Nonradiative Energy Transfer of Miscible Polymer Blends: Influence of the Concentration of Fluorescent Chromophores in Labeled Polymers

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The nonradiative energy-transfer (NRET) technique is a useful tool for the characterization of polymer blend miscibility, micelle formation in copolymers, chain interpenetration in solution, ion-pair interchange in ionomer solutions,[1] and morphology of polymer colloids.[2] The quantity measured is generally the emission intensity ratio of the fluorescent donor to acceptor, which are covalently attached to the polymer chains investigated. This quantity is related to the efficiency of energy transfer, E, from electronically excited donors to acceptors by a dipole–dipole interaction mechanism without the emission of photons. All these studies are made possible because E strongly depends on the distance r between the donor and the acceptor. In the case where donor–acceptor pairs are separated by a fixed distance, according to the theory of Forster,[3] E is given by

$$E = [1 + (r/R_0)^6]^{-1} \quad (1)$$

where R_0 is the characteristic distance at which nonradiative energy transfer and spontaneous decay of the excited state of the donor are equally probable; i.e., E equals 0.5. Although, in a real system, r is often not fixed and E should be averaged over the real spatial distribution of donor–acceptor pairs, eq 1 emphasizes, and that is the only important point here, that E varies rapidly with r in the vicinity of R_0.

More specifically, much attention has been paid to the use of the NRET technique to study the miscibility of polymer blends in the solid state.[4-13] The main interest of this method is its ability of monitoring changes in blend miscibility at a scale of ca. 3 nm, well below the scale of observation of differential scanning calorimetry. This is believed to be true under a suitable choice of the donor–acceptor pair, for example, naphthalene–anthracene (R_0 = 2.1 nm) or carbazole–anthracene (R_0 = 2.8 nm). Then, it may be assumed that changes in the efficiency of energy transfer between the donor and acceptor chromophores reveal differences of interpenetration (miscibility) of the labeled polymers at the scale of R_0.

The general experimental conditions for such studies have been well established. Comparative measurements of the efficiency of energy transfer can be made as a function of blend composition, copolymer composition, molecular weight, and tacticity of blend components, etc. However, the concentration of both donor and acceptor in blends must be kept constant and equal as an increase in their concentration decreases the average distance between them and, thereby, results in an increase in the efficiency of energy transfer. The concentration used for the donor and acceptor is generally between 10^{-3} and 10^{-2} mol L^{-1}.

In practice, not every chain is labeled with a certain number of fluorescent probes. Donor- and acceptor-labeled polymers are first prepared, and, then, they are diluted with the necessary amount of unlabeled polymers to attain the desired concentration of chromophores. As a typical example, to prepare a mixture of poly(methyl methacrylate) (PMMA) containing 10^{-2} mol L^{-1} of both the donor and the acceptor, about 17 wt % of labeled PMMA is needed if the concentration of chromophores in the labeled polymers, Φ, is 1.0 mol %. It is obvious that the number of labeled chains per unit volume depends on Φ. Very different values of Φ have been used in the literature, ranging from 0.24[12] to 2.63 mol %;[5] this difference means that, for chains of similar degrees of polymerization, the average number of chromophores per labeled chain varies by a factor of 10. However, no attention has been paid to Φ in these studies, except to verify that the amount of chromophores present should not modify significantly the properties of the polymer.

In this paper, however, we will demonstrate the significant influence of Φ on the efficiency of energy transfer, keeping all other conditions constant. For this purpose, let us first consider a reference blend often used in studies of polymer blend miscibility by NRET,[4,7,12] made from the mixture of chains of a single polymer but containing some chains labeled with the donor and other chains labeled with the acceptor. This blend can be considered to be a totally miscible mixture. Now, assuming a random distribution of the chromophores on the labeled chains as well as a random distribution of the labeled chains in the mixture, which are two basic assumptions of such studies, it is expected that a larger number of labeled chains per unit volume corresponds to a larger extent of interpenetration between them. In other words, keeping constant the concentration of chromophores in the mixture, an increase in Φ leads to a decrease of the number of labeled chains per unit volume and, hence, to a decrease of their interpenetration. This results in an increase of the average distance between the donor and acceptor chromophores and reduces the efficiency of energy transfer. This effect arises from the fact that the chromophores are *covalently* attached to the polymer chains and, therefore, their spatial distribution is determined by the chain conformation. This means that the chromophores on each chain are located in a volume determined by the radius of gyration of the random coil of the chain in the blend. This situation is different from that arising in mixtures where the chromophores are just embedded in a miscible matrix.

