Investigation of Polymer Miscibility by Spectroscopic Methods V. Effect of Molecular Weight and Block Copolymerization of Syndiotactic Poly(methyl methacrylate) on Its Miscibility with Poly(vinyl chloride)

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Synopsis

Investigated by nonradiative energy transfer (NRET), the state of mixing of PVC and s.PMMA which is on the dimensional scale of a few nanometers is significantly affected by the chain length. When PVC is blended with s.PMMA of increasing molecular weight (MW), the longest chains of s.PMMA are likely to segregate from a homogeneous blend formed by PVC and low-MW s.PMMA. The phase separation should therefore be of purely entropic origin and strongly dependent on both the relative percentage and the chain length of each component. These results are in qualitative agreement with conclusions previously drawn from DSC and transmission electron microscopy. NRET is a more powerful tool in probing heterogeneities compared to DSC and the thermally stimulated depolarization current method; it provides evidence against the previously suggested model of a 1:1 PVC/s.PMMA aggregate.

INTRODUCTION

Blending synthetic polymers is now recognized as an efficient means of achieving new polymeric materials with novel characteristics or improved performance.[1,2] Blends of miscible polymers can offer more appealing properties than those of the parent components. The development of Noryl is a convincing example of a system combining the advantages of an engineering thermoplastic [poly(2,6-dimethyl-1,4-phenylene oxide)] with the lower cost and ease of processing of a commodity polymer (polystyrene). Furthermore, there is much interest in immiscible polymer pairs which can combine in an additive way the physico-mechanical features of the associated partners, frequently yielding unexpected synergisms. While thermoplastics generally suffer from a dramatic brittleness, the dispersion of soft polydiene phases into polystyrene or poly(styrene-co-acrylonitrile) (SAN) is indeed able to promote the development of remarkable high-impact rigid materials (HIPS, ABS). For phase-separated systems, the interfacial adhesion between the respective phases, as well as the phase separation extent, have, however, a decisive influence on the ultimate mechanical properties. It is well known that poor adhesion and gross phase separation are responsible for ultimate properties significantly lower than those expected from the characteristics of the constituents. Depending on the ther-

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modynamics of mixing and the kinetics of the phase separation (or mixing) process, a broad range in the degree of mixing and related technological properties can be observed. It is therefore of prime importance to have a reliable and simultaneous insight onto the thermodynamic miscibility of a polymer pair and the morphology of the derived polymer blends.

Of the various methods used to analyze the morphology of polymer blends, electron microscopy and glass transition determination (using dynamic mechanical testing or differential scanning calorimetry DSC) are the most widely used. Recently, pulsed NMR[3-5] and fluorescence techniques[6-11] have received increasing attention because of their high sensitivity. Except for transmission electron microscopy (resolution down to a few angstroms), these techniques are probably the most powerful ones in probing spatial heterogeneity on a scale of a few tens of angstroms.

