

Investigation of Polymer Miscibility by Spectroscopic Methods IV. How Far is Poly(Vinyl Chloride) Miscible with s-Poly(Methyl Methacrylate) and Poly(styrene-co-acrylonitrile)? An Answer from Nonradiative Energy Transfer

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Synopsis

Miscibility of PVC with s.PMMA and SAN, respectively, has been investigated by nonradiative energy transfer. Blended by using a common solvent, the two polymer pairs are not homogeneous at a molecular level. They are likely to contain heterogeneities of a few nanometers depending on blend composition. At a comparable number average molecular weight, but a different polydispersity, SAN is seemingly less miscible with PVC than s.PMMA. That this behavior is of enthalpic or entropic origin, or mainly due to the method of mixing, cannot be settled so far.

INTRODUCTION

In the past decade, an ever increasing interest has been devoted to polymer blending and, as a consequence, to the investigation of polymer-polymer miscibility.^{1,2} Polymer blends are now recognized as the most efficient way of achieving commercially viable improved products, the other means (new monomers, new molecular structures, . . .) being generally less efficient to provide progress in polymer technology together with reduced cost. The differences between miscible versus immiscible polymer blends are comparable to those between random (homogeneous) and block (multiphase) copolymers, in terms of mediation or additivity of final bulk properties. Therefore present and future applications of blends strongly depend on the knowledge of the miscibility of commercial polymer pairs in order to achieve well-defined objectives.

Establishing miscibility in an unambiguous way is a very delicate task since it depends a great deal on both the blending methods used and the investigation techniques of the final state of mixing. The methods of preparation and the time and temperature to which the mixture is subjected are determinant to bracket reasonably the thermodynamic equilibrium. Of course, from an applied point of view it would be of minor importance to investigate the equilibrium state rather than that obtained reproducibly with industrial equipment. On the other hand, the actual level of molecular

mixing is hard to ensure because it depends on whether the investigation technique is able to probe mixing on a molecular scale. Numerous experimental techniques are based on bulk properties, such as glass transition. Nevertheless, microscopic evidence of two-phase structures has been reported in cases where glass transition measurements conclude to a single-phase behavior.¹ How large is the size of a domain required to be detected by a given experimental technique is thus an important question.

Transmission electron microscopy (TEM) is probably the most powerful technique with a resolution down to a few angstroms in the most favorable conditions. Unfortunately, low penetrating power, insufficient contrast in the sample and artifacts in the final image can drastically limit its usefulness.^{3,4} More recently, pulsed NMR has proved to be helpful in probing spatial inhomogeneity from molecular dimensions in the nanometer range up to microns or larger.⁵⁻⁷ In that respect, the transport of spin energy (spin diffusion) is a phenomenon quite suitable to derive information on small-size heterogeneities in polymers. Spectroscopy and more especially fluorescence techniques are also particularly valuable in the determination of the degree of polymer-polymer miscibility. Aside from the excimer fluorescence employed by Frank,⁸ and a fluorescence emission analysis reported by Monnerie,⁹ Morawetz has recently proposed a method relying on radiationless transfer between two fluorescing chromophores attached, one on each polymeric component of a binary blend.¹⁰⁻¹⁵ The emission spectrum of the first chromophore (the donor D) has to overlap the absorption spectrum of the second (the acceptor A). The energy selectively absorbed by the donor can be transferred to the acceptor through a nonradiative process over distances of a few nanometers. The ratio of the emission intensity of the donor and acceptor labels (I_D/I_A) is a measure of their mean mutual spacing and thus reflects the mutual interpenetration of two labeled polymers. The labeling of polymer pairs Morawetz has studied so far, was generally performed by copolymerization with monomers carrying the appropriate label. This procedure is of course inappropriate when preformed or commercial polymers have to be investigated by nonradiative energy transfer (NRET). It is the reason why we have reported elsewhere the chemical labeling of commodity polymers such as poly(vinyl chloride) (PVC), poly(methyl methacrylate) (PMMA) and poly(styrene-co-acrylonitrile) (SAN).¹⁶

