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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 is discussed for blends of PVC and PMMA of various tacticity. The sensitivity of that fluorescence technique depends on the range between the lower (total miscibility) and the upper value (complete immiscibility) of the ratio of the intensity emitted by naphthalene and anthracene (I_N/I_A) used to label PVC and PMMA, respectively. Although measurements of the lower limit are reproducible, determination of the upper limit is quite 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 I_N/I_A ratio of the PVC/PMMA blends changes with the tacticity of PMMA is interpreted as an effect of chain conformation on the probability of intermolecular interactions. For instance, the more rigid the PMMA is in relation to its tacticity, the more extended the intermolecular contacts with PVC seem to be. Finally, heating a monophase PVC/PMMA blend above the LCST does not lead to an increase in the I_N/I_A ratio great enough to detect phase separation.

Introduction

Most polymers are immiscible and form multiphase blends when mixed together.[3] A number of methods have been proposed to probe polymer blends and to determine whether they are homogeneous (monophase) or not.[4] 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 these techniques is different, a given blend might be declared miscible by using one method (i.e., T_g measurements) and immiscible according to a higher resolution technique (i.e., electron microscopy).

Today a great deal of attention is paid to novel techniques able to probe multicomponent system at a scale of a few nanometers, for example, solid-state NMR[5,6] and fluorescence techniques such as excimer fluorescence, fluorescence microscopy, and nonradiative energy transfer. Frank et al.[7] have used excimer fluorescence to characterize the miscibility of poly(2-vinylnaphthalene) with poly(methyl methacrylate) and polystyrene. Poly(2-vinylnaphthalene) (guest) comprises excimer-forming chromophores as constitutive pendant groups and has been mixed with a large percentage of the second partner (host). Using fluorescence microscopy, Monnerie et al.[8] have determined the boundaries (binodal and spinodal curves) of the phase diagram of anthracene-labeled polystyrene/poly(vinyl methyl ether). Finally, Morawetz et al.[9] and later on Teyssié et al.[10] 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

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Table I
Polymer Characteristics

polymer	acronym	tacticity (i:h:s)	$\bar{M}_n$, g·mol^{-1}	$\bar{M}_w$, g·mol^{-1}	T_g, °C	chromophore	
						nature	mol %
poly(vinyl chloride)	PVC		43 000	80 000	79	anthracene	1.05
						naphthalene	1.90
poly(methyl methacrylate)							
syndiotactic	s-PMMA 44K	0:22:78	44 000	55 000	122	anthracene	1.30
	s-PMMA 35K	0:20:80	35 000	47 000	122	naphthalene	1.65
atactic	a-PMMA 43K	8:35:57	43 000	73 000	113	anthracene	1.24
	a-PMMA 44K	10:33:57	44 000	78 000	113	naphthalene	1.78
isotactic	i-PMMA 32K	100:0:0	32 000	41 000	53	anthracene	1.76
	i-PMMA 51K	100:0:0	51 000	66 000	53	anthracene	1.97

NRET as a probing technique of polymer miscibility and especially of poly(vinyl chloride) (PVC) blended with poly(methyl methacrylate) (PMMA) of various tacticity. The question is whether NRET can improve the information already available from other experimental techniques.[11-14]

Förster nonradiative energy transfer[15] between two chromophores can occur when the emission spectrum of a donor chromophore overlaps the absorption spectrum of an acceptor chromophore. Then 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 (J) should be different from zero. The efficiency of energy transfer (E) between one donor and one acceptor separated by a constant distance r is expressed by Förster's relation

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

with $R_0^6 = (8.8 \times 10^{-25})Jn^{-4}K^2\phi_0$. R_0 is a characteristic distance at which half of the excitation energy is transferred. n is the refractive index of the medium, K^2 is a function of the mutual orientation of the donor and acceptor transition dipole moments, and ϕ_0 is 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 (I_N/I_A) 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 I_N/I_A, i.e., the maximum of energy transfer and the upper value (no energy transfer), have of course to be established. It will be shown that determining the upper limit is quite a problem. Finally, attention will be paid to the NRET technique as a means of investigating 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 RD258), was precipitated (three times) from tetrahydrofuran into methanol in order to eliminate both the stabilizer and the plasticizer. Molecular weights ($\bar{M}_n$ = 43K, $\bar{M}_w$ = 80K) were determined by size exclusion chromatography (SEC) (Waters 200) in tetrahydrofuran at 25 °C. PVC/PMMA blends heated at temperatures higher than 120 °C (phase separation experiments) were, however, added with 2 wt % of a stabilizer (thermolite 31).