Poly(vinyl Chloride) (PVC) is a widely used commodity thermoplastic. It exhibits compatibility with several other polymers such as syndiotactic poly(methyl methacrylate) (s.PMMA), SAN containing 28 wt % acrylonitrile, and poly(ϵ-caprolactone) (PCL).[2] The weakly proton-donating α-hydrogen of the vinyl chloride unit is likely to promote these situations of compatibility. Except in the isotactic configuration, PMMA is reported to be compatible with PVC by several authors whose conclusions are, however, at variance regarding the degree of that compatibility. By using neutron scattering, Jelenic et al.[12] concluded that the homogeneous a.PMMA/PVC pair is exothermic. Nevertheless, two unusual features are reckoned at 25°C: the second virial coefficient increases as the molecular weight of the components increases, whereas the PMMA coil expansion is independent of the chain length. This effect is tentatively accounted for by the assumed crystallinity of PVC. Using DSC, Schurer et al.[13] conclude that s.PMMA ($\overline{M}_v$ 370,000) and PVC ($\overline{M}_v$ 55,000) form a compatible system up to a composition corresponding to a monomer unit ratio of about 1:1. At higher s.PMMA contents, the 1:1 s.PMMA/PVC associate would segregate from the excess of pure s.PMMA. Although they detect only one T_g by DSC in the entire range of compositions, Razinskaya et al.[14] refer to transmission electron microscopy to assess that a.PMMA ($\overline{M}_v$ 102,000) and PVC ($\overline{M}_v$ 160,000) are only partly compatible: the compatibility limits would not be higher than 5% PMMA and 2% PVC, respectively. According to Vanderschueren et al.[15] a Maxwell–Wagner–Sillars (MWS) peak is evidenced by the thermally stimulated depolarization current method (TSDC) as the blend composition exceeds 10 wt % PMMA. This composition is therefore proposed as the upper limit of compatibility of s.PMMA ($\overline{M}_w$ 203,000) and PVC ($\overline{M}_w$ 85,000). It is worth noting that these blends were roughly prepared by grinding solid PVC and PMMA followed by molding at 160°C. It is obvious that no unified view of the s.PMMA/PVC miscibility emerges, mainly because of differences in the molecular parameters of the polymers mixed together, the methods of mixing used, and the variable sensitivity of the investigation techniques used. Recently, in an effort to rationalize all these viewpoints, carefully prepared s.PMMA ($\overline{M}_n$ 150,000)/PVC ($\overline{M}_n$ 54,000) blends have been characterized by pulsed NMR and nonradiative energy transfer (NRET).[5] Heterogeneities in the range from 2.5 to 12 nm are undoubtedly present in blends containing 25, 40, and 65 wt % of s.PMMA. Compared by NRET, PVC/SAN and PVC/s.PMMA pairs exhibit a small difference in their compatibility which, among other assumptions, could be attributed to a discrepancy in the number and stereostructure of the polar groups, as well as in the molecular parameters of SAN and s.PMMA used.[16]

This paper aims at reporting the effect of both the s.PMMA chain length and its block copolymerization with polystyrene (PS) on the miscibility level with PVC. The investigation is mainly performed by NRET whereas some data of glass transition are recorded for purposes of comparison.

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. By this procedure, PVC was expected to be freed from stabilizer and plasticizer. Molecular weights ($\overline{M}_n$ 43,000; $\overline{M}_w$ 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. After the addition of hydrochloric acid, the polymer was successively precipitated into methanol and hexane. Molecular weights ($\overline{M}_n$ 41,000; $\overline{M}_w$ 64,000 and $\overline{M}_n$ 150,000; $\overline{M}_w$: 190,000) were again measured by GPC. The stereostructure of the prepared PMMA was mainly syndiotactic (89% syndio, 11% hetero) as determined by 250-MHz NMR spectroscopy on a 5% solution in *o*-dichlorobenzene at 130°C with a CAMECA 250 RMN instrument.[17] Poly(styrene-*b*-methyl methacrylate) was synthesized by sequential anionic polymerization initiated by *sec*.butyllithium in THF at −78C°.[18]

Styrene was polymerized first into a 40,000-molecular-weight block, whereas the copolymer composition was adjusted to 50 wt % of each component. The tacticity of the PMMA block was exactly the same as that of the related homopolymers.

PVC was labeled with anthracene and naphthalene through the nucleophilic substitution of secondary chlorine atoms by 9-anthryl methyl lithium and α−naphthyl methyl lithium, respectively.[19] α-naphthyl methyl lithium was also used to label s.PMMA by reaction with the ester side group.[19] PVC contained 0.99 mol % of naphthalene and 1.20 mol % anthracene, respectively. The two samples of s.PMMA were labeled with 0.98 mol % anthracene ($\overline{M}_n$ 41,000) and 1.54 mol % anthracene ($\overline{M}_n$ 150,000), respectively. The same label was attached to the PMMA block of the copolymer at a rate of 2.7 mol %. The content of fluorescing chromophores in the labeled polymers was determined by UV spectroscopy. The spectroscopic characteristics of the labeled polymers were derived from those of the corresponding models,[9] i.e., 9-methylanthracene and α-methylnaphthalene (Table I).

