

A nonradiative energy transfer fluorescence spectroscopy study of poly(vinyl chloride)/poly(methyl methacrylate) blends

Yue Zhao* and Robert E. Prud'homme

Centre de Recherche en Sciences et Ingénierie des Macromolécules, Department of Chemistry, Laval University, Québec, Canada G1K 7P4

ABSTRACT

The miscibility of poly(vinyl chloride)/atactic poly(methyl methacrylate) (PVC/a-PMMA) blends was investigated by nonradiative energy transfer fluorescence spectroscopy using naphthalene-labeled PVC (PVC-N) with anthracene-labeled PMMA (PMMA-A), or anthracene-labeled PVC (PVC-A) with carbazole-labeled PMMA (PMMA-C). The two sets of results indicate an increase in energy transfer efficiency, corresponding to an increase in blend miscibility, as the PVC concentration increases and, more importantly, demonstrate that the same information about blend miscibility can be obtained using different donor-acceptor chromophore pairs and by changing the polymer to which the donor or the acceptor is attached. The effect of the tacticity of PMMA on its miscibility with PVC was also investigated using PMMA-C and PVC-A labeled polymers. The results confirm that PVC/a-PMMA blends are more miscible than PVC/i-PMMA blends over a large range of compositions.

INTRODUCTION

Following the studies of Morawetz and co-workers (1-4), the method of nonradiative energy transfer (NRET) fluorescence spectroscopy has been used by several groups to study the miscibility of polymer blends (5-13). This technique is based on the measurement of the nonradiative energy transfer from a donor chromophore to an acceptor chromophore, both being covalently attached to the polymers in the blend. The energy transfer efficiency, usually characterized by the fluorescence emission intensity ratio of donor to acceptor I_D/I_A , strongly depends on the average distance between the donor and acceptor molecules, thereby revealing the extent of interpenetration or miscibility of the polymers. Much effort has been made to improve our understanding of this method and to establish the most appropriate experimental conditions. These studies led to the conclusion that useful and unambiguous information about blend miscibility can be obtained by NRET measurements by taking into account possible effects of the fluorescence quenching by the polymers (10), the concentration of chromophores in labeled polymers (12), radiative energy transfer (13) and light scattering (13). It was shown to be particularly powerful to investigate the influence of different molecular parameters such as blend composition, molecular weight, tacticity, copolymer composition, and casting solvent, on the blend miscibility at the molecular scale.

Several NRET studies were carried out on blends of poly(methyl methacrylate) (PMMA) and poly(vinyl chloride) (PVC). Albert et al. (5) investigated the miscibility

*Present address: Département de chimie, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1

of PVC/PMMA blends as a function of blend composition using a naphthalene (donor)-labeled PVC (PVC-N) and an anthracene (acceptor)-labeled PMMA (PMMA-A). The measured I_N/I_A ratios increased with the PMMA concentration, which was interpreted as meaning a decrease in blend miscibility. Apparently, this is inconsistent with the measurements of nuclear magnetic resonance spectroscopy (5) which indicated the highest miscibility at 60% PMMA in the blend. This discrepancy could be due to the quenching of the naphthalene fluorescence by the chlorinated polymers (10). One of the objectives of the present study is to verify this hypothesis by using carbazole as the donor which is less sensitive to fluorescence quenching than naphthalene because of the shorter lifetime of its excited state, and to compare the trends observed as a function of composition with those obtained with naphthalene.

On the other hand, in a previous study (11), we used the NRET technique to investigate the influence of tacticity and molecular weight of PMMA on its miscibility with PVC. Based on the measured I_N/I_A values, we observed a decrease in blend miscibility with an increase in the isotactic content or the molecular weight of PMMA, in agreement with the results obtained from other techniques (14,15). Meanwhile, Henriouille-Granville et al. (8) also investigated PVC/PMMA blends with PMMA's of different tacticities (isotactic=i-PMMA, syndiotactic=s-PMMA and atactic=a-PMMA) and concluded that the tacticity of PMMA has no effect on its miscibility with PVC. They ascribed the observed increase in energy transfer in blends containing i-PMMA to a conformational effect of the chains; that is, i-PMMA chains have a more extended conformation than a-PMMA or s-PMMA chains and, hence, the i-PMMA-PVC contacts are favored as compared to the a-PMMA-PVC or s-PMMA-PVC contacts, which leads to more energy transfer.

