(11) Portugall, H.; Ringsdorf, H.; Zentel, R. *Macromol. Chem.* **1982**, *193*, 2311.
(12) Goldburt, E.; Shvartsman, F.; Fishman, S.; Krongauz, V. *Macromolecules* **1984**, *17*, 1225.
(13) Fischer, E. *Mol. Photochem.* **1970**, *2* (1), 99.
(14) Gray, G. W.; Lacye, D.; Nester, N.; Toyne, K. J.; White, M. S. *Abstracts*; International Conference on Liquid Crystal Polymers, Bordeaux, France, 1987.
(15) Sagane, T.; Lenz, R. *Polym. J.* **1988**, *20*, 923.
(16) Gegiou, D.; Muszkat, K. A.; Fischer, E. *J. Am. Chem. Soc.* **1968**, *90*, 3907.
(17) Meredith, G. R.; Vandusen, J. G.; Willimans, D. J. *Macromolecules* **1982**, *83*, 816.
(18) Meirovitch, E.; Shvartsman, F.; Krongauz, V.; Zimmerman, H. *J. Phys. Chem.* **1985**, *89*, 5522.
(19) Shvartsman, F.; Cabrera, I.; Weis, A.; Wachtel, E.; Krongauz, V. *J. Phys. Chem.* **1985**, *89*, 3941.

Registry No. M_6^{CN} (homopolymer), 83847-15-8; $(S_2^T)(M_6^{CN})$ (copolymer), 124401-69-0; $(S_2^T)(M_6^{OMe})$ (copolymer), 124401-70-3; $(S_5^R)(M_6^{CN})$ (copolymer), 108764-09-6; S_2^T, 25952-50-5.

A Nonradiative Energy Transfer Fluorescence Study: Blends of Poly(vinyl chloride) and Poly(methyl methacrylates) of Different Tacticities and Molecular Weights

Yue Zhao and Robert E. Prud'homme*

Centre de Recherche en Sciences et Ingênierie des Macromolécules, Chemistry Department, Laval University, Québec, Canada G1K 7P4. *Received February 22, 1989; Revised Manuscript Received July 17, 1989*

ABSTRACT: The nonradiative energy transfer (NRET) technique has been used to investigate the influence of tacticity and molecular weight of poly(methyl methacrylate) (PMMA) on its miscibility with poly(vinyl chloride) (PVC). These investigations were carried out by labeling PVC with both naphthyl (fluorescence donor) and anthryl (fluorescence acceptor) chromophores assuming that the efficiency of energy transfer is dependent upon the extent of random dispersion of the PVC chains. Comparative measurements lead to the observation of differences of miscibility at a molecular level between different PVC/PMMA blends prepared under identical conditions and all exhibiting a single glass transition temperature. These results indicate that an increase in isotactic content and molecular weight of PMMA results in more nonrandom dispersion of the PVC chains, i.e. reduces its miscibility with PVC. It is shown that this behavior can be related to a tacticity and molecular weight dependent lower critical solution temperature of these mixtures.

Introduction

The nonradiative energy transfer (NRET) technique has been used as a tool of investigation of ion-pair interchange in ionomer solutions,[1] chain interpenetration in bulk and solution,[2] morphology of polymer colloids,[3] miscibility of polymer blends,[4,5] and formation of micelles in block copolymers,[6] as reviewed recently by Morawetz.[7]

Morawetz et al. were the first to use this fluorescence technique to study the miscibility of polymer blends in the solid state,[4,7-9] which involves grafting fluorescent donor and acceptor molecules to the polymers. The efficiency of the nonradiative energy transfer, after the photoexcitation of the donor, depends upon the average distance between the donor and acceptor molecules; measurements of the relative emission intensities of the donor and acceptor, characterized by their emission intensity ratio, indicate the extent of interpenetration of the chains, giving information about the miscibility of the polymeric species. It has been demonstrated[4,5] that a suitable choice of the donor–acceptor pair, e.g. naphthalene–anthracene or carbazole–anthracene, leads to an efficient energy transfer over a distance of about 3 nm. It is then assumed that changes of the energy transfer efficiency is related to the evolution of the miscibility of the donor- and acceptor-containing polymers at this molecular level.

However, in a previous investigation, using naphthyl (donor) and anthryl (acceptor) chromophores,[10] we have critically examined this fluorescence method and shown that, in studies of the miscibility of polymer blends, the reference emission intensity ratio in the absence of energy transfer has to be measured in the bulk instead of being made in organic solutions. This ratio is important to establish an energy transfer scale. Furthermore, the fluorescence quenching effect of the polymers must be examined because it can lead to a variation of the relative fluorescence quantum yields of the donor and acceptor as a function of blend composition. In other words, if fluorescence quenching occurs, a change of the emission intensity ratio of the donor to acceptor can be observed without changing the miscibility level of the blend. Therefore, the interpretation of energy transfer data must be done with caution.

