules in solution. Some years ago, the dynamics of disentanglement diffusion were studied by measuring the rate of the change of the light scattering intensity (LSI) after very fast main-chain scission. In this case, the diminution of the average molecular weight gave rise to a decrease of the LSI after irradiation of the polymer solution with a 20-ns flash.[1]

Flash photolysis in conjunction with the LS detection method is also applicable to measure the rate of confor-

† Hahn-Meitner-Institut für Kernforschung Berlin.
‡ Osaka University.

0024-9297/85/2218-0394$01.50/0