It should be noticed that the NRET procedures used were different in these two series of experiments. In Ref. 8, anthracene-labeled PMMA's of different tacticities were used with naphthalene-labeled PVC. In contrast, in our previous study (11), both the donor and the acceptor were labeled onto the same polymer, namely PVC, but to different chains. Such differences in the experimental conditions could influence the results because the emission intensity ratio of donor to acceptor, which was used to characterize the efficiency of energy transfer in these studies, can be influenced by several factors (10,12). A second objective of the present study is to critically analyze the NRET measurements of PVC/PMMA blends and to clarify the situation. In order to do so, the PMMA tacticity effect was studied using the following experimental approach: a-PMMA and i-PMMA of similar molecular weights were used as matrices in which a small amount of a-PMMA-C was diluted; these PMMA's were then blended with a PVC containing PVC-A. In other words, both polymers were labeled, but the same labeled polymers were used in every blend, which has the advantage of eliminating some possible sources of the uncertainties in the NRET measurements, as will be discussed more extensively in the Discussion. The results will be discussed in terms of blend miscibility with a close look at the experimental procedures.

EXPERIMENTAL

PMMA-C and PMMA-A were prepared by the copolymerization of methyl methacrylate with 2-(N-carbazolyl)ethyl methacrylate and 9-anthrylmethyl methacrylate, respectively, in benzene at 60 °C with azobisisobutyronitrile as initiator. PVC-N and PVC-A were obtained by the reaction of PVC with (α -naphthylmethyl)lithium and (9-anthrylmethyl)lithium, respectively, under anhydrous conditions, in THF at 0 °C. More details about the synthesis of the labeled polymers are given in the literature (2,6,10).

The concentration of chromophores in the labeled polymers was determined by UV spectroscopy assuming that their extinction coefficients are the same before and after being attached to the polymers. The absence of unattached chromophores in the labeled polymers was verified by repeated dissolution in THF, precipitation into methanol and then into heptane, until the chromophores' concentration measured by UV spectroscopy remained constant. Molecular weights were measured by size-exclusion chromatography in toluene at room temperature, using standard polystyrene samples for calibration and Ultrastaygel columns.

The polymers used in this study are listed in Table I. PVC was provided by Aldrich Chemicals, whereas a-PMMA and i-PMMA samples were prepared by radical and anionic polymerization, respectively (14). The a-PMMA1 sample was used for the measurements of the effect of blend composition: two series of blends were prepared, one containing PVC-A and a-PMMA-C1, and the other one containing PVC-N and a-PMMA-A. The concentration of both donor and acceptor was $4 \times 10^{-3} \text{ mol.L}^{-1}$ in every case. In the measurements of the influence of PMMA tacticity, a-PMMA2 and i-PMMA were used, and the labeled polymers were PVC-A and a-PMMA-C2, with a concentration of $2 \times 10^{-3} \text{ mol.L}^{-1}$ for each chromophore in every blend. The tacticity of PMMA was determined by 200-MHz NMR spectroscopy in 5% chloroform solutions at room temperature.

Table I Characteristics of the polymers used

Polymer	M_n (kg/mol)	M_w/M_n	Mol% of label
PVC	90	1.54	----
PVC-N	79	1.56	0.24
PVC-A	85	1.51	0.50
a-PMMA1	40	1.58	----
a-PMMA2**	24	1.33	----
i-PMMA*	20	1.65	----
a-PMMA-C1	36	1.53	0.57
a-PMMA-C2	30	1.57	0.61
a-PMMA-A	37	1.59	0.33

*)NMR analysis: $mm=90$; $mr=4$; $rr=6$ **)NMR analysis: $mm=6$; $mr=36$; $rr=58$