NRET Measurements

The labeled polymers were diluted with the corresponding 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 (MEK) solutions

TABLE I
Spectroscopic Data for the Donor and Acceptor Chromophore[a]

Compounds	λ_{ex} (nm)	λ_{em} (nm)	ϵ_{ex} (M^{-1} cm^{-1})	$J \times 10^{15(9)}$ (cm^6 mol^{-1})	ϕ_D^0 [b]	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.
[b] From ref. 9.

on quartz plates. The solvent was allowed to evaporate slowly for two 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. 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 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.

DSC Measurements

The glass transition temperatures were measured with a Perkin-Elmer differential scanning calorimeter (DSC 2C) at a heating rate of 10°C min^{-1}. All samples were first scanned up to 180°C. T_g was taken as the temperature at which half of the heat capacity change during the glass transition has occurred.

TSDC Measurements

The thermally stimulated depolarization currents were recorded with a classical experimental device as described elsewhere.[20] 0.3-mm-thick films were prepared by slow evaporation of 2 wt % polymer solutions in MEK. They were provided with two measuring electrodes and a guard ring by painting with colloidal silver and then were vacuum-oven dried over P_2O_5 at 125°C for a week.

RESULTS AND DISCUSSION

Choice and Meaning of the Experimental Conditions

Polymer–polymer miscibility is a concept which can only be defined, and is best understood, in thermodynamic terms. From an experimental point of view the dimensional scale probed by an investigation technique defines its interest as a source of thermodynamic information on a polymer–polymer pair. As mentioned in the Introduction, this paper aims at investigating the state of mixing of PVC and s.PMMA by using a fluorescence technique developed by Morawetz and based on NRET between two fluorescing chromophores attached, one on each polymeric component of a binary blend. The sensitivity of this technique depends on both the mechanism of NRET and the nature of the chromophores used. The emission spectrum of the first chromophore (the donor) has to overlap the absorption spectrum of the second (the acceptor). The critical distance R_0 at which energy transfer and D^* deactivation by fluorescence or internal quenching (or other means) are of equal probability is defined by eq. (1) and estimated from Brikx's data[21]:

$$R_0^6 = 8.8 \times 10^{-25} K^2 J \phi_D^0 n^{-4} \tag{1}$$

ϕ_D^0 is the quantum yield of D in the absence of transfer, N is Avogadro's number, J is the overlap integral between the emission spectrum of D and the absorption spectrum of A, n is the refractive index of the medium ($n_{\mathrm{PMMA}} = 1.50$ and $n_{\mathrm{PVC}} = 1.55$), and K^2 is a dimensionless factor depending on the mutual spatial orientation of the transition dipole moments of D and A; it is worth 0.476 for a random orientation of D and A in a rigid medium.[22]

The efficiency E of NRET depends on both R_0 and the distance r between the D and A fluorescing chromophores according to eq. (2):

$$E = R_0^6/(R_0^6 + r^6) \tag{2}$$

From Table I we see that the naphthalene/anthracene pair is such that the nonradiative energy transfer is efficient over distances up to about 2 nm. As the energy transfer efficiency is characterized by the ratio I_N/I_A of the emission intensity of the naphthyl and anthryl labels, any modification in the mutual interpenetration of PVC and s.PMMA on a scale of 2 nm will be reflected by a change in the I_N/I_A value. The lower the miscibility level is, the higher the I_N/I_A ratio will be.

The conclusions derived from the investigation of the miscibility of a polymer pair are not only dependent on its resolution power but also on the method of mixing used. It is usually assumed that a polymer blend recovered from a solution in a common solvent is more likely to be in its equilibrium state than a melt-blended sample, provided suitable care is taken. It is furthermore required that the common solvent used does not disturb the polymer–polymer interactions and therefore the final equilibrium of the polymer mixture. In that respect, each polymer–solvent interaction parameter (χ_{12} and χ_{13}) should be of higher positive value than the polymer–polymer interaction parameter (χ_{23}). Based on this requirement, MEK is a suitable common solvent of PVC (component 2) and PMMA (component 3). χ_{12} and χ_{13} are indeed similar, 0.89 and 0.60, respectively, whereas χ_{23} is large and negative (ca. -3.0) as determined by inverse gas chromatography.[23] Having ascertained that under the experimental conditions used the I_N/I_A values are independent of the MEK evaporation rate, it may be assumed that the equilibrium state of the investigated PVC/s.PMMA blends is reasonably approached.