To experimentally confirm the effect of Φ on the efficiency of energy transfer, we used a series of labeled PMMA's of similar molecular weights but with different Φ values. Carbazole (donor)-labeled PMMA's (PMMA-c) and anthracene (acceptor)-labeled PMMA's (PMMA-a) were obtained from the copolymerization of methyl methacrylate with 2-(*N*-carbazolyl)ethyl methacrylate and 9-anthrylmethyl methacrylate, respectively, in benzene solution with azobis(isobutyronitrile) as initiator. Blends of PMMA/PMMA-c/PMMA-a, hereafter referred to as PMMA(c/a), were prepared with the same concentration of both the donor and the acceptor but from labeled PMMA's of different Φ. Furthermore, the effect of Φ was investigated in miscible PMMA/poly(vinyl chloride) (PVC) blends containing PMMA-c and anthracene-labeled PVC (PVC-a). This latter polymer was obtained by the reaction of PVC with (9-anthrylmethyl)lithium. Details about the synthesis of these labeled polymers are given in the literature.[4,8,12] In this study, Φ was determined by using UV spectroscopy, and the molecular weights were measured by size-exclusion chromatography. The absence of unattached chromophores in labeled samples was ensured by repeated dissolution in THF and precipitation into methanol and then into heptane, until the chromophores' concentration obtained from UV spectroscopy remained

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Table I
Polymer Characteristics

polymer	mol % of label	M_n, kg/mol	M_w/M_n
PMMA		40	1.58
PMMA-c-01	0.154	42	1.64
PMMA-c-03	0.316	36	1.64
PMMA-c-05	0.574	36	1.53
PMMA-c-06	0.605	30	1.57
PMMA-c-10	1.054	33	1.61
PMMA-a-01	0.124	42	1.74
PMMA-a-03	0.331	37	1.59
PMMA-a-06	0.628	44	1.57
PMMA-a-10	1.610	25	1.80
PVC		89	1.54
PVC-a	0.500	82	1.57

Table II
Blends of PMMA/PMMA-c/PMMA-a

blend	labeled PMMA	$(\Phi_c + \Phi_a)/2$
PMMA(c/a)-01	PMMA-c-01 + PMMA-a-01	0.14
PMMA(c/a)-03	PMMA-c-03 + PMMA-a-03	0.32
PMMA(c/a)-06	PMMA-c-06 + PMMA-a-06	0.62
PMMA(c/a)-10	PMMA-c-10 + PMMA-a-10	1.33

constant. The main characteristics of the polymers used and of the blends investigated in this study are given in Tables I and II, respectively. PMMA-c and PMMA-a of similar Φ values were used for a given blend, and the concentration of its chromophores is given by $(\Phi_c + \Phi_a)/2$.

Films with a thickness of ca. 25 μm were prepared by casting 3% butanone solutions onto quartz plates. The solvent was removed by slow evaporation at room temperature for 2 days under a nitrogen atmosphere, followed by vacuum drying at 90 °C for another 2 days and, then, at 125 °C for 15 h for the PMMA(c/a) blends and at 80 °C for 3 days for the PVC/PMMA blends. Fluorescence emission measurements were carried out with a Shimadzu RF-540 spectrofluorophotometer with a band pass of 5 nm. The samples were excited at 290 nm using front-face illumination with the film surface oriented 60 and 30° relative to the incident exciting beam and the axis of observation, respectively. The efficiency of energy transfer was characterized by the emission intensity ratio of the carbazolyl label to the anthryl label, I_c/I_a. I_c and I_a were measured at 360 and 413 nm, respectively, for the PMMA-(c/a) blends and at 362 and 419 nm, respectively, for the PVC/PMMA blends due to the red shift of the maximum emission of the chromophores in the presence of PVC.[12] The emission spectra were not corrected for the wavelength-dependent efficiency of the photomultiplier tube.

Before the results are discussed, it must be emphasized that the concentration of chromophores in blends has been carefully checked by UV spectroscopy in order to verify that the same relative amounts of donor and acceptor were present. Figure 1 gives a typical UV spectrum of a PMMA-(c/a) film, PMMA(c/a)-06, containing 10^{-2} mol L^{-1} of each chromophore. It is seen that the absorption intensity ratio of the carbazolyl label, measured at 290 nm, to the anthryl label, measured at 390 nm, is about 2; the same value was found for all PMMA(c/a) blends investigated. Similar verifications have been made for the PVC/PMMA blends. In the analysis, the radiative energy transfer, involving emission and reabsorption of photons, was not considered. Under the conditions of sample preparation used, all films had a very similar thickness. Consequently, the optical densities of donor and acceptor labels were approximately identical within a given series of samples, and no correction for such a contribution was needed.