Thin films with a thickness of *ca.* 20 μm were obtained by casting 2% butanone solutions onto quartz plates. The solvent was removed first by slow evaporation at room temperature for 2 days under a nitrogen atmosphere and, then, by vacuum drying at 70 $^\circ\text{C}$ for 2 days. No trace of residual solvent and impurity was found in the fluorescence spectra of the non-labeled samples prepared under the same conditions. The films were kept under vacuum before the fluorescence measurements. It should be mentioned that very similar thicknesses were obtained within a given series of films by casting a controlled amount of solution onto a known surface of the quartz plate. Consequently, the optical densities of both the donor and acceptor labels were approximately identical for every sample. Under these conditions, no correction for some possible contribution from radiative energy transfer, involving emission and re-absorption of photons, was needed. Moreover, under the experimental conditions used, even at the highest concentration of both donor and acceptor, $4 \times 10^{-3} \text{ mol.L}^{-1}$, the optical densities of the chromophores are very low, smaller than 0.04 with the anthryl

and naphthyl labels, and smaller than 0.08 with the carbazolyl label, to prevent significant radiative energy transfer. The emission spectra were not corrected for the wavelength-dependent efficiency of the photomultiplier tube.

Fluorescence emission measurements were performed on a Shimadzu RF-540 spectrofluorophotometer with a bandpass of 5 nm and using front-face illumination with the film surface oriented 60 and 30 ° relative to the incident exciting beam and the axis of observation, respectively. For samples containing PVC-N and PMMA-A, the naphthyl donor was excited at 288 nm and the emission intensities of naphthalene I_N and anthracene I_A were measured at 340 and 414 nm, respectively. For samples containing PVC-A and PMMA-C, the carbazolyl donor was excited at 290 nm and the emission intensities were measured at 362 nm for carbazole and 420 nm for anthracene. The difference in the wavelength of emission of the anthryl label in these two series of experiments is due to the red shift of its emission maximum (10) when anthracene is attached to PVC. As an example, the absorption and emission spectra of films of PVC/PMMA 50/50 blends containing, respectively, PVC-A/PMMA-C and PVC-N/PMMA-A (4×10^{-3} mol.L⁻¹) are given in Figure 1. It should be mentioned that, in the emission spectrum of the PVC-A/PMMA-C mixture, the anthracene band at 420 nm partly overlaps the carbazole band at 362 nm, but this factor does not influence the trends observed from their emission intensity ratio since the intensity ratio of 346 nm (carbazole) to 445 nm (anthracene) exhibits the same trend.

RESULTS

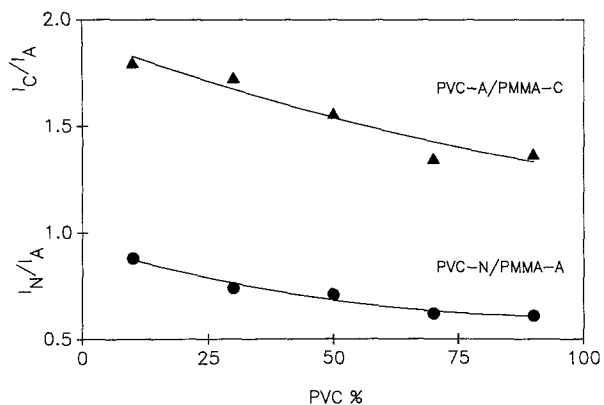
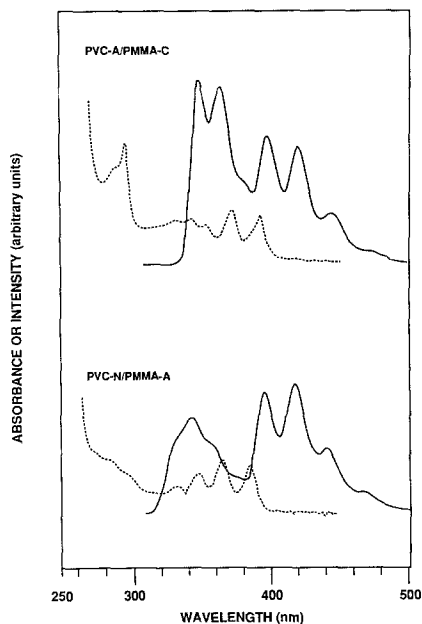
First of all, it must be emphasized that, under the conditions of sample preparation used, every PVC/PMMA blend (with both atactic and isotactic PMMA's) exhibits a single Tg with a width of the transition range of about 20 °C. In other words, differences in NRET efficiency observed in the present study reveal differences in these blends that cannot be detected from the Tg measurements and cannot be ascribed to a gross phase separation.