After polyolefins, PVC is probably the most widespread thermoplastic and, as a consequence, it is a major candidate in the development of new materials by polymer blending. Furthermore, PVC is reported as miscible with other commercial polymers, i.e., syndiotactic and atactic PMMA, SAN, and poly(ϵ -caprolactone) (PCL).¹ Accordingly, the following question arises: does PVC exhibit the same degree of miscibility with each of these three species? A NMR study of PCL/PVC and s.PMMA/PVC blends has already given partial answers to that specific question.^{6,7} The two kinds of blends are homogeneous on a dimensional scale of 12 nm, but heterogeneous at the 2nm scale. As the NMR study of the PVC/SAN pair is not straightforward, these polymer blends have been investigated by NRET in comparison with PVC/s.PMMA blends. This paper aims at reporting the preliminary results of that investigation.

EXPERIMENTAL

Materials

PVC was a commercial sample supplied by Solvay Belgium (PVC RD 258). It was purified by a twofold precipitation from tetrahydrofuran (THF) into methanol and finally dried under vacuum up to constant weight. In this way, PVC was expected to be freed from stabilizer and plasticizer. Molecular weights $\bar{M}_n = 43,000$, $\bar{M}_w = 80,000$ were determined in THF at 25°C by gel permeation chromatography (GPC).

Methyl methacrylate was anionically polymerized under anhydrous conditions in THF at -78°C using diphenyl methyl lithium as initiator. Polymerization was stopped by the addition of hydrochloric acid. The polymer was precipitated into methanol and hexane and dried under vacuum. Molecular weights ($\bar{M}_n = 41,000$ and $\bar{M}_w = 64,000$) were again measured by GPC. The tacticity of PMMA (89% syndio, 11% hetero) was determined by 250 MHz NMR spectroscopy; a 5% solution in *o*-dichlorobenzene was analyzed at 130°C with a CAMECA 250 RMN instrument.¹⁷

The commercial SAN material (SAN K11 from Labofina) contained 27 wt % acrylonitrile. It was purified by a twofold precipitation from THF into methanol and dried under vacuum ($\bar{M}_n = 54,000$ and $\bar{M}_w = 130,000$).

Labeling of SAN and s.PMMA

Naphthalene and anthracene were selected as donor and acceptor, respectively. 9-anthrylmethyl chloride was used as an alkylating agent to attach the anthracene moiety onto SAN in the presence of *N*-lithium diisopropylamide.¹⁶ PVC was labeled with anthracene or naphthalene through the nucleophilic substitution of secondary chlorine atoms by 9-anthrylmethyl lithium and α -naphthyl methyl lithium, respectively.¹⁶ α -naphthyl methyl lithium was also used to anchor the naphthalene label onto s.PMMA by nucleophilic attack on the ester groups.¹⁶ The crude labeled polymers were purified by repeated dissolution in THF and twofold precipitation into methanol and then into hexane. After that, the percentage of chromophores remained constant and any trace of impurities was removed. The content of naphthalene and anthracene residues in the labeled polymers was determined by UV spectroscopy. PVC contained 0.99 mol % naphthalene and 1.20 mol % anthracene, respectively. The blend of PVC labeled with naphthalene and anthracene respectively was used as a reference in the measurement of NRET. SAN and s.PMMA were labeled with 0.35 and 0.98 mol % anthracene, respectively. The spectroscopic characteristics (R_0 , J , . . .) of the labeled polymers were derived from those of the corresponding models,¹² i.e., 9-methylanthracene and α -methyl-naphthalene (Table I). R_0 was estimated from Brikx's data¹⁸ and eq. (1):

$$R_0^6 = \frac{8.8 \times 10^{-25} \cdot K^2 \cdot J \cdot \phi_D}{n^4} \quad (1)$$

TABLE I
 Spectroscopic Data for the Donor and Acceptor Chromophores

Compounds	λ_{ex} (nm)	λ_{em} (nm)	ϵ_{ex} ($M^{-1} \text{ cm}^{-1}$)	$J \times 10^{15 \ 12}$ ($\text{cm}^6 \text{ mol}^{-1}$)	$\phi_D^{0 \ 12}$	R_0 (nm)
Donor :						
α -methyl naphthalene	282	338	6.7			
				4.52	0.25	2.1
Acceptor :						
9-methyl anthracene	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.

