Evaluation of Nonradiative Energy Transfer as a Means of Probing Polymer Miscibility and Polymer Phase Separation

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ABSTRACT: The ability of nonradiative energy transfer (NRET) to probe polymer miscibility and polymer phase separation was explored for blends of PVC and PMMA of various compositions. It is shown that fluorescence techniques depend on the range between the lower (total miscibility) and the upper phase (complete immiscibility) of the ratio of the intensity emitted by naphthalene and anthracene (I₁/I₂)used to label PVC and PMMA, respectively. Although measurements of the lower limit are reproducible, determination of the upper limit is a problem, making uncertain the analysis of any system phase separated on a scale of at least 2-3 nm. At and above this dimension, solvent-cast PVC/PMMA blends appear to be completely miscible whatever the PMMA tacticity. That the I₁/I₂ ratio of the PVC/PMMA blends changes in a way that is consistent with the tacticity of PMMA is interpreted as an effect of chain confinement on the probability of intermolecular interactions. For instance, the more rigid the PMMA in relation to its tacticity, the more extended the intermolecular contacts with PVC seem to be. Finally, heating a monophase PVC/PMMA above the LST does not lead to an increase in the I₁/I₂ ratio great enough to detect phase separation.

Introduction
Most polymers are immiscible and form multiphase blends when mixed together. A number of methods have been proposed to probe polymer blends and to determine whether they are homogeneous (monophase) or not. Optical clarity is the simplest test, which is only convenient when both the difference in the refractive index of the mixed polymers is large enough and the information is at a scale larger than 100 nm. The most commonly used techniques to measure the glass transition are differential scanning calorimetry, dynamic mechanical testing, and microscopy (optical or electron depending on the miscibility level). Since the resolution power of all of these techniques is different, a given blend might be declared miscible by using one method (i.e., Tg measurement) and immiscible by another (i.e., electron microscopy). Today a great deal of attention is paid to novel techniques able to probe multiphase systems at a scale of a few nanometers, for example, solid-state NMR and fluorescence techniques such as excimer fluorescence, fluorescence microscopy, and nonradiative energy transfer. Frank et al. have used excimer fluorescence to characterize the miscibility of poly(2-vinylpyridine)/naphthalene with poly(vinyl methyl acrylate) and poly(naphthalene). Poly(2-vinylpyridine) (guest) comprises excimer-forming chromophores as constituent pendant groups and has been mixed with a large percentage of the second partner (host). Using fluorescence microscopy, Monnerie et al. have determined the boundaries (binodal and spinodal curves) of the phase diagram of polymer-polymer excimer-polymer (poly(vinyl methyl ether)). Finally, Morawetz et al. have used nonradiative energy transfer (NRET) to estimate the degree of miscibility of several polymer pairs.

The main purpose of this study is a critical analysis of NRET as a probing technique of polymer miscibility and especially of poly(vinyl chloride) (PVC) blended with poly(vinyl methyl methacrylate) (PMMA) of various tacticity. The question is whether NRET can improve the information already available from other experimental techniques. For nonradiative energy transfer, two different chromophores can occur when the emission spectrum of a donor chromophore overlaps the absorption spectrum of an acceptor chromophore. Thus, the excitation energy absorbed by the donor can be transferred to the acceptor. Moreover, the overlap integral between the normalized emission spectrum of the donor and the absorption spectrum of the acceptor (Iₐ) should be different from zero. The efficiency of energy transfer (ϕ) between one donor and one acceptor separated by a constant distance r is expressed by Förster's relation

\[ \phi = \frac{R_0^6}{R^6} \]

with \[ R_0^6 = (8.8 \times 10^{-4}) \text{J} \cdot \text{cm}^2 \cdot \text{mol}^{-1} \] as a characteristic distance at which half of the excitation energy is transferred. I is the peak intensity of the medium, Ω is a function of the mutual orientation of the donor and acceptor. The concentration dipole moment of the donor, \( \mu_D \), in the fluorescence quantum yield of the donor in the absence of an acceptor.

Since the ratio of the fluorescence emission intensities of the donor and the acceptor (I₁/I₂) is related to the efficiency of the energy transfer, this ratio is a measure of the degree of miscibility of two polymers labeled with the donor and the acceptor, respectively. The lower limit of I₁/I₂, i.e., the maximum energy transfer and the upper limit of I₁/I₂ (I₁/I₂ = 1) of course to be established. It will be shown that this determination upper limit is quite a problem. Finally, attention will be paid to the relative LST inducing a phase separating phase separation in polymer blends exhibiting a LCST phase diagram. Results from NRET will be compared with DSC data.

Experimental Section
Materials. PVC, as supplied by Solvay (PVC RDSB), was precipitated (three times) from tetrachloroethylene into methanol in the presence of anthracene and naphthalene. Ultrapure water (18.2 MΩ cm) and ultrapure naphthalene (99.9%) and anthracene (99.9%) were used. The temperature was set at 35 °C. PVC/PMMA blends heated at constant temperature higher than 130 °C (phase separation experiments) were, however, subsequently subjected to a heating rate of 2 °C/min (thermal analysis). Sodicitoff actinide PMMA (PMMA 4K) was prepared by anionic polymerization of methyl methacrylate under anhydrous conditions in THF at -60 °C, with tetrabutylammonium cations as initiator. Polymerization was stopped by the addition of hydroxide after a few minutes. The PMMA sample was then precipitated into methanol. Weight average molecular weights, determined by SEC in THF at 25 °C, were \( M_w = 44k \) and \( M_M = 65k \). Sodicite PMMA was comprised of 78% styric triblocks and 22% heterotactic triblocks as determined by 1H NMR with C6D6 as solvent. PMMA containing a few mole percent (1.8 mol %) of tert-butyl acrylate was prepared as described above. Molecular weights were \( M_w = 35k \) and \( M_M = 47k \), and tacticity was 95% syndiotactic tris and 30% heterotactic triblocks. The two samples of s-PMMMA were amorphous, in agreement with the observation of Karam et al. that PMMA containing 70% syndiotactic triads did not show evidence of any melt or recrystallization phenomena up to 460 °K.

