

NOTE

폴리스티렌 및 폴리(α -메틸스티렌)과 폴리(비닐메틸에테르)
블렌드의 상용성에 대한 비복사성에너지이동에 의한
형광분광학적 연구

하 창 식[†] · 손 현 희 · 조 원 제

부산대학교 고분자공학과

(1993년 7월 1일 접수)

Fluorescence Spectroscopic Studies on the Miscibility
of Polystyrene or Poly(α -methyl styrene) with Poly(vinyl methyl ether)
by Nonradiative Energy Transfer

Chang-Sik Ha[†], Hyun-Hee Son, and Won-Jei Cho

Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea

(Received July 1, 1993)

INTRODUCTION

Fluorescence spectroscopy has been recently recognized as one of the new and sensitive techniques to study the miscibility of polymer blends. Two main methods have been utilized for the fluorescence spectroscopic investigation on the miscibility: viz, excimer fluorescence and nonradiative energy transfer(NRET) techniques.¹

The first method is generally employed for blends in which one of the polymers contains aromatic rings and exhibits an intrinsic fluorescence.

The second method can be used to characterize the compatibility of polymer blends by labeling the first polymer with fluorescence residue-donor-whose emission spectrum overlapped the absorption spectrum of another fluorescent moiety-acceptor-attached to the second polymeric species.^{2,3} Energy absorbed by the donor can then be transferred by a nonradiative process to the acceptor over distances of the order of 2 nm so that the relative donor and acceptor emission intensity of a

sample irradiated in the donor absorption band is dependent on the mutual interpenetration of two polymeric species.

In general terms, it is useful to describe two labeling pathways that can be followed. The first one involves a free radical polymerization with a comonomer carrying the desired fluorescence label.³ The second pathway of labeling involves a reaction between a preformed polymer and a fluorescent compound. In this brief article, we report on the effect of different donor and acceptor labels on the fluorescence intensity ratio in the blends of poly(vinyl methyl ether) (PVME) with polystyrene (PS) or poly(α -methyl styrene)(PMS). For this work, the labeling of different chromophores was performed by first introducing a reactive chloromethyl group to PS, PMS, or PVME and then by reacting the chloromethylated polymers with potassium carbazole and (9-anthryl)methanol. To our knowledge the work presented here describes the first use of NRET technique to determine the miscibility of PVME with PS or PMS, even though the

excimer fluorescence technique has been extensively used to investigate the miscibility of the PS/PVME as well as PS/P(2-vinylnaphthalene) blend systems by Frank and his coworkers.⁴⁻⁶

EXPERIMENTAL

Materials. Styrene (Junsei Chemical) was washed with 10% aqueous solution of NaOH to remove inhibitor, followed by washing with distilled water until it became neutral. After drying with CaCl_2 for 2 days, it was purified by distillation. Azobisisobutyronitrile (AIBN) (Yakuri Pure Chemical) and benzoyl peroxide (BPO; Hayashi Chemical) were purified by recrystallization from ethanol and methanol, respectively. Insoluble part of the saturated ethanol solution of AIBN at 50°C was filtered off. Purified AIBN was obtained by lowering the temperature of the solution to 5°C. Poly(vinyl methyl ether) (PVME) (Scientific Polymer Products) was reprecipitated at toluene and n-heptane and dried in vacuum before use. Poly(α -methylstyrene) (PMS) (Aldrich) was reprecipitated at toluene and methanol and dried in vacuum to a constant weight.

Polystyrene (PS) was prepared at 60°C for 4 hrs in toluene using 1 wt% of AIBN in a glass ampoule charged with nitrogen. Purification was accomplished by reprecipitation in methanol from its toluene solution followed by drying in a vacuum oven to a constant weight. Molecular weights of polymers were measured by GPC (Waters 244) using THF as an effluent. The characteristics of the polymers used in this study are summarized in Table 1.

Attachment of Fluorescent Labels. PS and PMS were chloromethylated with 1 wt% of ZnCl_2 in a 10 wt% chloromethyl ethyl ether solution at room temperature by the same method as described by Jones.⁷ Chloromethylated PS of chlorine contents of $10.72\% \pm 0.5$ and chloromethylated PMS of chlorine contents of $10.67\% \pm 0.5$ were obtained in this way. To ensure complete removal of the ZnCl_2 , the chloromethylated polymers were dissol-

Table 1. Characteristics of the Polymers used in This Work

Polymers	M_n	M_w	M_w/M_n^{a1}	Source
PS	29,300	43,950	1.50	Synthesized
PMS	39,760	52,090	1.31	Aldrich
PVME	64,190	154,700	2.41	Scientific Polymer Product

^{a1} From GPC

ved in dioxane and reprecipitated in water.