Dependence of the PVC/s.PMMA Miscibility on the Molecular Weight of s.PMMA

That the thermodynamics of polymer blends is markedly affected by the high molecular weight of both components is plain. Therefore, when the mutual interpenetration of a polymer pair is investigated the conclusions drawn from experiments are only valid in the limits of the considered chain lengths. The effect of this determinant parameter is sometimes disregarded or at least underestimated and partial conclusions might improperly be considered as a general truth.

As NRET displays a resolution of a few nanometers, it could be helpful to estimate whether the state of mixing is markedly affected by the chain length on this dimensional scale or not. Figure 1 (curves 1 and 3) reports the emission intensity ratio I_N/I_A plotted against composition of PVC/s.PMMA blends constituted of the same PVC and s.PMMA of two different molecular weights ($\overline{M}_n$ 4×10^4 and 15×10^4). The fluorescence data have to be compared to the I_N/I_A ratio $\simeq 0.18$ for a blend of PVC chains labeled with naphthyl and anthryl moieties, respectively, and used as a reference of homogeneity. In the absence of NRET, the value of I_N/I_A can be approximated from solutions of 9-methylanthracene and α-methylnaphthalene of equal absorbancy. At the excitation wavelength of 282 nm, the emission intensity ratio at 338 and 417 nm is measured (1.24). Taking into account the ratio of the molecular extinction coefficient of the labels (10.7), an I_N/I_A ratio of 13.2 is predicted for equimolar concentrations in donor and acceptor in the absence of energy transfer.

Up to about 60 wt % of low-molecular-weight s.PMMA, the investigated blends are practically free from heterogeneities on a scale of 2 nm (curve 1, Fig. 1). The I_N/I_A ratio (0.28) is just a little higher than the value for the homogeneous reference blend (0.18). A slight departure from homogeneity

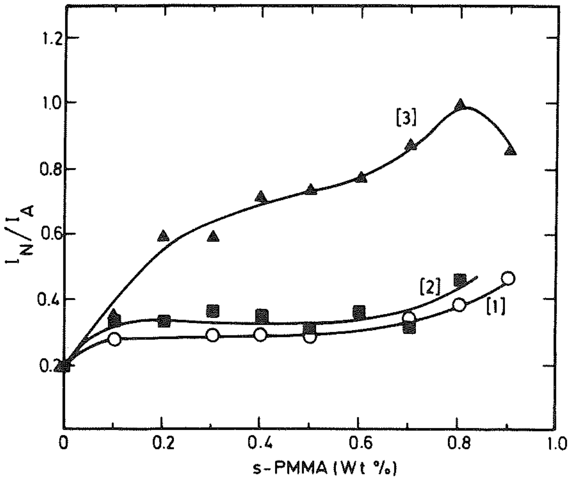

Fig. 1. Emission intensity ratio I_N/I_A vs. weight composition of binary blends constituted of PVC and s.PMMA ($\overline{M}_n$ 41,000) (○), s.PMMA ($\overline{M}_n$ 150,000) (▲), poly(styrene-*b*-methyl methacrylate) (■), respectively.

is observed for the s.PMMA-rich blends (> 60%). When the molecular weight of s.PMMA is increased from 4×10^4 up to 15×10^4, the I_N/I_A ratio goes up in the whole range of composition; a twofold increase is observed for the PVC-rich blends and a threefold increase when s.PMMA is the major component (curve 2, Fig. 1). These results put clearly in evidence a loss in the mixing ability of PVC and s.PMMA when the size of PMMA has increased fourfold. On a dimensional scale of a few nanometers the PVC/s.PMMA (15×10^4) blends contain heterogeneities which are likely to be of extremely small size as the I_N/I_A ratio does not exceed 1.0, compared to 0.18 for a homogeneous blend and 13.2 for a completely phase-separated system. The NRET technique is therefore a powerful tool in probing heterogeneities in polymer blends, but it has the disadvantage that it gives only comparative and not quantitative information on the mean size of the segregated domains. A parallel investigation of the same PVC/s.PMMA (15×10^4) blends has however provided a more quantitative picture, suggesting an apparently intimate mixture on the dimensional scale of 12 nm, but including heterogeneities on the 2.5-nm scale.[5] The agreement between pulsed NMR and NRET gives of course support to the results derived from NRET and allows a more thorough examination of these data.