Syndiotactic PMMA (s-PMMA 44K) was prepared by anionic polymerization of methyl methacrylate under anhydrous conditions in THF at -78 °C by using *sec*-butyl lithium as an initiator. Polymerization was stopped by the addition of hydrochloric acid and the polymer was precipitated into methanol. Molecular weights, determined by SEC in THF at 25 °C, were $\bar{M}_n$ = 44K and $\bar{M}_w$ = 55K. s-PMMA 44K was comprised of 78% syndiotactic triads and 22% heterotactic triads as determined by ^{1}H NMR with $CDCl_3$ as solvent. PMMA containing a few mole percent (1.8 mol %) of *tert*-butyl acrylate was prepared as described above. Molecular weights were $\bar{M}_n$ = 35K and $\bar{M}_w$ = 47K, and tacticity was 80% syndiotactic triads and 20% heterotactic triads. The two samples of s-PMMA were amorphous, in agreement with the observation of Karasz et al. that PMMA containing 70% syndiotactic triads did not show evidence of any melting or recrystallization phenomena up to 460 K.[16]

Atactic PMMA (a-PMMA 43K) was a commercial polymer supplied by ICI (Diakon), which was purified by precipitation from THF into methanol. The molecular weights were $\bar{M}_n$ = 43K and $\bar{M}_w$ = 73K (SEC in THF at 25 °C). The tacticity was 57% syndiotactic triads, 35% heterotactic triads, and 8% isotactic triads.

Isotactic PMMA (i-PMMA) was prepared by anionic polymerization in toluene at -78 °C by using t-C_4H_9MgBr as initiator. Polymerization was stopped by adding hydrochloric acid and the polymer was precipitated into methanol. Two isotactic PMMA's were prepared with $\bar{M}_n$ = 32K, $\bar{M}_w$ = 41K (i-PMMA 32K) and $\bar{M}_n$ = 51K, $\bar{M}_w$ = 66K (i-PMMA 51K). According to ^{1}H NMR, i-PMMA was ca. 100% isotactic. Table I lists the polymers used in this study. i-PMMA is known to be a very slowly crystallizing polymer.[17,18] Nevertheless, it has been observed that i-PMMA of $\bar{M}_n$ = 32K can crystallize in blends containing up to 50% PVC and annealed at 120 °C for 3 h. In contrast, i-PMMA of $\bar{M}_n$ = 51K does not crystallize at all when blended with 50% PVC under the same experimental conditions. This completely amorphous blend will be used to evaluate NRET as a means of detecting phase separation. Furthermore, a rapid quenching of the blends containing i-PMMA of the lower $\bar{M}_n$ (32K) as a major component and heated above the melting point (~150 °C) prevents any crystallization to occur. It is thus possible to characterize the PVC/PMMA blends by fluorescence independently of any crystallization effect, whatever the PMMA tacticity.

Attachment of Fluorescent Chromophores. Naphthalene and anthracene were selected as the donor and the acceptor, respectively. The characteristic distance, R_0, was 2 nm for the naphthalene/anthracene pair.[19] (9-Anthrylmethyl)lithium was used to graft anthracene moieties onto PVC by nucleophilic substitution of secondary chlorine atoms and onto PMMA by reaction with the ester side group. The grafting reaction[20] proceeded under anhydrous conditions in THF at 0 °C. (9-Anthrylmethyl)lithium was prepared by metalation of 1,2-di(9-anthryl)ethane by lithium in THF under anhydrous conditions.[10b] 1,2-Di(9-anthryl)ethane was prepared by reducing 9-anthraldehyde with lithium aluminum hydride in refluxing THF.[21]