Two series of PMMA(c/a) blends, containing a total of 10^{-2} and 5×10^{-3} mol L^{-1} of each chromophore, were prepared. The results of NRET measurements are shown in Figure 2, where the I_c/I_a ratio is plotted as a function of $(\Phi_c + \Phi_a)/2$ (the error bar refers to the standard deviation of measurements made with different films of the same sample). First, it is observed that blends containing 10^{-2} mol L^{-1} of both the donor and acceptor exhibit smaller I_c/I_a values, i.e., higher energy-transfer efficiencies, as compared to blends containing 5×10^{-3} mol L^{-1} of each chromophore. Second, and more importantly, Figure 2 shows that, with the two chromophores' concentrations used, the I_c/I_a ratio is not constant but increases significantly with increasing $(\Phi_c + \Phi_a)/2$. This result gives evidence of the effect of Φ on the nonradiative energy transfer; that is, an increase in the concentration of chromophores in the labeled polymers reduces the efficiency of energy transfer despite the fact that the total concentration of chromophores remains constant in the blend; in other words, the maximum efficiency of energy transfer, at a given concentration of chromophores, is reached when the chromophores (both donors and acceptors) are randomly distributed on each of the chains.

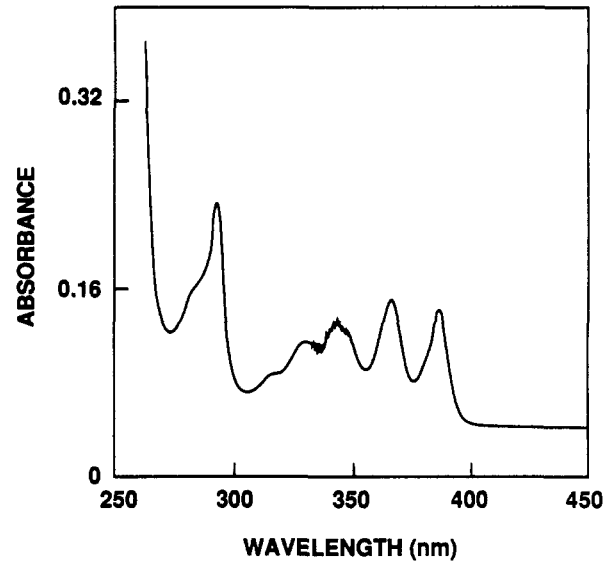

Figure 1. UV spectrum of the PMMA(c/a)-06 blend film containing 10^{-2} mol L^{-1} of both the carbazolyl label and the anthryl label.

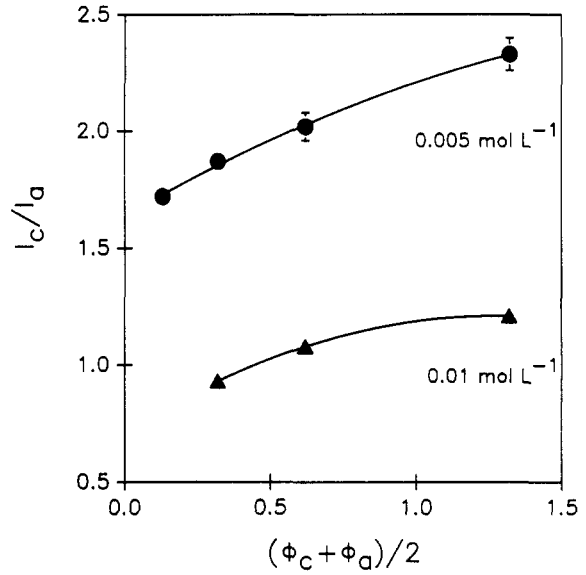

Figure 2. I_c/I_a vs $(\Phi_c + \Phi_a)/2$ for PMMA(c/a) blends containing two different concentrations of both chromophores.