Emission intensity ratios of donor to acceptor obtained for the two series of PVC/PMMA blends containing, respectively, PVC-A/PMMA-C and PVC-N/PMMA-A are depicted in Figure 2 as a function of the PVC concentration in the blend. The higher values of the I_C/I_A ratio as compared to those of I_N/I_A may be attributed 1) to the higher extinction coefficient of the carbazole moiety at the excitation wavelength and 2) to the higher quantum yield of the carbazole fluorescence as compared to that of the naphthyl donor (see Figure 1). The fluorescence quenching by PVC (11), resulting from an increased intersystem crossing from the singlet to the triplet state, is less important for carbazole than for naphthalene because of the shorter fluorescence lifetime of the excited carbazole (16.1 ns for carbazole as compared to 67 ns for α -methyl-naphthalene in cyclohexane (16)).

The most important feature of Figure 2 is that the same trend is observed for I_C/I_A and I_N/I_A : both ratios decrease as the PVC concentration increases, corresponding to an increase in the energy transfer efficiency and, hence, indicating an increase in the PVC/PMMA blend miscibility. Based on these results, it seems that low-concentration PMMA is more miscible in PVC than does low-concentration PVC in PMMA. These measurements clearly demonstrate that the same information about blend miscibility can be obtained by labeling the polymers with different donor-acceptor pairs.

Figure 1

Absorption and emission spectra of PVC/PMMA 50/50 blends containing PVC-N/PMMA-A and PVC-A/PMMA-C labeled chains ($\lambda_{ex}=290$ nm).

**Figure 2**

Fluorescence emission intensity ratio of donor to acceptor of PVC/PMMA blends containing PVC-N/PMMA-A and PVC-A/PMMA-C as a function of the PVC content (concentration of donor and acceptor: 4×10^{-3} mol.L⁻¹).

It is interesting to note that, in addition to the use of different chromophores, PMMA is labeled with the donor (carbazole) in one series of blends and with the acceptor (anthracene) in the other series of samples. Therefore, it is also clear that changing the polymer to which the donor or the acceptor is attached leads to the same trends and the same conclusions.

The effect of the tacticity of PMMA on its miscibility with PVC was then investigated using labeled PMMA and labeled PVC. A small amount of the labeled PMMA, PMMA-C, was diluted in the unlabeled a-PMMA or i-PMMA at a concentration of $2 \times 10^{-3} \text{ mol.L}^{-1}$ and, therefore, the fraction of labeled PMMA is 24.5, 8.4, 5.2, 3.8 and 3.0% for PMMA concentrations of 10, 30, 50, 70 and 90%, respectively. Under these conditions, it can be assumed that the labeled PMMA chains are equally (and randomly) dispersed in i-PMMA and in a-PMMA, and that their spatial distribution in the blend, which determines the energy transfer efficiency, is controlled by the miscibility of all PMMA chains with PVC.

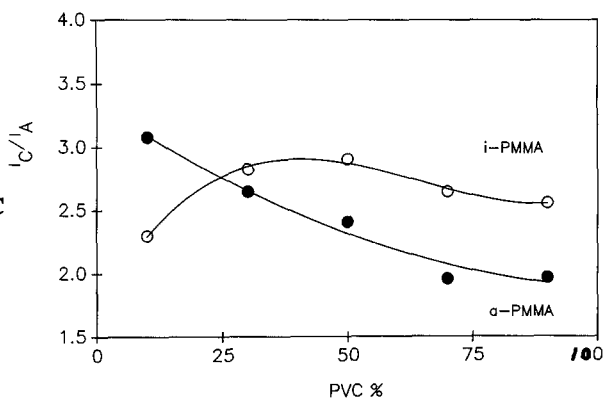
In Figure 3, the I_C/I_A ratios obtained for blends of PVC/a-PMMA and PVC/i-PMMA are plotted as a function of PVC concentration. Over a large range of blend compositions, more efficient energy transfers (smaller I_C/I_A values) are observed in blends with a-PMMA as compared to blends with i-PMMA, thereby indicating a higher miscibility of PVC with a-PMMA than with i-PMMA. This observation is in agreement with the results of a previous study using the doubly labeled-PVC approach (11), in which the higher PVC/a-PMMA miscibility was revealed by a lower energy transfer efficiency. However, for blends with low PVC concentrations, smaller than *ca.* 20%, the energy transfer is more efficient in PVC/i-PMMA blends than in PVC/a-PMMA blends. In addition, the variation of the I_C/I_A ratio with blend composition is in agreement with that observed in Ref. 8 (I_N/I_A) using labeled PMMA's of different tacticities in the corresponding PVC/PMMA blends.