The naphthalene moiety was similarly attached onto PVC by reaction of (α-naphthylmethyl)lithium with PVC in THF at 0 °C. (α-Naphthylmethyl)lithium was synthesized by metalation of 1,2-bis(α-naphthyl)ethane by lithium under anhydrous conditions in THF.[10b] 1,2-Bis(α-naphthyl)ethane was prepared according to procedures reported by Copeland et al.[22] When the naphthalene moiety was attached onto PMMA by reaction of (α-naphthylmethyl)lithium with the ester side groups, a ketone was formed and the emission intensity of the naphthalene chromophore was very low. This could be explained by an intramolecular energy transfer from the excited naphthalene to the ketone carbonyl, as was reported elsewhere.[23] In order to avoid this drawback, naphthalene was attached to atactic PMMA by radical copolymerization of methyl methacrylate and naphthyl methacrylate using AIBN as an initiator in ethyl acetate at 60 °C (a-PMMA 44K). Naphthyl methacrylate[24] was synthesized by esterification of methacryloyl chloride with the lithium salt of 1-naphthol in dried toluene. The monomer was purified by repeated washings with NaOH and water, dried over $CaCl_2$, and finally distilled. Molecular weights determined by SEC were $\bar{M}_n$ = 44K and $\bar{M}_w$ = 78K. ^1H NMR showed that the copolymer contained 57% syndiotactic triads, 33% heterotactic triads, and 10% isotactic triads. Naphthalene was attached to s-PMMA by transalcoholysis of the *tert*-butyl acrylate units incorporated into the s-PMMA 35K chains by using 1-naphthalene methanol in toluene with *p*-toluenesulfonic acid as a catalyst. This reaction was performed in refluxing toluene for several days.

All the labeled polymers were purified by repeated dissolution in THF and precipitation into methanol and finally into heptane, until the chromophore content remained constant and any trace of grease was removed. The content of naphthalene and anthracene in the labeled polymers was determined by UV spectroscopy using the extinction coefficient of a model chromophore. α-Methylnaphthalene and 9-methylanthracene were used when the polymers were labeled by reaction with (α-naphthylmethyl)lithium and (9-anthrylmethyl)lithium, respectively. Naphthyl methacrylate and 1-naphthalenemethanol were used as model compounds for the labeled a-PMMA 44K and s-PMMA 35K, respectively. The anthracene content was 1.3 mol %, 1.24 mol %, 1.76 mol %, 1.97 mol %, and 1.05 mol % for s-PMMA 44K, a-PMMA 43K, i-PMMA 32K, i-PMMA 51K, and PVC, respectively (Table I). The naphthalene content was 1.78 mol %, 1.65 mol %, and 1.9 mol % for a-PMMA 44K, s-PMMA 35K, and PVC, respectively (Table I).

Sample Preparation and Fluorescence Measurements. Labeled polymers were diluted with the corresponding unlabeled polymers in order to prepare films containing 10^{-2} mol·L^{-1} of chromophore. Films were cast from solutions onto quartz plates. Methyl ethyl ketone (MEK) was used for blending PVC with s-PMMA, a-PMMA, and i-PMMA 32K. Due to the insolubility of i-PMMA 51K in MEK, THF was used as a common solvent for PVC and i-PMMA 51K. The solvent was allowed to evaporate at room temperature under a nitrogen atmosphere for 1 or 2 days and the films were finally dried under vacuum between 50 and 70 °C for several days and finally at ca. 120 °C (i.e., above T_g and below the LCST) for a few hours. Then fluorescence measurements were independent of further thermal treatments. Film thickness was about 25 μm for blends of any composition and 12.5 μm when the upper limit of I_N/I_A had to be measured. Emission spectra were recorded with a Spex Fluorolog spectrofluorimeter. Energy transfer efficiency was characterized by the ratio of the emission intensity of naphthalene and anthracene (I_N/I_A) measured at the maximum of emission, i.e., 338 nm for the donor and 417 nm for the acceptor. The donor was excited at 282 nm. I_N/I_A ratios were plotted as a function of blend composition. DSC measurements were performed by using a Du Pont DSC 910 apparatus.

Results and Discussion

1. Blends of PVC with PMMA of Different Tacticity. PVC is blended with PMMA of approximatively the same molecular weight but of a different tacticity (Table I). All the binary blends of various compositions are characterized by the NRET technique as MEK cast films in which naphthalene is attached onto PVC and anthracene onto PMMA. The experimental I_N/I_A ratios are plotted on Figure 1 as a function of the weight percentage of PMMA. The thermal history of the solvent-cast films is of critical importance. Cast from MEK at 25 °C, films are dried as described in the Experimental Section, and the I_N/I_A ratio is observed to increase during that process. Values reported on Figure 1 are the constant ratios recorded at 25 °C after 3 or 4 h of heating at 120 °C. The initial values could be attributed to a possible energy transfer from naphthalene to residual MEK.[23] Therefore heating blends, especially above T_g (Table I), allows any residual solvent to be removed and the experimental I_N/I_A ratios to increase up to a constant value. Reproducibility of the I_N/I_A ratios characteristic of the PVC/PMMA blends is quite good (~0.015).