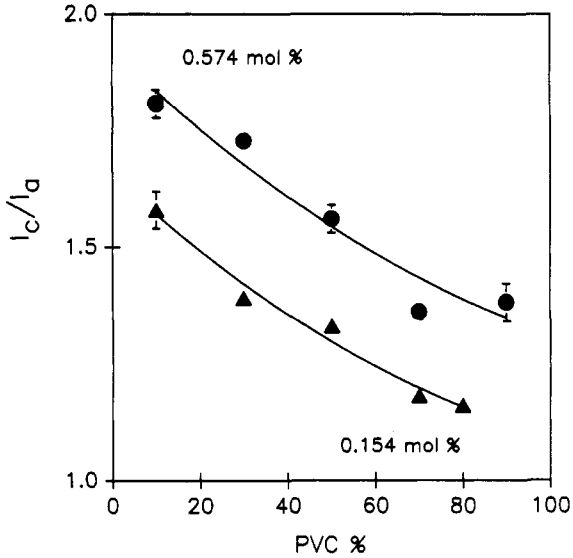

Figure 3. I_c/I_a vs PVC content in PVC/PMMA blends containing 4×10^{-3} mol L^{-1} of both chromophores. Φ of PVC-a is 0.5 mol %, whereas Φ of PMMA-c is indicated on the figure.

Now, we make comparative measurements of energy transfer with different values of Φ and check for variations of miscibility. In order to do this, PVC/PMMA blends were investigated as a function of composition. Two series of blends were prepared by using PVC-a and PMMA-c; the concentration of each chromophore was kept at 4×10^{-3} mol L^{-1}. In the first series, PMMA-c-01 (Φ = 0.154 mol %) was used, while the second series was prepared by using PMMA-c-05 (Φ = 0.574 mol %) with a Φ value almost 4 times greater than that of PMMA-c-01; the same PVC-a (Φ = 0.5 mol %) was used in all blends.

In Figure 3, the I_c/I_a ratio of these blends is plotted as a function of PVC concentration. It can be seen that, in spite of the same concentration of chromophores, a systematic difference exists between the two series of PVC/PMMA blends, with smaller I_c/I_a values for the blends prepared from PMMA-c-01. These results are consistent with those of Figure 2: a larger number of labeled chains with a smaller chromophores' concentration in each of them favors the mutual interpenetration and increases the probability of approach between the donor and acceptor. But more significantly, the same variation of the I_c/I_a ratio with blend composition is observed in the two series of blends: I_c/I_a decreases with increasing the PVC content, indicating that PMMA is more miscible in PVC than PVC is in PMMA. This is consistent with previous measurements using PMMA-a and naphthalene-labeled PVC.[7] Therefore, from Figure 3, it can be concluded that different Φ values of nonradiative energy transfer lead to the same relative information about the blend miscibility. It should be mentioned that differential scanning calorimetry measurements indicate, for blends prepared under the conditions described above,[13,14] a single glass transition temperature.

In conclusion, it has been demonstrated that, at a given concentration of chromophores in a given blend, the efficiency of nonradiative energy transfer depends on Φ; an increase in Φ reduces the energy transfer between donors and acceptors. Nevertheless, different Φ values lead to the same relative variation of the intensity ratio, at least in the example investigated in this paper. Therefore, the conclusions reached about blend miscibility seem to be independent of this parameter. However, this effect of Φ must be taken into account in studies where comparisons are made between different systems involving labeled polymers with different Φ values since a difference in the efficiency of energy transfer may result not only from a difference in blend miscibility but also from differences in Φ; in other words, Φ values must be similar in each of the systems under comparison.

Finally, it must be mentioned that other factors can contribute to variations in NRET efficiency with Φ. As the density of donor labels in a polymer chain increases, energy migration between donor moieties can become significant, leading to an increase in the efficiency of energy transfer from the donor to the acceptor.[15] On the other hand, as the density of acceptor labels in a polymer chain increases, some "overlap" of acceptor moieties can take place in the region of interpenetration between donor and acceptor coils, leading to a decrease in the NRET efficiency. However, these two factors are probably negligible in the present study because of the low donor and acceptor concentrations used; for example, at a value of Φ of 1.6 mol % (the maximum used in this study), we have on average 7 label moieties per PMMA chain of molecular weight 40 000 g/mol, separated on average by 57 repeat units. Under these conditions, energy migration is not possible. Therefore, we believe that the effect of the spatial distribution of chromophores is the main factor influencing the NRET, as discussed in the previous paragraphs.

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Registry No. PMMA (homopolymer), 9011-14-7; PVC (homopolymer), 9002-86-2; (2-(*N*-carbazolyl)ethyl methacrylate)-(methyl methacrylate) (copolymer), 82729-08-6; (9-anthrylmethyl methacrylate)(methyl methacrylate) (copolymer), 33773-67-0.