If the presence and the mean size of heterogeneities are now rather well bracketed, still nothing is known about the nature of the separated phases. In a previous work, Challa et al. proposed the formation of a 1:1 PVC/s.PMMA associate miscible with excess PVC but immiscible with any excess of s.PMMA.[13] If any kind of 1:1 complex was really formed between the two homopolymers they should be most thoroughly intermixed at a composition of 60 wt % s.PMMA (i.e., a 1:1 monomer ratio). As no minimum in I_N/I_A is reported for such a blend (curve 2, Fig. 1), Challa's model cannot be supported by the present investigation and another scenario has to be devised.

It is worth noting the the I_N/I_A vs. composition curve is asymmetric and passes through a maximum at 80 wt % s.PMMA (15×10^4) (Fig. 1, curve 2). This tendency is already nascent when the low-molecular-weight s.PMMA is blended with PVC. The only difference in the blends corresponding to curves 1 and 3 (Fig. 1) lies in the molecular weight of s.PMMA. As long as this component is of sufficiently short chain length, the PVC-rich blends (< 60% s.PMMA) appear to be perfectly homogeneous on a 2 nm scale. Therefore, when the molecular weight of s.PMMA has increased up to 15×10^4, the longer chains of this sample are likely to segregate from the major, homogeneous, and probably continuous mixture of PVC, and lower-molecular-weight s.PMMA. A fractionation then takes place, leaving the too long chains of s.PMMA (and perhaps of PVC too) as small separated phases. There is evidence in the pulsed NMR data to indicate the presence of immiscible PVC, the origin of which is however questionnable.[5] Indeed, small amounts of "paracrystalline phase" in PVC are generally referred to[24,25]; they are mentioned by Jelenic et al. to explain some unusual features in the neutron scattering investigation of PVC/a.PMMA blends.[12] Along the same line of thought, when PVC is added to higher-molecular-weight s.PMMA, phases constituted of the added PVC plus lower-molecular-weight s.PMMA should segregate from a continuous PMMA matrix. Thus, depending on the composition range, either both PVC and s.PMMA form the continuous phase in which the longer chains of at least s.PMMA are dispersed as discrete domains, or the inverse situation occurs. Of course, at an intermediate composition a phase inversion is expected to occur; this phenomenon seemingly takes place at 80 wt % s.PMMA. The asymmetry of the experimental curve might be accounted for by a difference in the volume fraction of the dispersed phases. At 80 wt % s.PMMA, the added PVC (20 wt %) mainly forms discrete domains in mixing with a fraction of low-molecular-weight s.PMMA. On the other hand, at 20 wt % s.PMMA, the dispersed phases would contain only a part of this added component, corresponding to a smaller volume fraction compared to the preceding situation. According to this scheme, the phase inversion should occur earlier starting from pure s.PMMA than from neat PVC. Figure 2 is a schematic illustration of the phase separation mechanism, which is of purely entropic origin and strongly dependent on both the relative percentage and the chain length of each component.

It is noteworthy that the PVC/s.PMMA blends investigated herein are found to be heterogeneous by NRET whereas the technique of neutron scattering concludes in the complete miscibility of PVC and a.PMMA, the molecular parameters of which are unfortunately unspecified. This conclusion is amazing as neutron scattering is generally expected to be an important source of detailed fundamental thermodynamic information on polymer–polymer systems[26] and since a.PMMA is probably less miscible than the syndiotactic isomer. By reference to the previous investigations