R_0 is the critical distance at which energy transfer and D^* deactivation by fluorescence or internal quenching are of equal probability, ϕ_D^0 is the quantum yield of the donor in the absence of transfer, J is the overlap integral between the emission spectrum of the donor and the absorption spectrum of the acceptor, n is the refractive index of the medium ($n_{\text{PMMA}} = 1.50$ and $n_{\text{PVC}} = 1.55$), and K^2 is a dimensionless factor depending on the mutual spatial orientation of the transition dipole moments of the donor and acceptor. $K^2 = 0.476$ for a random orientation of donor and acceptor in a rigid medium.¹⁹

NRET Measurements

The labeled polymers were diluted with the corresponding unlabeled polymers in order to prepare films containing $10^{-2} \text{ mol L}^{-1}$ of donor and acceptor, respectively. Films were cast from 2% methyl ethyl ketone solutions on quartz plates. The solvent was allowed to evaporate slowly for 2 days at room temperature under a nitrogen atmosphere; the films were finally dried under vacuum at 50°C for 48 h. They were kept under nitrogen before measurement. The film thickness was adjusted to about 25 μm . Emission spectra were recorded with a Hitachi-Elmer MPF-2A spectrophotometer. The exciting beam was directed at 60° to the surface of the sample sandwiched between quartz plates; emission was observed at 30° from the surface. Energy transfer efficiency was characterized by the ratio of the fluorescence 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 versus blend composition.

RESULTS AND DISCUSSION

To define the resolution power of NRET using naphthalene and anthracene as donor and acceptor, respectively, the efficiency (E) of NRET has to be defined. E depends on the distance r between donor and acceptor according to:

$$E = R_0^6 / (R_0^6 + r^6) \quad (2)$$

The sensitivity of this fluorescence technique is therefore directly related to the R_0 value. By reference to Table I, the selected donor/acceptor pair

is such that nonradiative energy transfer is efficient over distances of about 2 nm. The miscibility of PVC with SAN and s.PMMA can thus be probed on this dimensional scale. Decreasing miscibility means an increase in the average distance between donor and acceptor and a consequent reduction of the transfer efficiency, i.e., an increasing I_N/I_A ratio.

Figure 1 reports the emission intensity ratio (I_N/I_A) as a function of blend composition for as well PVC/SAN as PVC/s.PMMA pairs. It is noteworthy that the two kinds of blends contain the same PVC ($\bar{M}_n = 43,000$) whereas the \bar{M}_n of SAN (54,000) and s.PMMA (41,000) are not very different from each other. The main difference in the molecular parameters of SAN and s.PMMA is the polydispersity which is worth 2.41 and 1.54, respectively.

The fluorescence data may be compared with the ratio $I_N/I_A \approx 0.18$ for a blend of PVC chains labeled with the donor and the acceptor chromophore, respectively, and used as a reasonably homogeneous reference blend. In the absence of energy transfer, the value of the I_N/I_A ratio can be approximated by the following rough calculation. Solutions of 9-methylanthracene and α -methyl naphthalene of equal absorbancy at the excitation wavelength of 282 nm were excited and the emission intensity ratio at 338 and 417 nm recorded as 1.24. As the ratio of the molecular extinction coefficients of the chromophores was 10.7, an emission intensity ratio of 13.2 would be expected for equimolar concentrations in donor and acceptor in the total absence of energy transfer.