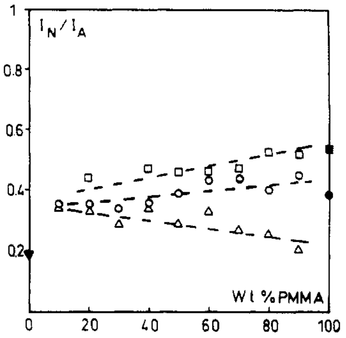

Figure 1. Dependence of I_N/I_A on weight percentage of PMMA in PVC/PMMA blends. I_N and I_A are the intensity emitted by naphthalene and anthracene, respectively. (▼) pure PVC; (△) i-PMMA 32K/PVC blends; (○) a-PMMA/PVC blends; (□) s-PMMA/PVC blends; (●) pure a-PMMA; (■) pure s-PMMA.

PMMA has been claimed to be miscible with PVC at room temperature whatever its tacticity.[25,26] Actually these polymer pairs exhibit a phase diagram with a lower critical solution temperature (LCST) above T_g. Accordingly, no difference should be observed in the degree of miscibility of PVC with PMMA of various tacticity at 25 °C. The experimental I_N/I_A values of Figure 1 might indicate that the miscibility of PMMA with PVC is enhanced when the PMMA isotacticity increases, especially for blends containing more than 50% PMMA. For the comparison to be meaningful, values reported for each series of blends have to be referred to the appropriate limits, i.e., I_N/I_A characteristic of total miscibility (maximum of energy transfer) and complete immiscibility (no Förster energy transfer).

Total miscibility has been characterized by using a 25-μm-thick film of a homopolymer in which half of the chains are labeled by the donor and the other half by the acceptor. This blend should be an ideal model for the intimate mixing of donor-labeled chains and acceptor-labeled chains, respectively. Surprisingly enough, the experimental I_N/I_A ratio (Figure 1) depends on the homopolymer used. It increases from 0.19 for PVC to 0.38 for a-PMMA and to 0.54 for s-PMMA. The relatively low value measured for PVC (0.19) compared to those obtained for PMMA's (0.38 and 0.54) could be accounted for by a quenching of the chromophore fluorescence by PVC. Prud'homme has observed a similar effect in PVC/CPVC blends. This quenching was more important for naphthalene than for anthracene.[27] In order to assess the quenching of the naphthalene fluorescence emission by PVC, the fluorescence quantum yield of α-methylnaphthalene has been measured in different solvents. It amounts to 0.2 in THF, 0.19 in isooctane, and 0.05 in dichloromethane. The fluorescence quantum yield of naphthalene groups attached onto PVC and measured in THF is 0.12. These values suggest that chlorine is responsible for a decrease in the fluorescence quantum yield of the naphthalene chromophore in a naphthalene-labeled PVC.

Quenching further explains why the I_N/I_A ratio for the total miscibility is smaller when measured using PVC rather than PMMA. Other evidence for the same conclusion is found in the initial increase in I_N/I_A when PVC is blended with even small amounts of PMMA (e.g., 10 wt %) whatever the tacticity of PMMA (Figure 1). Actually, the NRET occurs now between naphthalene attached onto PVC and anthracene bonded to PMMA. Accordingly the *local environment of the chromophores* has changed from pure PVC to a medium in which the chlorine content has decreased significantly. Since naphthalene and anthracene concentrations are 10^{-2} mol·L^{-1}, whatever the blend composition, the PMMA and PVC composition in the very close vicinity of each N/A pair is expected to be largely independent of the macroscopic blend composition. This might explain why I_N/I_A changes sharply upon the addition of a few percent of PMMA to PVC and then very smoothly as a function of the blend composition (Figure 1).