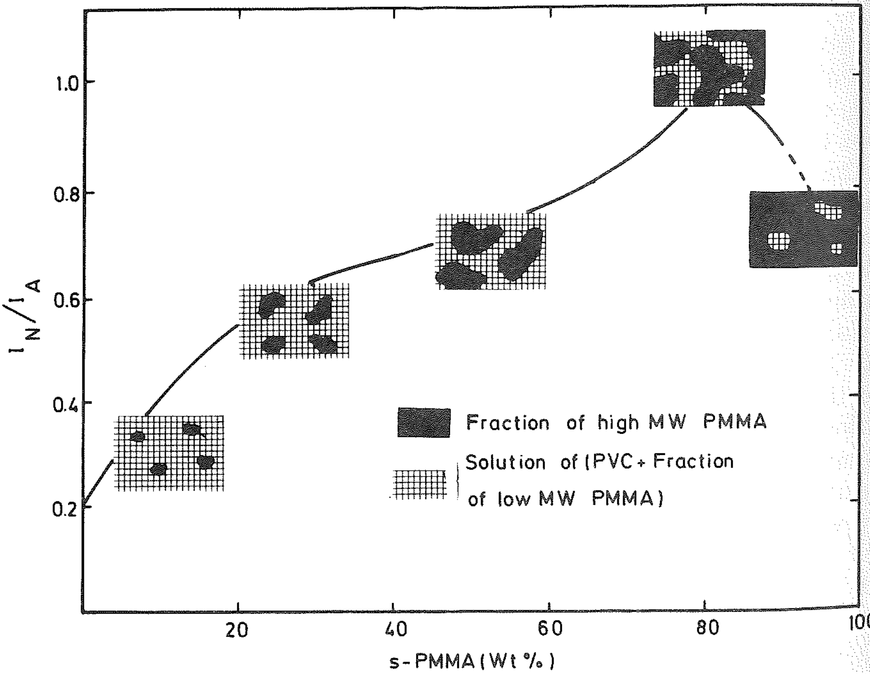

Fig. 2. Schematic illustration of the phase morphology of PVC/s.PMMA ($\overline{M}_n$ 150,000) blends.

of PVC/s. or a.PMMA blends, NRET is in qualitative agreement with the results derived by Razinskaya et al. from transmission electron microscopy.[14] NRET thus appears as a technique very sensitive to the presence of small heterogenities and able to detect modifications in the mixing level due to changes in the molecular parameters of the polymeric components. This is in agreement with results from excimer fluorescence as published by Semerak and Frank.[6]

Finally, in the light of this investigation, some observations reported by Mikes et al. deserve renewed interest. Studied by NRET, blends of polystyrene (PS) ($\overline{M}_n = 11.3 \times 10^4$ and $\overline{M}_w/\overline{M}_n = 1.51$) and poly($\alpha$-methylstyrene) (PMS) ($\overline{M}_n$ 9.5×10^4 and $\overline{M}_w/\overline{M}_n = 1.25$) also exhibit an asymmetry of the energy transfer efficiency versus composition curve.[10] Morawetz's suggestion that this effect could emerge from the difference in the molecular parameters of PS and PMS is thus corroborated, particularly in light of the broader distribution of the PS. In another paper concerned with the miscibility of SAN and PMMA, Amrani et al.[9] observe a minimum in the dependence of the energy transfer efficiency on the acrylonitrile content of SAN. The authors report that this minimum, which defines the range of miscibility (between ca. 20 and 45 mol % AN) "is distinctly higher with the longer PMMA suggesting that the interpenetration with SAN is somehow less perfect."

This observation resulting from an independent experiment lends support to the information from this work and outlines the adequacy of NRET for a detailed evaluation of polymer miscibility. Finally, in an attempt to explain the gradual change from miscibility to immiscibility as evidenced by NRET, Morawetz et al.[9] suggest, among other interpretations, that, since the polymers are polydisperse, incompatibility might gradually extend to lower-molecular-weight fractions. Figure 2 is not at all incompatible with this view. Of course, the gradual decrease in the energy transfer efficiency as the composition changes from a neat component might be the consequence of the increase in the volume fraction of the separated phases. As this factor increases, the mean size of the discrete domains grows to progressively approach and finally exceed the detection limit of NRET.