In a broad range of composition, the PVC/s.PMMA blends are practically free from heterogeneities on a dimensional scale of 2 nm. The values of the I_N/I_A ratio (0,28) are indeed of the same order of magnitude as that reported for PVC used as a reference for homogeneity. A very slight departure from a homogeneous situation is observed for the s.PMMA rich blends (> 60%). These experimental results are in qualitative agreement with the NMR

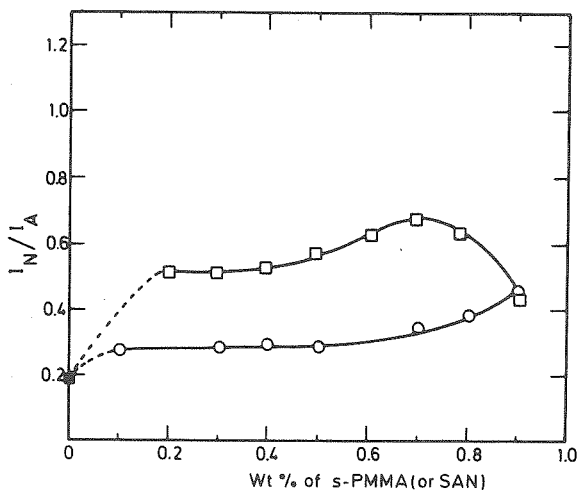


Fig. 1. Emission intensity ratio (I_N/I_A) versus weight composition (W) of (○) PVC/s.PMMA and (□) PVC/SAN blends.

investigation of blends made up of the same PVC and a higher molecular weight s.PMMA (\bar{M}_n : 150,000). That work concluded to the presence of heterogeneities the mean size of which was likely to range from 2.5 to 12nm (7,20). According to NRET, blends of PVC and lower molecular weight s.PMMA would not contain separated phases much larger than 2 nm.

At a comparable \bar{M}_n , SAN is obviously less miscible with PVC than s.PMMA is (Fig. 1). Nevertheless, no gross phase separation occurs in PVC/SAN blends, as the I_N/I_A ratio is still at the edge of homogeneity (on a scale of 2 nm) with an extreme value of 0.6 compared to 0.18 and 13.2 for homogeneous and completely phase separated systems, respectively. The I_N/I_A ratio versus composition curve is again dissymmetric showing that both SAN and s.PMMA accommodate PVC less efficiently than PVC does for them both. Phase diagrams of systems consisting of a single polymer in a single or a binary solvent mixture exhibit a striking dissymmetry too, which is attributed to the great disparity in the sizes of the mixed molecules. The same is true for mixtures of polymers with a sufficiently different chain length. The critical point is then shifted towards higher compositions of the polymer with the shorter average molecular weight.¹ That the slight difference in \bar{M}_n of PVC (43,000) and SAN (54,000) or s.PMMA (41,000) might be responsible for the marked dissymmetry of Figure 1 is doubtful.

It is worth noting here that NRET is not in disagreement with previous investigations reporting the compatibility of SAN and PVC. Although this polymer pair has not been directly characterized, information has been derived from the study of PVC and ABS (polybutadiene grafted with SAN) blends.²¹ Two glass transition temperatures (T_g) were observed. The T_g at high temperature shifted towards higher temperature with increasing ABS content in the blends and was attributed to a mixed PVC/SAN phase. The second T_g was independent of the blend composition and characteristic of polybutadiene. NRET now makes it clear that the mixing of PVC and SAN is not intimate at the molecular level but well at a few nanometers, depending on composition.