The I_N/I_A ratio of the blends (i.e., 90% PMMA/10% PVC composition) is found to depend on the PMMA tacticity (Figure 1). Interestingly, it is known that PMMA conformation changes with tacticity. Isotactic PMMA in the crystalline state exhibits a helix conformation,[28] whereas syndiotactic PMMA displays a slightly curved planar zigzag conformation.[29] The characteristic ratio $\langle r^2\rangle/nl^2$, where $\langle r^2\rangle$ is the unperturbed average square end-to-end length, n the number of bonds, and l the length of the valence bonds, has been reported to increase as PMMA is more isotactic.[30,31] Since $\langle r^2\rangle/nl^2$ is related to the chain stiffness, isotactic PMMA chains are thus stiffer and more extended than their syndiotactic counterparts. Actually, Jenkins and Porter have assessed that i-PMMA is 30% more extended than s-PMMA in the unperturbed state.[32] Finally, it has been calculated[33] that syndiotactic PMMA chains can circle back on themselves in agreement with a limited chain stiffness. From all these results it might be anticipated that transfer between naphthalene on PVC and anthracene on PMMA is easier when anthracene is attached onto i-PMMA because of a higher probability of PVC-PMMA heterocontacts. It is worth recalling that Mc Brierty et al.[5] have shown that the ester side groups in PMMA are in a better contact with PVC than the methyl groups of the same PMMA. The effect of PMMA conformation is also supported by the I_N/I_A values for total miscibility, which decreases from s-PMMA to a-PMMA (Figure 1). Accordingly, the I_N/I_A ratio for pure i-PMMA might be extrapolated to ca. 0.2. So far, this value has not been measured because of problems of labeling i-PMMA with naphthalene. Although PMMA tacticity seems to have the same effect on the NRET from PMMA/PMMA references and PMMA/PVC blends, no straightforward comparison is allowed because of a difference in the way the PMMA/PMMA references are labeled with anthracene and naphthalene, respectively.

If we compare the I_N/I_A values of the PVC/PMMA's blends, it is obvious that PMMA tacticity has no effect on its level of miscibility with PVC. In each series of binary blends, I_N/I_A changes linearly from the apparently common value observed when PVC is modified by a low percentage of PMMA and the value for a 90% PMMA/10% PVC blend. This means that the lack of superposition of the experimental curves does not indicate a difference in the thermodynamic miscibility but rather a difference in the probability of PVC–PMMA heterocontacts in relation to PMMA conformation. Let us recall that a-PMMA and s-PMMA are completely amorphous, whereas i-PMMA (32K) crystallizes in blends containing up to 50% PVC and annealed at 120 °C for a few hours. It has been observed that a rapid quenching of these blends, previously heated above the melting point, prevents the crystallization to occur and does not change the I_N/I_A ratio significantly (ca. 5% discrepancy). Thus, it can be concluded that the results collected in Figure 1 are independent of any crystallization effect, whatever the PMMA tacticity.

To our best knowledge, this is the first time that a technique probing a polyblend at a very small scale shows conformational effects in relation to chain tacticity.

2. Determination of the Immiscibility References for PVC/PMMA Blends. For the investigation to be complete, I_N/I_A values corresponding to the total immiscibility have to be determined. So far the upper limit of the I_N/I_A ratio has been calculated from the intensity emitted by solutions in cyclohexane of α-methylnaphthalene and 9-methylanthracene, respectively, upon excitation at the naphthalene maximum absorption wavelength. A value of 13.2 has been proposed for the naphthalene/anthracene pair.[10b] The reliability of that value is based, however, on the assumption that the extinction coefficient and the quantum yield of both the donor and the acceptor are the same in solution as in polymer films. As already noted by Prud'homme, this assumption is groundless,[27] and the reference in the absence of energy transfer has to be determined from two individual polymer films, one containing naphthalene and the other one labeled with anthracene.