Nevertheless, in the present article, we will show that, under suitable conditions, the NRET technique provides useful information about the miscibility of polymer blends. It is particularly sensitive to small differences of polymer miscibility at the molecular level, differences which cannot be detected by other conventional techniques such as, for example, differential scanning calorimetry (DSC).

More specifically, the NRET technique will be used to investigate the influence of the tacticity and molecular weight of poly(methyl methacrylate) (PMMA) on its miscibility with poly(vinyl chloride) (PVC). Miscibility is generally observed in these blends, under suitable conditions of blend preparation.[11-13] The origin of this miscibility is attributed to the presence of hydrogen-bonding interactions involving the carbonyl group of PMMA and the α-hydrogen[14] as well as the β-hydrogens[11] of PVC. It will be shown that the NRET technique allows direct measurements of small miscibility differences between

0024-9297/90/2223-0713$02.50/0

Table I
Polymer Characteristics

polymer	sample	M_w, kg/mol	M_w/M_n	tacticity mm	mr	rr	mol % of label
PVC	PVC	138	1.54				
	PVC-N	123	1.56				0.24
	PVC-A	128	1.51				0.50
PMMA	a-PMMA1	30	1.09	...	...	...	
	a-PMMA2	60	1.10	7	41	52	
	a-PMMA3	98	1.08	6	43	51	
	a-PMMA4	200	1.10	5	43	52	
	a-PMMA5	350	1.15	6	44	50	
	i-PMMA1	7	1.4	88	4	8	
	i-PMMA2	14	2.0	89	4	7	
	i-PMMA3	27.5	2.5	93	2	5	
	i-PMMA4	31	2.2	96	2	2	
	i-PMMA5	47	1.24	98	1	1	
	s-PMMA1	117	1.17	0	18	82	

these (miscible) blends, all exhibiting a single glass transition temperature (T_g).

In the present investigation, PVC was attached by naphthyl and anthryl labels (none of the chromophores was grafted to PMMA). It is assumed that miscibility corresponds to a random dispersion of the PVC chains in those of PMMA, leading to the largest possible average distance between donor and acceptor molecules and, therefore, to the lowest energy transfer; any decrease in the degree of miscibility implies some nonrandom dispersion of the PVC chains, leading to a decrease of the average distance between donor and acceptor molecules and to an increase in the energy transfer efficiency. It should be noted that donor- and acceptor-labeled polystyrenes (PS) were previously used to study the interpenetration of this polymer in solution and in the bulk by Torkelson et al.[2] and that a PS labeled by two different chromophores was used to investigate its penetration into an unlabeled matrix by Liu et al.[15]

Finally, some measurements of the fluorescence anisotropy of the anthryl label in blends were performed. It will be shown that the nonradiative energy transfer from the naphthyl label to the anthryl label causes a fluorescence depolarization. A correlation between the magnitude of energy transfer and the fluorescence anisotropy of the anthryl label can be established.

Experimental Section

The preparation of the labeled PVC's was described previously;[10] the attachment of the naphthyl and anthryl moieties was achieved by the reaction of (α-naphthylmethyl)lithium and (9-anthrylmethyl)lithium, respectively, with PVC. The chromophores' content was determined by UV spectroscopy.

The main characteristics of the polymers used in this study are given in Table I (N and A stand for the naphthyl label and anthryl label, respectively). Isotactic and syndiotactic PMMA's of different molecular weights were prepared by anionic polymerization at the University of Liège.[16] Atactic PMMA's were purchased from Polysciences (i-PMMA, s-PMMA, and a-PMMA mean respectively isotactic, syndiotactic, and atactic PMMA). Molecular weights were measured by size-exclusion chromatography. Tacticities were determined by 200-MHz NMR spectroscopy, in 10% *o*-dichlorobenzene solutions at 135 °C for isotactic and syndiotactic PMMA's and in 5% chloroform solutions at room temperature for atactic PMMA's.

The concentrations of naphthyl and anthryl labels were both kept at 10^{-3} mol·L^{-1} in each blend. It is worth noting that, with this concentration of the chromophores, the amount of labeled polymers diluted in the corresponding unlabeled polymer is very small. For example, in a PVC/PMMA blend of 50/50 ratio, the total weight percent of donor- and acceptor-labeled PVC's is about 6%. Only one blend composition, namely, 50% in PVC, was investigated throughout this study.

Films were cast from 2.5% butanone solutions onto quartz plates. The solvent was allowed to evaporate very slowly for 2 days at room temperature under a nitrogen atmosphere. Then, the films were peeled off the quartz plates and dried under vacuum at 60 °C for 48 h, ensuring the complete removal of the solvent. No evidence of residual solvent and impurity was found in the fluorescence spectra of nonlabeled polymer films prepared under these conditions. The films were kept under vacuum before the measurements.