Polymer-polymer miscibility is generally explained in terms of specific interactions. As far as the miscibility of PVC and s.PMMA is concerned, reference is made to hydrogen bonds between the tertiary hydrogen atom in the vinyl chloride unit (a proton donor) and the oxygen atom in the carbonyl group of PMMA (a proton acceptor).²² If a similar situation prevails between PVC and acrylonitrile units in SAN, the concentration of interacting groups smaller in SAN than in PMMA could possibly account for the difference in miscibility reported for PVC/SAN and PVC/s.PMMA pairs (Fig. 1). This argument has however to be considered carefully. First, the intermolecular interactions are very sensitive to steric factors as convincingly demonstrated by the immiscibility of PMMA with PVC when its configuration is changed from syndiotactic to isotactic.²² Furthermore, the acrylonitrile content of SAN plays determinant role in the achievement of miscibility with other partners. SAN and poly(ϵ -caprolactone) are for instance compatible only when the acrylonitrile weight percentage in SAN ranges from 8 to 28.³³ A miscibility "window" is also reported in blends of PVC and acrylonitrile-butadiene copolymers (NBR).²⁴ Similarly, SAN and

PMMA form compatible systems when SAN contains from 9 to 27 wt % of acrylonitrile units.²⁵ Paul and Barlow have recently developed a binary interaction model which explains such a behavior.²⁶ According to these authors, the net exothermic heat of mixing required for miscibility of high molecular weight polymer mixtures might result from appropriate considerations of both intermolecular and intramolecular interactions of component units, without an exothermic interaction existing between any individual pair of units. It would therefore be helpful to investigate by NRET the effect of the acrylonitrile content in SAN on the miscibility of the SAN/PVC pair, and to analyze the experimental results by the light of the binary interaction model proposed by Paul and Barlow.

It could also be argued that the increase in the I_N/I_A ratio when s.PMMA is substituted by SAN results from the difference in their molecular parameters and more especially in their polydispersity. As the SAN sample contains a number of longer chains than the s.PMMA sample, a decrease in miscibility could be accounted for by entropic considerations. A forthcoming paper will focus on that important point in order to determine the sensitivity of NRET to a change in the molecular weight of at least one of the component polymers of a binary blend.

Finally, due to a possible disparity of its interactions with SAN and PMMA, methylethyl ketone (MEK) could impart slight differences in the state of mixing of PVC with SAN and s.PMMA, respectively. The χ_{ij} interaction parameter of the PVC/MEK pair has been estimated to 0.89 by inverse gas chromatography,²⁷ whereas, to our knowledge, this one of the SAN/MEK pair has not yet been determined. In principle Hildebrand's equation allows for the calculation of χ_{ij} :

$$\chi_{ij} = \frac{V_r}{RT} (\delta_i - \delta_j)^2 \quad (3)$$

where V_r is the reference volume. Unfortunately, the validity of eq. (3) is questionable especially for favorably interacting pairs. When applied to the PVC/MEK pair, eq. (3) provides a result (0.0068) largely different from the experimental value (0.89). In such conditions, possible effects of the solvent on the morphology of the investigated blends cannot be ascertained. It is worth recalling that a binary polymer blend prepared by using a common solvent could be affected by a too large difference between each polymer-solvent interaction parameter. It has indeed been shown that the miscible polystyrene/poly(vinyl methyl ether) pair exhibits a miscibility gap in solvents for which the strength of the polymer-solvent interactions is too high ($|\Delta\chi| \gg$ individual χ_{ij}).²⁸ Therefore, if the evaporation of these solutions is not slow enough, the final blends can be cloudy, i.e., in a nonequilibrium state, reminiscent of the "closed" two-phase region and brought about by the high viscosity of the system. Needless to say, the polymer displaying the larger χ_{ij} would preferentially come out from the solution as the solvent evaporation proceeds. In the actual case of PVC/SAN blends, it has been ascertained that the NRET results remained in the limits of experimental errors when tetrahydrofuran was substituted for MEK as a common solvent.

In conclusion, NRET is a very sensitive technique in the determination of polymer-polymer miscibility. At the level of 2 nm, a small but definite difference in miscibility is reported between PVC/s.PMMA and PVC/SAN pairs. Further investigation is required to establish the origin of this discrepancy. Interference of the common solvent used in the polymer mixing as well as entropic contributions due to a small disparity in the molecular parameters of SAN and s.PMMA cannot indeed be completely disregarded thus far.

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