T_g Measurements in Comparison with NRET Results

The disagreement between Challa's model resulting from DSC measurements and the conclusions of this work relying upon NRET data is obvious. It is worth noting that the two studies are concerned with practically the same PVC ($\overline{M}_v = 55{,}000$ for Challa et al.; $\overline{M}_n = 43{,}000$ in this study) contrary to the s.PMMA sample which is of shorter chain length in this study ($\overline{M}_n$ 150,000) compared to that of Challa et al. ($\overline{M}_v$ 370×10^3). Unfortunately, the mixing techniques cannot be compared as Challa et al. propose three different procedures but do not mention the one applied to samples characterized by DSC. Nevertheless, keeping in mind some differences in the blends investigated, DSC measurements reported by Challa et al. are in qualitative agreement with the NRET data in assessing that the phase separation extent is largest in the s.PMMA-rich blends.

In order to seek for a more reliable comparison between DSC and NRET, the PVC/s.PMMA ($\overline{M}_n$ 150,000) samples have been analyzed by the former method. In the whole composition range, only one glass transition temperature T_g is reported, one which is, however, greatly broadened at 80 wt % s.PMMA (Fig.3). From these observations, it is not surprizing that Challa et al. detect separate T_g's in blends rich in a higher-molecular-weight s.PMMA. That one of these T_g's would be characteristic of s.PMMA is in agreement with the picture suggested in Figure 2. The T_g values reported by DSC are systematically lower than the values calculated from the Fox equation [eq.(3)] (Table II):

$$\frac{1}{T_g} = \frac{W_A}{T_{gA}} + \frac{W_B}{T_{gB}} \tag{3}$$

where W_i is the weight fraction of component i.

Departure from eq. (3) probably means that PVC/s.PMMA blends cannot be reduced to a system constituted of two single components whatever the composition range. According to Figure 2, at least one of the phases should be composed of PVC and s.PMMA in a ratio depending on the blend compositions. This is probably the simplest way of describing the small-scale demixing in the investigated blends. Although there is apparent agreement between DSC and NRET, the latter method provides undoubtedly a more sensitive, if not quantitative, criterion of miscibility than calorimetric data. This item has already been pointed out by Morawetz et al.[6,11]

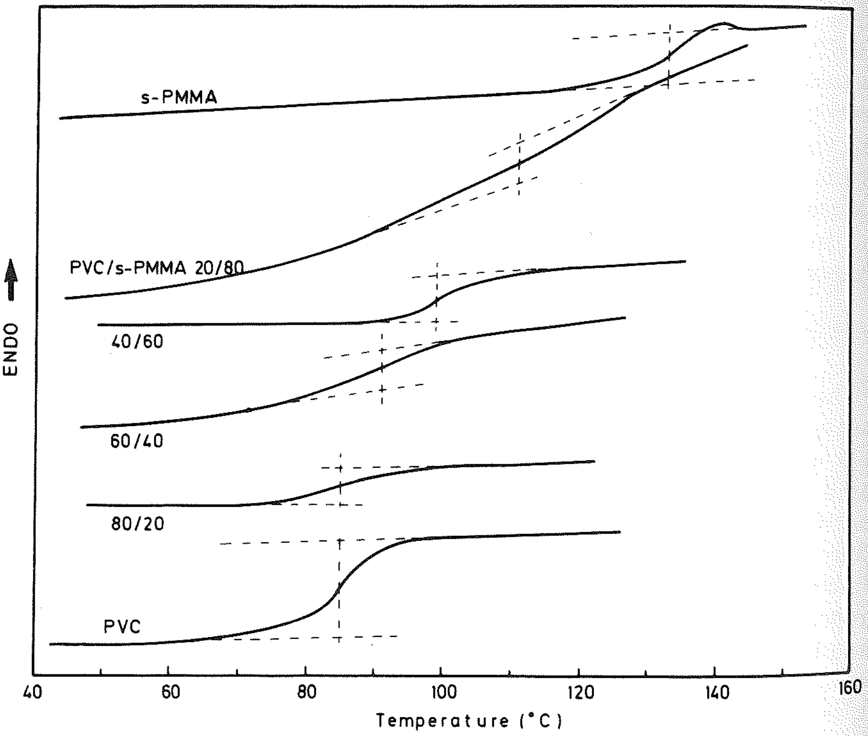

Fig. 3. Differential scanning calorimetry of PVC, s.PMMA ($\overline{M}_n$ 150,000), and PVC/s.PMMA blends of different composition (20/80, 40/60, 60/40, and 80/20).