Fluorescence emission and anisotropy measurements were made by using a Shimadzu RF-540 spectrofluorometer with a bandpass of 5 nm. The films were mounted between quartz plates with the incident excitation beam oriented at 60° and the axis of observation oriented at 30° with respect to the sample surface. The samples were excited at 288 nm which is near the maximum absorption of the naphthyl label in the labeled polymers.[10] The efficiency of energy transfer was characterized by the ratio of the emission intensity of the naphthyl label to that of the anthryl label, I_N/I_A, measured at 340 nm for the former and 421 nm for the latter. The emission spectra were not corrected for the wavelength-dependent efficiency of the photomultiplier tube.

The fluorescence anisotropy of the anthryl label, r, was determined at its wavelength of maximum emission using the singel-channel method[17] according to

$$r = (I_{VV} - GI_{VH})/(I_{VV} + 2GI_{VH}) \tag{1}$$

where I is the fluorescence emission intensity (the first and second subscripts indicate the orientation of the excitation and emission polarizers, respectively: V, vertical; H, horizontal) and G is the ratio of the sensitivities of the detection system of the fluorometer for vertically and horizontally polarized light. The G factor was calculated from

$$G = I_{HV}/I_{HH} \tag{2}$$

Results and Discussion

Method Used. Before discussing the results obtained about the miscibility of PVC/PMMA blends, it is important to emphasize the conditions of observation used in the present study to prevent any ambiguity in the interpretation of the experimental data.

Generally, the fluorescence donor and acceptor labels are attached to the different polymers present in the blend.[4,5,8-10] As has been pointed out,[9] some ambiguity arises in such energy transfer investigations from the fact that the efficiency of energy transfer depends not only upon the extent of interpenetration (miscibility) of the donor- and acceptor-labeled polymers but also upon the size and geometry of phase domains; energy transfer can take place via the interface. This ambiguity has been eliminated in the present investigation by having the naphthyl and anthryl labels attached to the same polymer (not to the same chains). It is obvious, in this case, that miscibility implies a random dispersion of the chains, hence the largest possible average distance between donor and acceptor molecules; any decrease in the degree of miscibility results in an increased efficiency of energy transfer, with a maximum for the completely immiscible blend, whatever the size and geometry of phase domains. In other words, the increase of efficiency of energy transfer depends upon the extent of nonrandom dispersion of the fluorescence donor- and acceptor-labeled polymer chains, i.e. the local concentration of the chromophores.

The efficiency of energy transfer as a function of the concentration of chromophores was examined by using a PVC/PVC-A/PVC-N blend. The emission spectrum of a film of this sort containing 2 × 10^{-3} mol·L^{-1} of donor and the same concentration of acceptor is given in Figure 1. It shows a maximum emission intensity at 340 nm for the naphthyl label and at 421 nm for the anthryl label. As shown in Figure 2, the I_N/I_A ratio of this mix-

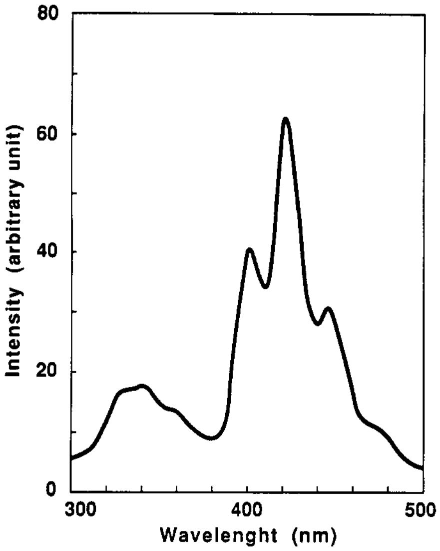

Figure 1. Emission spectrum of a PVC/PVC-A/PVC-N blend containing 2 × 10^{-3} mol·L^{-1} naphthyl label and 2 × 10^{-3} mol·L^{-1} anthryl labels (λ_{ex} = 288 nm).

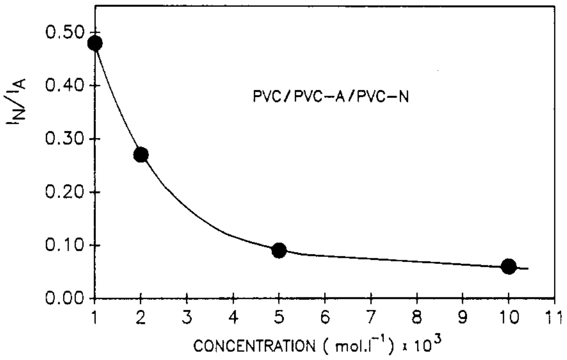

Figure 2. I_N/I_A values as a function of the concentration of naphthyl and anthryl labels in blends of PVC/PVC-N/PVC-A.