PVME was chloromethylated with 1 wt% of BPO in a 10 wt% chloromethyl ethyl ether/dichloromethane (1/2 v/v.) solution at 80°C under nitrogen atmosphere. After 2 hrs, purification of the chloromethylated PVME was carried out by reprecipitation in ether five times.

Carbazole-labeled PS and PMS were prepared by condensing the chloromethylated PS and PMS with potassium carbazole by the same method as described by Gibson and Bailey.⁸ The polymers were dissolved and reprecipitated five times with intermittent washing by the precipitants until the absorption peak stopped decreasing due to carbazole in the 270~320 nm range on UV spectra.

To obtain anthracene-labeled PS and PMS, the chloromethylated polymers were treated with (9-anthryl)methanol and sodium hydride by the procedure used for the benzylation of carbohydrates.⁹ This method is based on the observation¹⁰ that benzyl chloride does not react with sodium hydride below 170°C.

The carbazole-labeled PVME and the anthracene-labeled PVME were prepared from the chloromethylated PVME by the similar methods as described for PS and PMS. The chloromethylation of PVME was carried out according to the work of Mikes, et al.,¹¹ assuming that the chloromethylation rate of PVME proceeds at a similar relative rate as in PS or PMS.

Sample Preparation and Fluorescence Measurement. Blend films were cast from tetrahydrofuran solutions (5 wt%) of PS and PVME or PMS and PVME mixtures having various different compositions. Labeled polymers were diluted with unlabeled

Fluorescence Spectroscopic Studies on the Miscibility of Polystyrene or Poly(α -methyl styrene) with Poly(vinyl methyl ether) by Nonradiative Energy Transfer

led polymers so as to reach a concentration of 12 mM of the carbazole and anthracene chromophore. Reflectance fluorescence spectra of films irradiated in the carbazole absorption band at 297 nm were recorded as previously described elsewhere.² The nonradiative energy transfer was characterized by the ratio of the emission intensities of the donor, carbazole, at 365 nm (I_C) and the acceptor, anthracene, at 413 nm (I_A). Fluorescence measurements were carried out with a KONTRON SFM 25 fluorescence spectrophotometer. Fig. 1 illustrates typical fluorescence spectra of PS-C/PVME-A blend having 50/50 composition by weight % as well as PS-C and PVME-A labeled homopolymers.

Light Scattering Measurement. Cloud points of a polymer mixture were measured using a laboratory-made light scattering apparatus.¹² A low-po-

wer He/Ne laser was used as a light source. A photodiode (EG & G HAV-1000 with a sensitivity of 7×10^6 V/W at $R_f = 20$ M Ω for 6328 Å wavelength) was used as a detector. All measurements were performed at a 90° scattering angle with heating and cooling rates of 2°C/min. The temperature at which the turbidity appeared on heating was taken as the cloud point.

RESULTS AND DISCUSSION

Resulting polymers were characterized by their FT-IR and UV spectra. Fig. 2 shows a typical FT-IR spectrum of PS, which exhibited characteristic absorption bands at 3000 cm^{-1} (stretching vibration of =C-H), 1000–650 cm^{-1} (out-of-plane bending of =C-H) and 1660–1600 cm^{-1} (stretching vibration of C=C). The FT-IR spectrum of chloromethylated-PS (PS-CH₂Cl) showed similar characteristic