Since there is a quenching effect of PVC on the chromophore fluorescence, the upper limit of the I_N/I_A ratio is expected to depend on the composition of the PMMA/PVC blends. Thus, for a given composition, two films have to be prepared that are identical except for the chromophore they contain. For example, when the 50/50 PMMA/PVC composition is used, a film is prepared that comprises 50% PMMA and 50% naphthalene-labeled PVC, whereas the second film of the same thickness comprises 50% anthracene-labeled PMMA and 50% PVC. The chromophore concentration is the same within the two films (10^{-2} mol·L^{-1}). From an experimental point of view, the I_N/I_A ratio can be measured in two different ways. Either the absolute I_N and I_A intensities, emitted by each film when excited at 282 nm, are measured, or the two films are sandwiched face to face and excited at 282 nm and the I_N and I_A intensities are measured at the appropriate emission wavelength of each chromophore. In the latter case, relative intensities are recorded and the relative position of the film assembly toward the incident beam can be modified: either the naphthalene-containing film is in front of the incident light or the reverse. The reported I_N/I_A ratio is the average of values measured when the orientation of the film assembly toward the incident beam is changed.

When the two methods are compared, measurements of relative intensities give more reproducible results than those of absolute intensities. In the latter case, when measurements are repeated after an interval of one or several days, results depend on possible absolute intensity fluctuations. Therefore, the former technique has been selected because of its independence of any apparatus fluctuations. I_N/I_A values are, however, reproducible only when the incident exciting beam hits the same local area of a given film assembly. If another section of the sample surface is excited or another pair of films used, sharp discrepancies are observed as illustrated in Table II. Control and reproducibility of the solvent-cast film is thus questionable. In this regard, it has been observed that the film thickness is not uniform and can change by as much as a factor of 2 from one local area to another. The distribution of these irregularities also varies with

Table II
Reference of Total Immiscibility As Measured for Two Different Pairs of Films

polym comp, wt %	I_N/I_A 1st pair	I_N/I_A 2nd pair
s-PMMA/PVC		
25/75	0.85	0.59
50/50	0.77	1.05
75/25	1.27	1.09
100/0	2.04	1.22
a-PMMA/PVC		
25/75	0.87	0.83
50/50	0.93	1.09
75/25	0.72	1.20
100/0	0.91	0.70
i-PMMA 32K/PVC		
25/75	0.75	
50/50	0.77	
75/25	0.67	0.78

Table III
Effect of Thermal Treatments on I_N/I_A (NRET) and T_g (DSC) for the 50% i-PMMA 51K/50% PVC Blend

thermal treatments	I_N/I_A	T_g, °C
4 days at 25 °C[a]	0.31	20–40
65 h at 70 °C	0.27	45–70
65 h at 70 °C + 3 h at 120 °C	0.30	50–60, 65–85
65 h at 70 °C + 3 h at 120 °C + 4 h at 170 °C	0.35	50–60, 65–85

[a] THF-cast films dried under vacuum, at 25 °C, for 4 days.

the sample preparation. It might be concluded that the fluctuations observed in the experimental upper I_N/I_A values are unavoidable as long as films that have to be assembled do not display a highly uniform thickness. It is worth recalling that the PVC/PMMA blends of various compositions are characterized by using one film (and not a two-film assembly), the thickness of which has no effect on the experimental values of I_N/I_A. Although the measurements of the immiscibility references using polymer films are not yet reproducible, they are more meaningful than measurements from solutions. In the latter case a value as high as 13.2 has been calculated whatever the blend composition, in strong contrast to the order of magnitude of the values reported in Table II.

3. Can NRET Probe Polymer Phase Separation? It is also the purpose of this paper to evaluate NRET as a means of detecting phase separation, especially in PVC/PMMA blends, which are known to exhibit a lower critical solution temperature (LCST). Several films of the same 50% PVC/50% i-PMMA 51K blend have been cast from THF at 25 °C. Each film has been submitted to a well-defined thermal treatment and characterized by NRET (I_N/I_A value) and differential scanning calorimetry (T_g value). The purpose is to state whether there is a sharp transition in the I_N/I_A ratio when the phase separation occurs and especially when two T_g's are observed. As shown in Table III, I_N/I_A decreases from 0.31 to 0.27 when the film is dried under vacuum for 65 h at 70 °C, while the unique T_g is shifted toward higher temperatures by ca. 25 °C (Figure 2).

These observations can be accounted for by the elimination of THF left in the sample after drying under vacuum at room temperature (4 days). The solvent is expected to be completely removed, when the sample has been treated at 70 °C, i.e., above T_g of the blend and above the boiling point of THF under reduced pressure. No further change in I_N/I_A and T_g is indeed observed when the thermal treatment at 70 °C is repeated for several extra hours. In contrast, heating that blend at 120 °C for 3 h is sufficient to reach the two-phase region of the phase diagram since two T_g's are now observed: one T_g between 50 and 60 °C and the other one between 65 and 85 °C.