ture decreases when the concentration of the naphthyl and anthryl labels increases, indicating an increase in energy transfer (in this figure, and, hereafter, each data point is the average value of at least five measurements with different samples); in particular, a change of concentration for each chromophore from 10^{-3} to 2 × 10^{-3} leads to an important variation of the I_N/I_A ratio, from 0.48 to 0.27. This result indicates that, in the PVC/PMMA 50/50 blends investigated in the present study, a change of the local concentration for each chromophore between 10^{-3} and 2 × 10^{-3} can be monitored, with reasonable precision, by measuring the I_N/I_A ratio. However, it must be realized that the I_N/I_A values measured in a PVC/PVC-A/PVC-N blend are not equal to those found in a PVC/PMMA 50/50 blend, since the fluorescence quenching effect of PVC,[10] particularly with naphthyl chromophores, will be more important in the former system than in the latter one.

Another advantage of labeling the same polymer with both donor and acceptor molecules is that systematic investigations can be performed with a chosen polymer without the need of labeling several samples. However, blends containing a large concentration of the labeled polymer cannot be investigated because, in this case, the difference in local concentration of the fluorescence donor and acceptor is small, whatever the degree of miscibility of the system.

On the other hand, comparisons can be made between blends having the same concentration of PVC. Under this condition, the fluorescence quenching effect of PVC is necessarily the same and it cannot alter the relative quantum yields of the naphthyl and anthryl labels in different blends.

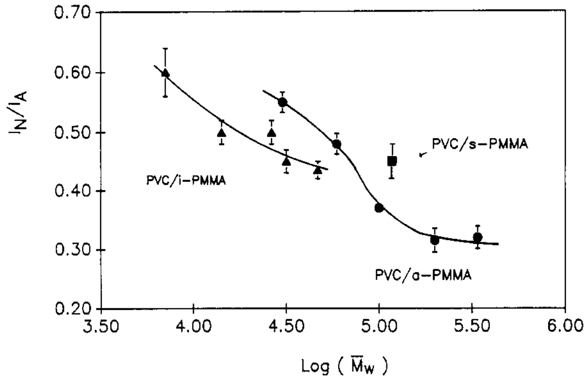

Figure 3. I_N/I_A values of PVC/i-PMMA, PVC/s-PMMA, and PVC/a-PMMA blends of 50/50 ratios as a function of the molecular weight of PMMA.

Influence of the Tacticity and Molecular Weight of PMMA on Its Miscibility with PVC. PVC was blended with one syndiotactic, five atactic, and five isotactic PMMA's of different molecular weights. Using the conditions of preparation described in the Experimental Section, DSC measurements do not indicate any difference between these samples: each blend exhibits a single T_g, and no variation in the glass transition width (about 18 °C) was observed from one sample to another. However, energy transfer measurements indicate a difference between these blends. As shown in Figure 3, where the I_N/I_A values are plotted as a function of the logarithmic value of the molecular weight, the I_N/I_A ratio (energy transfer efficiency) varies, with both the tacticity and molecular weight of PMMA.

More specifically, the I_N/I_A values decrease with an increase of the molecular weight of both atactic and isotactic PMMA, indicating that, in the molecular weight range investigated, an increase of the molecular weight of PMMA decreases the extent of random dispersion of PVC chains in the blend, i.e. reduces the miscibility. No difference in the I_N/I_A ratio was found between two blends prepared from different high molecular weight atactic samples (a-PMMA4 and a-PMMA5). On the other hand, the I_N/I_A values of PVC/atactic PMMA blends are larger than those of PVC/isotactic PMMA blends of similar molecular weights (Figure 3), indicating a higher degree of miscibility in blends made with atactic PMMA's. Also, a PVC/syndiotactic PMMA blend (a PMMA containing 82% syndiotactic triads) exhibits a still smaller energy transfer value than the PVC/atactic PMMA (a PMMA containing 50% syndiotactic triads) of similar molecular weight (Figure 3), indicating an increase of the blend miscibility with the syndiotactic content of PMMA. Finally, it is interesting to note, in Figure 3, that the smallest molecular weight isotactic PMMA (i-PMMA1) exhibits a larger I_N/I_A value than all atactic PMMA's investigated, indicating that the unfavorable PMMA isotacticity effect can be compensated by a decrease of molecular weight.

Qualitatively, the results obtained in the present investigation using the NRET technique are in agreement with the DSC and light scattering observations;[12,13] PVC is miscible with syndiotactic as well as with isotactic PMMA. However, the comparative NRET measurements indicate differences in the extent of random dispersion of PVC chains in blends made with PMMA's of different tacticities and molecular weights, PVC chains being more randomly dispersed in syndiotactic and low molecular weight PMMA than in isotactic and high molecular weight PMMA.