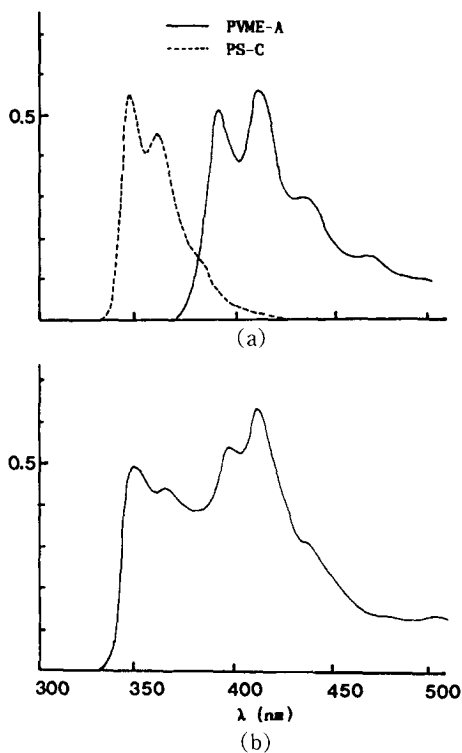


Fig. 1. Typical fluorescence spectra of PS-C, PVME-A labeled homopolymers (a) and PS-C/PVME-A blend having 40/60 composition by weight % (b).

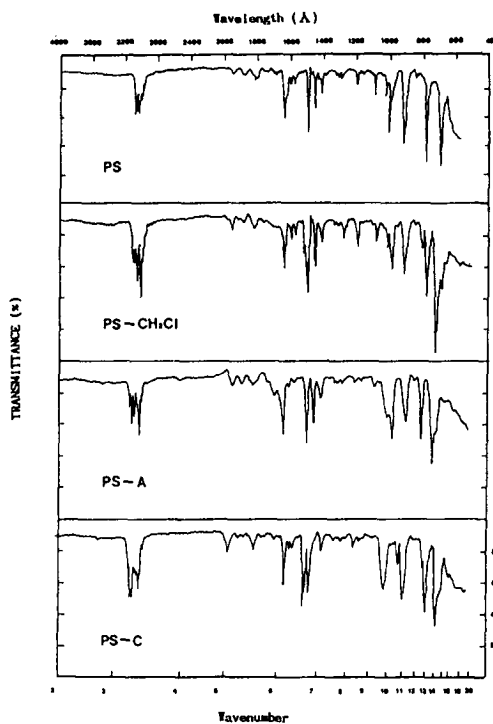


Fig. 2. FT-IR spectra of polystyrene, chloromethylated PS (PS-CH₂Cl), anthracene-labeled PS (PS-A) and carbazole-labeled PS (PS-C).

bands except for the strong characteristic peak of C-Cl exhibited at 680 cm^{-1} . The labeling of anthracene and carbazole on PS was identified by the remarkable decrease in the C-Cl peak at 680 cm^{-1} , which appeared due to the chloromethylation. However, as is expected, the characteristic peaks of anthracene and carbazole were not observed for the anthracene-labeled PS(PS-A) and the carbazole-labeled PS(PS-C). The FT-IR spectrum of chloromethylated-PVME(PVME-CH₂Cl) showed similar peaks as that of PVME, except for the characteristic peak of C-Cl around 800 cm^{-1} . The FT-IR spectra of PVME and PVME-CH₂Cl were illustrated in Fig. 3.

As in the anthracene-labeled PS(PS-A) and the carbazole-labeled PS(PS-C), the characteristic peaks of anthracene and carbazole were not observed for the anthracene-labeled PVME(PVME-A) and the carbazole-labeled PVME(PVME-C). The anthracene-labeled and carbazole-labeled PS were also confirmed by their UV spectra, as shown in Fig. 4. The characteristic peak shape and fine structure were observed around the wavelength ranges of $340\sim 380\text{ nm}$ for the anthracene-labeled PS and around $270\sim 320\text{ nm}$ for the carbazole-labeled PS, respectively. Similarly, the labeling of anthracene and carbazole on PMS and PVME was also characterized by their FT-IR and UV spectra. The

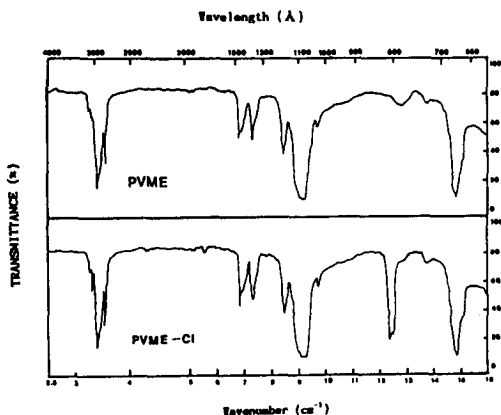


Fig. 3. FT-IR spectra of poly(vinyl methyl ether), chloromethylated PVME(PVME-CH₂Cl).