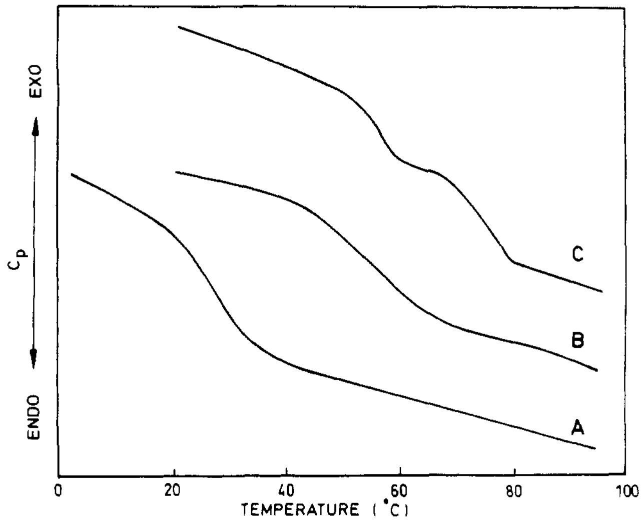

Figure 2. Effect of annealing on DSC thermograms of the 50/50 PVC/i-PMMA 51K blend (THF cast films). (A) 4 days at 25 °C; (B) 65 h at 70 °C; (C) 65 h at 70 °C + 3 h at 120 °C.

As a result of the phase separation, I_N/I_A increases only from 0.27 to 0.30 (Table III). Finally, it reaches 0.35 after further thermal treatment at 170 °C for 4 h. These data have been duplicated and show that the measurement of I_N/I_A is not sensitive enough to detect the phase separation that occurs when the temperature is increased above LCST. This disappointing observation might be explained by the formation of a great number of very small domains, the composition of which should be intermediate of that of the initial blend and the binodal points. The energy transfer can thus take place through a large interfacial area as well as inside the individual domains. Although the I_N/I_A ratio has to be different for phases of different composition, the experimental measurement provides an average value that might not be very different from the initial ratio. Progress of the phase separation upon heating the sample at a higher temperature (170 °C compared to 120 °C) promotes a slight increase in I_N/I_A from 0.30 to 0.35. That increase can rise slowly when the sample is heated at 170 °C for longer periods of time. As expected, phases coalesce and the interfacial area decreases while the purity of the phases is improved. All these experiments support that NRET is not a convenient technique to detect a phase separation in an initially monophase polyblend. Progress of the phase separation promotes too small changes in the I_N/I_A ratio, so that the kinetics cannot be followed accurately.

4. Conclusion. This study has focused on the possible use of NRET as a probing technique of polymer miscibility and polymer phase separation. Experimental data have shown that this fluorescence technique can provide information of the miscibility level of PVC and PMMA binary blends. The upper and lower values of the I_N/I_A ratio have to be determined in a reliable way since the range between these two limits defines the sensitivity of the technique. Although the lower limit corresponding to the total miscibility is reproducible, experimental knowledge of the upper limit is quite a problem. The best way to determine it consists of an assembly of two films modeling the complete phase separation. Inhomogeneity in the thickness of the individual films seems to affect strongly the value of I_N/I_A and makes the upper limit and hence the conclusion about polymer miscibility very unaccurate. In the very particular case of solvent-cast PVC/PMMA binary blends, no effect of the PMMA tacticity 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 NRET is the first fluorescence technique that has shown evidence for effect of chain tacticity on the molecular mixing in monophase polyblends. From that point of view, NRET is a sensitive technique to probe chain interactions.

Finally, heating a monophase PVC/PMMA blend above the LCST does not produce an increase in the I_N/I_A ratio great enough to detect phase separation. In this regard NRET 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 Horsky[34] and might be dominated by radiative, rather than nonradiative, 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

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Registry No. PVC, 9002-86-2; PMMA, 9011-14-7; s-PMMA, 25188-97-0; i-PMMA, 25188-98-1; (MMA)(*tert*-butyl acrylate) (copolymer), 30525-32-7; (MMA)(1-naphthyl methacrylate) (copolymer), 38783-77-6.