This behavior must be related to the presence of a tacticity and molecular weight dependent lower critical solution temperature (LCST) in these mixtures. In a recent study, Lemieux et al.[12] pointed out to a difference of about 65° between the LCST of PVC/i-PMMA blends and PVC/s-PMMA blends, the former being found at about 100 °C and the latter at 165 °C. Similarly, the influence of molecular weight on the phase diagram of polymer blends were predicted theoretically[18] and observed experimentally in several systems, such as chlorinated polyethylene/PMMA,[19] polystyrene/poly(vinyl methyl ether),[20] and PVC/PMMA.[13] Generally, a decrease of the molecular weight of one component, the molecular weight of the second one being kept constant, leads to an increase of the LCST, resulting from the favorable combinatorial entropy contribution, and favoring miscibility.

The difference in LCST observed with PVC/PMMA blends as a function of the tacticity of PMMA can be ascribed both to the "chemical" difference between i-PMMA and s-PMMA and to the free volume differences between PVC and i-PMMA and PVC and s-PMMA. According to the equation-of-state theory, the thermodynamic interaction parameter χ between two polymers is the sum of three contributions: an entropic (χ_s), an enthalpic or interactional (χ_H), and a free volume (χ_v) contribution with

$$\chi = \chi_s + \chi_H + \chi_v \qquad (3)$$

On the one hand, i-PMMA has been shown to be more flexible than s-PMMA.[21-23] Assuming that the miscibility of PMMA with a chlorinated polymer depends primarily on the specific interactions[11] between the two sorts of chains, it can be postulated that these interactions are stronger or more numerous with s-PMMA than with i-PMMA[24] since i-PMMA is found in a 10/1 helical chain conformation with a repeat distance of 2.11 nm whereas s-PMMA is in an all-trans conformation, in agreement with the observation of a weaker molar cohesion and closer packing of i-PMMA. This involves a more favorable interactional contribution, i.e. a more negative χ_H value with s-PMMA than with i-PMMA.

On the other hand, the free volume contribution can be expressed by

$$\chi_v = (C_p/2R)\tau^2 \qquad (4)$$

where C_p is the heat capacity of the system, R the gas constant, and τ the free volume difference between PMMA and PVC, which is given by

$$\tau = 1 - (T_1^*/T_2^*) \qquad (5)$$

where T_i^* is the characteristic temperature of polymer i. From the literature,[12,13,35] it is known that τ is equal to 0.066 and 0.116 with s-PMMA and i-PMMA, respectively, meaning a smaller positive χ_v with s-PMMA. Therefore, a larger favorable interactional contribution and a smaller unfavorable free volume effect in the PVC/s-PMMA mixture relative to the PVC/i-PMMA mixture (χ_s is assumed to be constant, and probably negligible, in both cases) lead to a larger LCST of the former.

The differences of miscibility observed in the present study can be related to tacticity and molecular weight dependent LCST's. We have to keep in mind that all PVC/PMMA blends were prepared from solution with a very slow rate of evaporation of the solvent at room temperature for 2 days and then an annealing period of 2 days at 60 °C. We suggest that differences of miscibility were induced during the removal of the solvent, when the T_g of the mixture was below the annealing temperature, i.e. before freezing in the mixture below its T_g. Indeed, as illustrated in Figure 4, at 60 °C, the mixture is at about 40 °C from its LCST with i-PMMA but at about 100 °C from its LCST with s-PMMA. Similarly, it is known[13] that the LCST decreases, for a given mixture, with an increase of molecular weight. This means that, at 60 °C, a PVC/PMMA mixture is closer to its LCST if the molecular weight and isotactic content of PMMA is high.

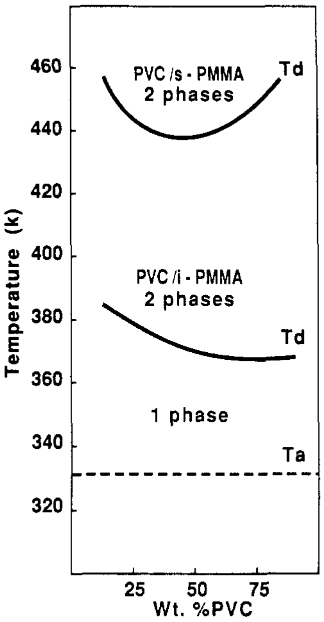

Figure 4. Phase diagrams of PVC/i-PMMA and PVC/s-PMMA blends, drawn from ref 11. T_d is the temperature of phase separation and T_a the annealing temperature.

More precisely, when the PVC/PMMA mixtures were placed at 60 °C, a large amount of solvent (>20%) remained during a certain period of time and made their T_g's below 60 °C. Assuming that the presence of solvent reduces the LCST's of the different PVC/PMMA mixtures with the same magnitude, which was found to be the case for poly(styrene-*co*-acrylonitrile)/PMMA mixture with two different molecular weights of PMMA in the presence of up to about 50% dimethyl phthalate,[26] as mentioned above, mixtures with high molecular weights and high isotactic contents of PMMA were, at 60 °C, closer to their LCST than those mixtures with low molecular weights and high syndiotactic contents of PMMA. Taking this factor into account, two possible interpretations can be considered.