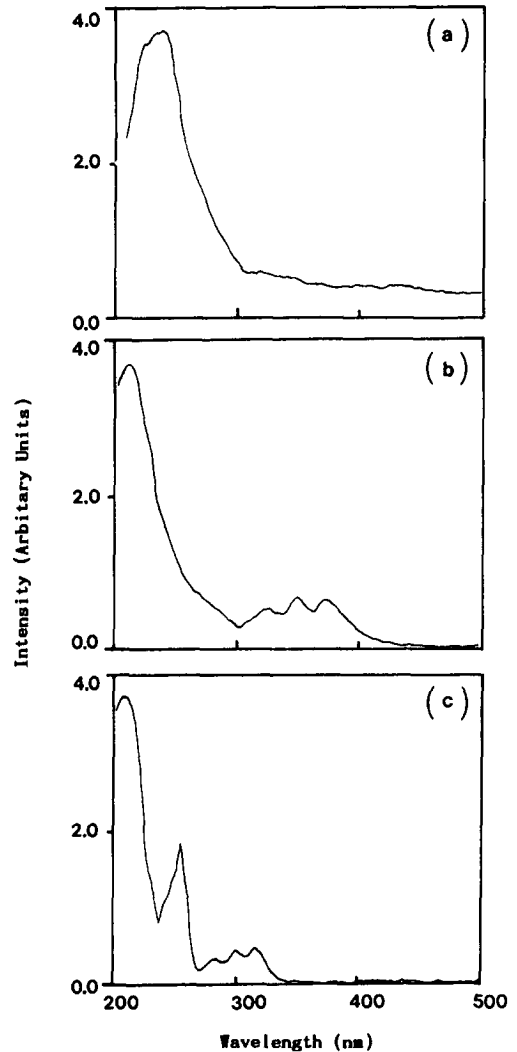


Fig. 4. UV spectra of Polymers (a) PS-CH₂Cl, (b) PS-A, (c) PS-C.

contents of anthracene and carbazole moieties in the labeled polymers were determined by UV spectroscopy and were listed in Table 2. The result summarized in Table 2 indicates that the contents of anthracene and carbazole moieties in the labeled polymers are almost constant and that the miscibility of the unlabeled component polymers are not dependent on the contents of fluorescence moieties in the labeled polymers.

Table 2. The Contents of Carbazole(C) and Anthracene(A) Moieties in Labeled Polymers.

Polymers	mol %
PS-A	1.26
PS-C	1.20
PMS-A	1.23
PMS-C	1.15
PVME-A	1.01
PVME-C	0.98

PS or PMS formed clear films when blended with PVME. From the standpoints of optical clarity, all of the blends cast from tetrahydrofuran showed compatibility over the whole concentration range examined in this study.

The observed cloud points of mixtures of PS and PVME or PMS and PVME are plotted in Fig. 5. The LCST behavior of PS/PVME blends is well known.^{13,14} The specific interaction between PS and PVME, giving rise to their compatibility, was reported to reside on phenyl group of styrene monomer and $-\text{COCH}_3$ group of PVME. It is seen that the mixtures of PVME with PMS also exhibit

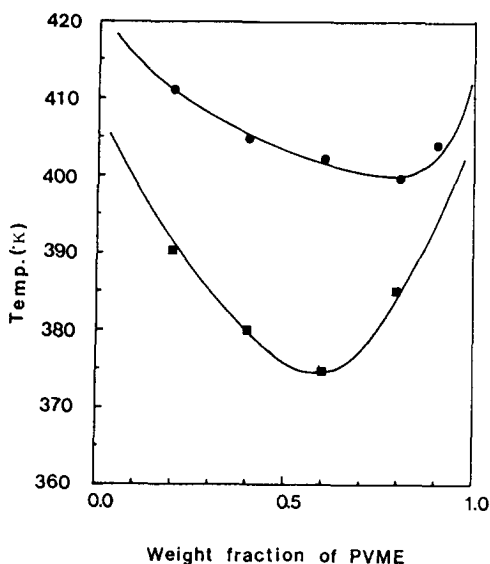


Fig. 5. Cloud points of mixtures containing PVME and one of PS(●) and PMS(■).

LCST behavior and the LCST is observed around the PVME composition of 60 wt%.