Actinic PMMA (PMMA 63K) was a commercial polymer supplied by ICI (Dialon), which was purified by precipitation from THF into methanol. The concentration [PMMA], in THF at 25 °C, was \( M_w = 44k \) and \( M_M = 73k \) (SEC in THF at 25 °C). The tacticity was 57% syndiotactic triads, 35% heterotactic triads, and 8% isotactic triads.

Isotactic PMMA (PMMA 63K) was prepared by anionic polymerization in toluene at -78 °C under N2, c-C3H7MgI as initiator. Polymerization was stopped by adding hydrochloric acid and the polymer was precipitated into methanol. Two isotactic PMMA's were prepared with \( M_w = 32k \), \( M_M = 41k \) (PMMA 32k) and \( M_w = 51k \), \( M_M = 68k \) (PMMA 68K). According to 1H NMR, PMMA was a monosynthetic tactic. The samples of PMMA label all when blended with 50% PVC under the same experimental conditions. This completely amorphous sample was used to evaluate NRET as a means of detecting phase separation. Furthermore, a rapid quenching of the chains containing 1PMMA of the lower \( M_w = 32k \) as a major component and heated above the melt temperature (120 °C) prevents any crystallization to occur. It is thus possible to determine the presence or absence of intra- and intermolecular interactions. This fluorescence intensity of any crystallization effect, whatever the PMMA tacticity.

Attachment of Fluorescent Chromophores. Naphtha- lene and anthracene were selected as the donor and the acceptor, respectively. The chromophore, 1n, cm, was used for the naphthalene/anthracene pair. 2-[2-1H]Naphthaldehyde was used to graft anthracene moieties onto PVC by naphthalene/anthracene pair. 2-1H]Naphthaldehyde was used to graft anthracene moieties onto PVC by naphthalene/anthracene pair. 2-[1H]Naphthaldehyde was used to graft anthracene moieties onto PVC by naphthalene/anthracene pair. 2-[1H]Naphthaldehyde was used to graft anthracene moieties onto PVC by naphthalene/anthracene pair.

Table 1

<table>
<thead>
<tr>
<th>Polymer Characteristics</th>
<th>PVC</th>
<th>PMMA 4K</th>
<th>PMMA 32K</th>
<th>PMMA 51K</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(vinyl chloride)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>poly(methyl metacrylate)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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The naphthalene moiety was similarly attached onto PVC by reaction of naphthalene with the ester side groups, a ketone was formed and the emission intensity of the naphth}-{
that the choline cation is found in the initial increase in \(I_{PMMA}\) when PVC is blended with a mixture of PMMA (e.g., 10% by weight) and N,N-dimethylacetamide in water. Later, the same PMMA in the presence of a NaA/PMMA blend is observed to give a smaller increase in the PMMA/PVC blend. These results confirm that the choline cation is not responsible for the cholinergic effect in the PMMA/PVC blend, and suggests that the presence of NaA in the PMMA/PVC blend is necessary for the cholinergic effect to be observed. This is consistent with previous observations that the cholinergic effect is only observed in blends containing NaA, and not in blends containing NaCl or NaBr. Further experiments are needed to confirm this result and to further understand the mechanisms involved in the cholinergic effect in the PMMA/PVC blend.

2. Determination of the Immmiscibility Refer-
ence Points for PVC/PMMA Blends. The aim of this work is to investigate the phase behavior of PVC/PMMA blends as a function of composition and processing conditions. The immiscibility reference points for PVC/PMMA blends are determined by monitoring the viscosity of the blends as a function of composition and processing conditions. The viscosity of the blends is measured by a rotational viscometer at a constant shear rate. The immiscibility reference points are defined as the compositions at which the viscosity of the blends shows a significant change, indicating the onset of immiscibility. The immiscibility reference points for PVC/PMMA blends are determined at different shear rates and temperatures, and are found to be dependent on the composition of the blends. The results of this work are in good agreement with previous studies and provide new insights into the phase behavior of PVC/PMMA blends.
the thickness of the individual films seems to affect strongly the value of $I_{P2}/I_{P1}$ lower limit and hence the conclusion about polymer miscibility very unaccurately.
In the very particular case of solvent-cast PVC/ PMMA binary blends, the $I_{P2}/I_{P1}$ ratio on the polymer miscibility has been evidenced, and the miscibility seems to be complete. It is, however, worth noting that any change in the PMMA conformation caused by a change in the tacticity affects the frequency of chain interactions for PMMA blended with PVC. The more rigid, and thus extended, the PMMA chains, the more frequent are the interchain contacts. It is believed that NRT is the first fluorescence technique that has shown evidence for effect of chain tacticity on the molecular mixing in monophasic polyblend.

Finally, heating a monophasic PVC/PMMA blend above the LCST does not produce an increase in the $I_{P2}/I_{P1}$ ratio, great enough to detect phase separation. In this regard NRT is much less sensitive than DSC.

Let us finally mention that fluorescence measurements on solutions of donor and acceptor-labeled polymers have been performed by Morawetz and Hershkovitz and might be dominated by radiation, rather than non-radiative, energy transfer. This might also occur in polymer films and enhance limitations of the fluorescence technique for probing blends of labeled polymers.

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References and Notes

2. Visiting Scientist from Unilever Ltd, Kyoto, Japan.