First, let us consider the thermodynamic interaction parameter χ which is known to vary, as a function of temperature, as

$$\chi = A + B/T \qquad (6)$$

where A and B are two constants. Assuming the same variation of χ with temperature for PVC/i-PMMA and PVC/s-PMMA, a χ value much closer to the critical χ value (χ_c) is found with PVC/i-PMMA blends than with PVC/s-PMMA blends; in other words, at 60 °C, χ is larger in PVC/i-PMMA blends than in PVC/s-PMMA blends, meaning that the former system is less miscible than the latter.

Secondly, from another point of view, it has been shown that thermal (and periodic) concentration fluctuations are present in polymer liquid–liquid mixtures.[27,28] These fluctuations are characterized by a wavenumber $q(t)$ and a wavelength $\Lambda(t)$ (both depend upon time t). They are present in the liquid–liquid mixtures in the disordered state and lead to phase separation at high temperatures when the q modes, those below a certain characteristic wavenumber q_c, have the thermodynamic potential to grow; below the LCST, they are also present but do not grow. Their decay rate is much larger than their growth rate.

It has been theoretically predicted[28] and experimentally observed[28,29] that the magnitude of these fluctuations increases when the temperature approaches the LCST, i.e. with an increase of the χ value. Moreover, the wavenumber q also depends upon temperature. This dependence is given by[27]

$$q(T) \sim (T_d - T) \qquad (7)$$

where T_d is the spinodal temperature. This means that the thermal fluctuations increase when getting close to T_d. This phenomenon implies larger fluctuations for a system which is close to T_d, like the PVC/i-PMMA blend, as compared to a system which is far from T_d, like the PVC/s-PMMA blend. This could explain some nonrandomness in the dispersion of i-PMMA with PVC which is not seen in the dispersion of s-PMMA with PVC. With i-PMMA (close to T_d), thermal fluctuations are characterized by a smaller wavenumber and decay rate but larger correlation length and relaxation time. This involves less random dispersion at the molecular level and a somewhat smaller degree of miscibility, as seen in Figure 3.

It is then seen that both approaches (the variation of χ with temperature and the theory of thermal fluctuations) lead to the conclusion that the PVC/s-PMMA system, which is far from its LCST, is more miscible than the PVC/i-PMMA, which is close to its LCST. Similar arguments can be drawn for two PVC/PMMA blends where the tacticity of PMMA is kept constant but its molecular weight varied.

Finally, the influence of the solvent used in the preparation of the samples upon the miscibility of blends as a function of tacticity has been ignored. However, it has been shown, by Chen and Morawetz,[30] through NRET measurements, that a preferential solvation of one component of the polymer blend by the casting solvent reduces the level of miscibility reached. Therefore, if stronger interactions exist between butanone and one specific PMMA, this effect could contribute to increase or decrease somewhat the differences observed herein.

Measurements of Fluorescence Depolarization Resulting from the Nonradiative Energy Transfer. The nonradiative energy transfer from the naphthyl label to the anthryl label can result in fluorescence depolarization. An excitation with polarized light results in the emission of fluorescence which is also polarized due to the photoselection of the chromophores according to their orientation relative to the direction of the polarized excitation. Generally, the rotational diffusion of the chromophores and the nonradiative energy transfer between the chromophores are the primary causes of fluorescence depolarization.[17]

In the present study, the samples containing the naphthyl and anthryl labels were excited at 288 nm. At this wavelength, the naphthyl chromophore is excited to its second singlet state, assigned to be ^1L_a,[31] and the anthryl chromophore to its first singlet state which is also ^1L_a because its second excited state (^1L_b) is not observed at excitation wavelengths between 255 and 386 nm.[32] Then, before the energy transfer, the excited naphthyl molecules relaxe rapidly to their lowest singlet state, ^1L_b, which direction of dipole oscillation is perpendicular to that of ^1L_a. In this case, the excited naphthyl molecules transfer their energy preferably to the anthryl molecules which orientation is perpendicular to that of those molecules excited directly by the polarized excitation light. Hence, the nonradiative energy transfer from the naphthyl label to the anthryl label leads to a randomnization of the emission dipoles of the anthryl molecules, which should induce a fluorescence depolarization of the chromophores.