DISCUSSION

Before discussing the results obtained concerning the effect of the tacticity of PMMA on the structure of the blends, it is important to take a closer look at the possible experimental procedures for such studies. It may at first seem better to label each PMMA with one chromophore, and PVC with another one. However, it should be recognized that many factors can exert a significant influence on the experimentally measured I_D/I_A values when using different labeled PMMA's, and if a certain number of conditions are not met, unexpected variations of I_D/I_A will be recorded.

Figure 3

Fluorescence emission intensity ratio of donor to acceptor of PVC/a-PMMA and PVC/i-PMMA blends containing PVC-A/PMMA-C as a function of the PVC content (concentration of donor and acceptor: $2 \times 10^{-3} \text{ mol.L}^{-1}$).



First, the fluorescence quantum yield of the chromophore in different labeled polymers must be same, without fluorescence quenching and spectral modification. Second, the chromophores' concentration in each sample must be rigorously the same (12) (without even considering errors arising from the determination of the chromophores concentration in each labeled polymer). Based on these considerations, it seems preferable to use the same labeled polymers in comparative NRET studies, and to eliminate such sources of uncertainty, whenever possible. This is the main advantage of using a polymer, for example PVC, containing both donor- and acceptor-labeled PVC chains in systematic study of PVC/PMMA blends, changing only the PMMA (different tacticities or molecular weights), but without any chromophores attached to PMMA, as demonstrated in a previous study (11). The same advantage is found with the approach used in the present study; although the two polymers were labeled, the same labeled PMMA and the same labeled PVC were used in each sample, therefore keeping the possible influence arising from the aboved mentioned factors constant in all samples of a given series of blends.

Generally speaking, a higher level of blend miscibility means more contacts between the dissimilar chains at the molecular level. This requires primarily a random distribution (or random dispersion) of the chains of both polymers. However, for a given degree of dispersion, the number of contacts can be enhanced by an extended chain conformation since it will increase the interpenetration of the dissimilar chains. In other words, the effect of chain random dispersion and chain conformation should both be considered in the analysis of NRET measurements. For example, an extended conformation of the donor- and acceptor-labeled chains does not necessarily result in a smaller average distance between the two sorts of chromophores and, hence, a higher NRET efficiency, if there is more nonrandom dispersion of the two polymers.

In view of the above considerations, let us look again at the results of Figure 3. As discussed in Ref.8, the tacticity of PMMA has an effect on its unperturbed dimension which increases with the content of the isotacticity (17,18): *i*-PMMA has a more extended chain conformation than *a*-PMMA. If the only difference between PVC/*i*-PMMA and PVC/*a*-PMMA blends is a difference in chain conformation, assuming the same chain dispersion of both polymers in these two blends, there will be more PVC-*i*-PMMA contacts than PVC-*a*-PMMA contacts and, hence, more energy transfer (a smaller I_D/I_A ratio). However, the results of Figure 3 indicate more energy transfer in PVC/*a*-PMMA than in PVC/*i*-PMMA blends at most compositions. These results cannot be explained by a difference in chain conformation between isotactic and atactic PMMA. This leads us to the conclusion that there is more nonrandom chain dispersion in the PVC/*i*-PMMA mixture than in PVC/*a*-PMMA blends. In other words, PVC is more miscible with *a*-PMMA than with *i*-PMMA at most compositions because of a larger favorable interactional (enthalpic) contribution combined with a smaller unfavorable free volume effect in the former system (11). This conclusion is reached here using a mixture containing a labeled PMMA and a labeled PVC, in contrast with our previous study where PMMA was not labeled, but where PVC contained donor- and acceptor-labeled chains (11).