TABLE II
Glass Transition Temperatures of PVC/s.PMMA ($\overline{M}_n$ 150,000) Blends

Blend Compositions (wt %)		T_g (°C)	
PVC	s.PMMA ($\overline{M}_n$ 150,000)	Theoretical	Experimental
...	Neat		133
Neat	...		84
80	20	93	84
60	40	102	91
40	60	112	99
20	80	122	111

Referring to the work of Vanderschueren et al.,[15] we see that the thermally stimulated depolarization current method applied to our samples supports the main information provided by DSC measurements. Only one α peak (correlated to T_g) is observed as well for blends rich in PVC as in s.PMMA. Furthermore, no Maxwell–Wagner–Sillar (MWS) polarization is detected. Such MWS polarization is generated by the trapping of charge carriers at large phase boundaries and is usually observed as an α' peak at a temperature a little higher than the α peak. The absence of any α' peak lends support to the small size of the demixed phases or particles.

From the in-depth investigation of PVC and s.PMMA blends, it may be concluded that these two polymers are not homogeneously mixed at the molecular level, and are even less so at higher molecular weights of s.PMMA. This conclusion is in apparent contradiction with the exothermic behavior reported for polymethacrylates and PVC ($\chi_{23} < 0$),[27] and is only precisely valid for samples prepared as described in this paper.

Influence of the Block Polymerization of s.PMMA on Its Miscibility with PVC

Curve 1 plotted on Figure 1 unambiguously shows that the low-molecular-weight s.PMMA is well miscible with PVC on a scale of a few nanometers. This situation is therefore favorable to estimation of whether the block copolymerization of s.PMMA has a detrimental effect on its mutual interpenetration with PVC. In that respect, a poly(styrene-*b*-methyl methacrylate) containing 50 wt % of each component has been prepared in such a way that the PMMA block displays the same molecular features (ca. 90% syndio, $\overline{M}_n$ 4×10^4) as the homopolymer studied above. Polystyrene and PMMA are known indeed as being immiscible.[28] Figure 1 (curve 2) clearly demonstrates that, whatever the percentage of the s.PMMA block mixed with PVC, the I_N/I_A ratio is scarcely increased compared to the blends of the two homopolymers (curve 1). It means that the linking of s.PMMA to an immiscible PS block does not significantly disturb the probability of interactions between PVC and PMMA. It must be concluded that PS forms very small and finely dispersed phases which are unable to localize the s.PMMA component in limited interfacial regions leaving out a part of neat PVC. From a thermodynamic point of view it then appears that the present blends are more stable (lower free energy) when the intermixing of s.PMMA and PVC is maximum despite the formation of some interfacial area between PS and the "homogeneous" PVC/s.PMMA phase. In other words, a reduction of the interface at the expense of interactions between PVC and the s.PMMA block is an unfavorable process. Again this is true in the particular case of the investigated blends, and mixing of PVC with diblock copolymers of increasing molecular weight should be of prime interest; a forthcoming paper will focus on that problem.

Nevertheless, reference can be made again to Morawetz's results dealing with binary mixtures of acceptor-labeled PS ($\overline{M}_n$ 6 × 10^4) and a poly(styrene-*b*-*p*-tert-butylstyrene) copolymer, the PS block of which is donor labeled and immiscible with poly(*p*-tert-butylstyrene) (33 mol % styrene, $\overline{M}_n$ 76,000).[11] For low PS concentrations, the homopolymer is effectively mixed with the PS block of the copolymer and the energy transfer is highly efficient. As the homopolymer concentration is increased, more and more of it is removed from the block copolymer, and the efficiency of the energy transfer decreases. This behavior is in sharp contrast to that reported in this work and might find (at least partly) its origin in the discrepancy of the molecular weight of the two PS components. It is indeed well known that a homopolymer can only be accommodated to a significant extent in the phase domains of a block copolymer when its chain length is equal to or shorter than that of the parent block,[29] and this is not the case in the example analyzed by Morawetz et al.

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