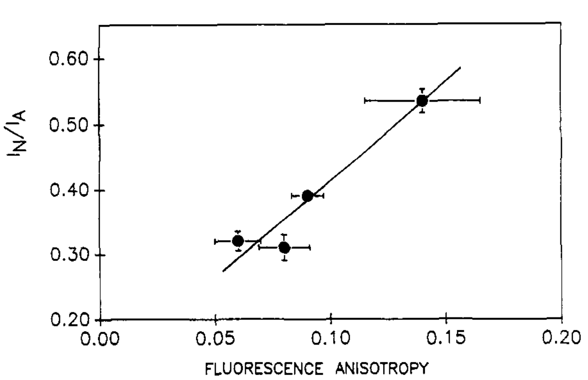

Figure 5. I_N/I_A values of PVC/a-PMMA blends of 50/50 ratios as a function of the fluorescence anisotropy of the anthryl label.

An investigation of fluorescence depolarization of the anthryl label was performed by measuring the fluorescence anisotropy, r, which is defined as

$$r = (I_{\parallel} - I_{\perp})/(I_{\parallel} + 2I_{\perp}) \qquad (8)$$

where $I_{\parallel}$ and $I_{\perp}$ are the fluorescence intensities with the emission polarizer oriented parallel and perpendicular, respectively, to the direction of the polarized excitation. The measurements were carried out by using the PVC/a-PMMA blends that exhibit (Figure 3) the smallest error bars.

The results are shown in Figure 5. Despite some scatter in the measurements, a decrease of the fluorescence anisotropy of the anthryl label is observed with a decrease of the I_N/I_A ratio, i.e., the larger the magnitude of energy transfer, the smaller the anisotropy. A value of about 0.2 was obtained with a PVC/PVC-A blend prepared under identical conditions, in which there is no energy transfer.

Conclusions

The NRET technique can be used to study the miscibility of polymer blends by labeling fluorescence donor and acceptor molecules to the same polymer component (but to different chains) instead of attaching the donor to one polymer and the acceptor to the other polymer as is usually done. Under suitable conditions of blend composition and concentration of chromophores, the I_N/I_A ratio is sensitive to the extent of random dispersion of the chains; an increase of the extent of random dispersion, corresponding to an increase of blend miscibility, leads to a decrease of the energy transfer efficiency. Please note that in a previous paper,[10] the donor and acceptor were attached to the different polymers present in the blend, which led to an increase in the efficiency of energy transfer with blend miscibility, contrary to the situation found in the present article.

With PVC/PMMA blends, using PMMA's of different molecular weights and tacticities, prepared in the single-phase regime, comparative measurements of the efficiency of energy transfer lead to the observation of differences of miscibility at a molecular level, which cannot

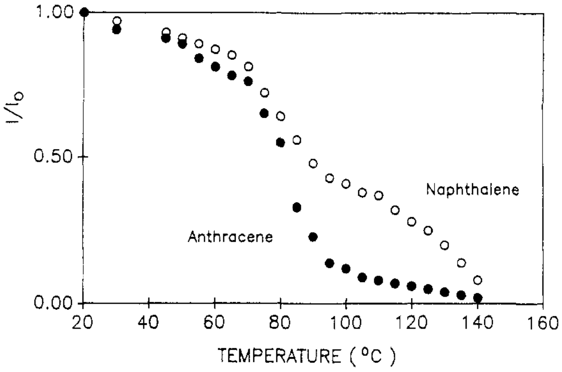

Figure 6. Temperature dependence of the fluorescence quenching of naphthyl and anthryl labels in PVC. I_0 and I are the fluorescence intensities measured at room temperature and temperature T, respectively.

be detected by DSC. An increase of the molecular weight or isotactic content of PMMA results in more nonrandom dispersion of the PVC chains. This behavior was related to the LCST observed with PVC/PMMA blends, which depends on both the molecular weight and tacticity of PMMA. Therefore, in agreement with expectations, the NRET technique is more sensitive to small differences of miscibility at the molecular level than DSC because of differences in the scales of observation: 10–15 nm by DSC[33,34] and about 3 nm by NRET.[4,5,10]

With an excitation wavelength of 288 nm, the nonradiative energy transfer from the naphthyl label to the anthryl label results in fluorescence depolarization for the anthryl chromophore. A correlation was found between the fluorescence anisotropy of the anthryl label and the efficiency of energy transfer as given by the emission intensity ratio I_N/I_A.

Finally, it is worth while to mention that all attempts made so far to determine temperatures of phase separation by NRET measurements have failed. As has been pointed out previously,[10] the chlorine atoms in PVC are an important source of fluorescence quenching, which is highly temperature dependent. An example showing such a fluorescence quenching is given in Figure 6, with a PVC/PVC-A/PVC-N blend examined under continuous illumination. In this figure, the fluorescence intensities of the naphthyl and anthryl labels, normalized to the values measured at room temperature, are plotted as a function of the temperature of measurement, at a heating rate of about 3 °C/min. It can be seen that the fluorescence intensities of both naphthyl and anthryl chromophores drop between 70 and 100 °C, which corresponds to the glass transition of PVC. It seems that the fluorescence quenching, under continuous illumination, is considerably enhanced by the chain mobility of PVC. Work is now in progress to solve these problems.