However, even if *a*-PMMA is more miscible than *i*-PMMA at most compositions, as discussed above, at low PVC concentrations, e.g. 10% (left side of Figure 3), the chain conformation could play an important role. The polymer matrix is PMMA and, consequently, the conformation of the diluted labeled PMMA-C chains could be influenced by the chains of the matrix PMMA and adopt a more extended conformation in the *i*-PMMA than in the *a*-PMMA matrix, which favors the contacts

between the PVC-A and PMMA-C chains. In order to confirm this hypothesis, we prepared PVC/a-PMMA and PVC/i-PMMA blends with a PVC concentration of only 2.1%. At such a low concentration of PVC, we can assume a similar random dispersion of the PVC chains in both the a-PMMA and i-PMMA matrices, i.e., there is no difference in miscibility due to different extents of random dispersion in these two blends. The measured I_C/I_A ratios are 2.8 for the PVC/a-PMMA blend and 1.5 for the PVC/i-PMMA blend. This difference in energy transfer efficiency has to be ascribed to the conformational effect: in the i-PMMA matrix, the labeled PMMA-C chains are more extended than in the a-PMMA matrix. This seems to confirm our hypothesis, although more measurements need to be done.

In conclusion, the NRET results presented in this paper indicate an increase in energy transfer efficiency, corresponding to an increase in the level of PVC/PMMA miscibility, as the PVC concentration increases. It is also demonstrated that the same information about blend miscibility can be obtained by using different donor-acceptor chromophore pairs and by changing the polymer to which the donor or the acceptor is attached. From one series of experiments to the other, the energy transfer ratio is obviously different, but the same trends are observed in each series. Finally, the NRET measurements confirm that, over a large range of blend compositions, PVC is more miscible with atactic PMMA than with i-PMMA.

ACKNOWLEDGMENT: We thank Dr. P. de Grandpré (Faculty of Medicine, Laval University) for the use of the spectrofluorometer. Financial support from N.S.E.R.C. (Canada) and F.C.A.R. (Québec) is also acknowledged.

REFERENCES

1. Morawetz, H., Amrani, F. *Macromolecules* 1978, **11**, 281
2. Amrani, F., Hung, J.M., Morawetz, H. *Macromolecules* 1980, **13**, 649
3. Mikes, F., Morawetz, H., Dennis, K.S. *Macromolecules* 1980, **13**, 969
4. Morawetz, H. *Science* 1988, **240**, 172
5. Albert, B., Jérôme, R., Teyssié, P., Smyth, G., Boyle, N.G., McBrierty, V.J. *Macromolecules* 1985, **18**, 388
6. Albert, B., Jérôme, R., Teyssié, P. *J. Polym. Sci., Chem. Ed.* 1986, **24**, 537
7. Albert, B., Jérôme, R., Teyssié, P. *J. Polym. Sci., Chem. Ed.* 1986, **24**, 551
8. Henriouille-Granville, M., Kuyde, K., Jérôme, R., Teyssié, P., De Schryver, F.C. *Macromolecules* 1990, **23**, 1202
9. Major, M.D., Torkelson, J.M., Brearley, A.M. *Macromolecules* 1990, **23**, 1711
10. Zhao, Y., Lévesque, J., Roberge, P.R., Prud'homme, R.E. *J. Polym. Sci., Polym. Phys. Ed.* 1989, **27**, 1955
11. Zhao, Y., Prud'homme, R.E. *Macromolecules* 1990, **23**, 713
12. Zhao, Y., Prud'homme, R.E. *Macromolecules* in press
13. Wang, Y., Koberstein, J.T. *Macromolecules* 1990, **23**, 3088
14. Lemieux, E., Prud'homme, R.E., Forte, R., Jérôme, R., Teyssié, P. *Macromolecules* 1988, **21**,
15. Vorenkamp, E.J., ten Brinke, G., Meijer, J.G., Jager, H., Challa, G. *Polymer* 1985, **26**, 1725
16. Berlman, I.B. *Handbook of Fluorescence Spectra of Aromatic Molecules*, Academic Press, New York, 1965.
17. Sundararajan, P.R. *Macromolecules* 1986, **19**, 415.
18. Jenkins, R., Porter, R.S. *Polymer* 1982, **23**, 105.