Acknowledgment. We thank Dr. Pierre C. Roberge (Laval Unversity) and Dr. Takeji Hashimoto (Kyoto University) for useful discussions. We also thank Dr. R. Jérôme (University of Liège) for providing some of the PMMA samples and Dr. Pierre de Grandpré (Laval University) for the use of the spectrofluorometer. We finally thank the National Sciences and Engineering Research Council of Canada and the Department of Education of the Province of Quebec (FCAR program) for supporting this study.

References and Notes

(1) Morawetz, H.; Wang, Y. *Macromolecules* **1988**, *21*, 107.
(2) Torkelson, J. M.; Gilbert, S. R. *Macromolecules* **1987**, *20*, 1860.
(3) Winnik, M. A. *Polym. Eng. Sci.* **1984**, *24*, 87.
(4) Amrani, F.; Hung, J. M.; Morawetz, H. *Macromolecules* **1980**, *13*, 649.
(5) Albert, B.; Jérôme, R.; Teyssié, P.; Smyth, G.; Boyle, N. G.; McBrierty, V. J. *Macromolecules* **1985**, *18*, 388.
(6) Major, M. D.; Torkelson, J. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, *29*, 444.
(7) Morawetz, H. *Science* **1988**, *240*, 172.
(8) Mikes, F.; Morawetz, H.; Dennis, K. S. *Macromolecules* **1980**, *13*, 969.
(9) Mikes, F.; Morawetz, H.; Dennis, K. S. *Macromolecules* **1984**, *17*, 60.
(10) Zhao, Y.; Lévesque, J.; Roberge, P. C.; Prud'homme, R. E. *J. Polym. Sci., Polym. Phys. Ed.* **1989**, *27*, 1955.
(11) Tremblay, C.; Prud'homme, R. E. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 1857.
(12) Lemieux, E.; Prud'homme, R. E.; Forte, R.; Jérôme, R.; Teyssié, P. *Macromolecules* **1988**, *21*, 2148.
(13) Vorenkamp, E. J.; ten Brinke, G.; Meijer, J. G.; Jager, H.; Challa, G. *Polymer* **1985**, *26*, 1725.
(14) Varnell, D. V.; Moskala, E. J.; Painter, P. C.; Coleman, M. M. *Polym. Eng. Sci.* **1983**, *23*, 658.
(15) Liu, C. Y.; Morawetz, H. *Macromolecules* **1988**, *21*, 515.
(16) Forte, R. D.Sc. Thesis, Université de Liège (Belgique), 1987.
(17) Lakowicz, J. R. In *Principles of Fluorescence Spectroscopy*; Plenum Press: New York, 1983; Chapter 5.
(18) McMaster, L. P. *Macromolecules* **1973**, *6*, 760.
(19) Zhikuan, C.; Ruona, S.; Walsh, D. J.; Higgins, J. S. *Polymer* **1983**, *24*, 263.
(20) Ubrich, J. M.; Ben Cheikh Larbi, F.; Halary, J. L.; Monnerie, L.; Bauer, B. J.; Han, C. C. *Macromolecules* **1986**, *19*, 810.
(21) Bywater, S.; Toporowsky, P. M. *Polymer* **1972**, *13*, 94.
(22) Brownstein, S.; Wiles, D. M. *Can. J. Chem.* **1966**, *44*, 153.
(23) Pohl, H. A.; Zabusky, H. H. *J. Phys. Chem.* **1962**, *66*, 1390.
(24) Quach, A.; Wilson, P. S.; Simha, R. *J. Macromol. Sci., Phys.* **1974**, *B9*, 533.
(25) Lemieux, E. Ph.D. Thesis, Laval University, 1988.
(26) Bernstein, R. E.; Cruz, C. A.; Paul, D. R.; Barlow, J. W. *Macromolecules* **1977**, *10*, 681.
(27) Hashimoto, T.; Kumaki, J.; Kawai, H. *Macromolecules* **1983**, *16*, 641.
(28) Mori, K.; Tanaka, H.; Hashimoto, T. *Macromolecules* **1987**, *20*, 381.
(29) Mori, K.; Hasegawa, H.; Hashimoto, T. *Polym. J.* **1985**, *17*, 799.
(30) Chen, C. T.; Morawetz, H. *Macromolecules* **1989**, *22*, 159.
(31) ^1L_a and ^1L_b are the singlet states corresponding to weak dipole oscillations with polarizations perpendicular and parallel to the molecular axis, respectively.
(32) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: New York, 1970.
(33) Fried, J. R.; Karasz, F. E.; MacKnight, W. J. In *Polymer Blends*; Paul, D. R., Newman, S., Eds.; Academic Press: New York, 1978.
(34) Kaplan, D. S. *J. Appl. Polym. Sci.* **1976**, *20*, 2616.