The ratios of carbazole and anthracene emission intensities, I_C/I_A , in blends of polystyrene and poly(vinyl methyl ether) are presented in Fig. 6 as a function of the blend compositions.

I_C/I_A increased with increasing PVME compositions in the blends of donor-labeled PS and acceptor-labeled PVME. Zhao and Prud'homme¹ reported that efficient energy transfer occurs when the polymers in binary blends, to which the donor and the acceptor are attached, are randomly dispersed (miscible); in contrast, if a blend is heterogeneous (immiscible), no energy transfer can occur, except for a small amount via the interface. Thus, the result shown in Fig. 6 implies that the mutual interpenetration of the two polymeric species is decreased as PVME composition increases. Therefore, the NRET efficiency is decreased, indicating a decrease in blend miscibility.

It is also seen in Fig. 6 that blends of acceptor-labeled PS and donor-labeled PVME showed same I_C/I_A behavior although the exact I_C/I_A values are slightly different.

Fig. 7 shows plots of I_C/I_A for blends of PMS with PVME. I_C/I_A ratio increased with increasing

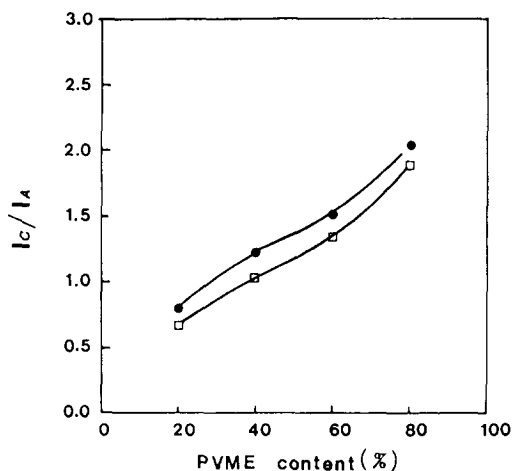


Fig. 6. Fluorescence intensity ratio versus PVME contents in PS/PVME blends containing PS-C/PVME-A(●) and PS-A/PVME-C(□), respectively. C and A stand for carbazole and anthracene.

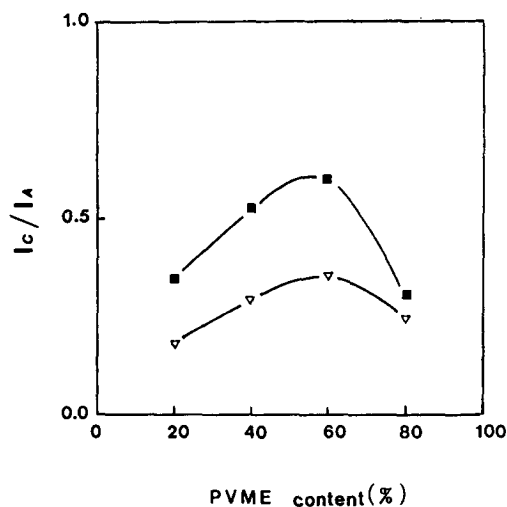


Fig. 7. Fluorescence intensity ratio versus PVME contents in PMS/PVME blends containing PMS-C/PVME-A(■) and PMS-A/PVME-C(▽), respectively. C and A stand for carbazole and anthracene.

PVME composition, but showed a maximum at around 60 wt% of PVME composition. As is in the case of PS/PVME blends, the result implies that the miscibility decreased with increasing PVME composition up to 60 wt%, but increased with further increasing PVME compositions. It is interesting to note that this result was in accord with our previous light scattering results to exhibit the LCST around the blend composition for the PMS/PVME blends, as shown in Fig. 5.

It should be pointed out that the same I_C/I_A behaviors were observed both for the donor-labeled PMS/acceptor-labeled PVME and the acceptor-labeled PMS/donor-labeled PVME system, although the absolute values of their emission intensity ratios are different because of different optical densities and fluorescence quantum yields.

Thus, it is believed that either of the two com-

ponent can be labeled with donor(or acceptor) to investigate the miscibility of PVME and PS or PMS, or other polystyrene analogues by NRET.

A more detailed study on the fluorescence spectral features on the miscibility of the styrene containing copolymers with PVME will be reported in a future publication, based on the present preliminary results.

REFERENCES

1. Y. Zhao and R. E. Prud'homme, *Chemtracts-Macromolecular Chemistry*, JAN/FEB., 1 (1991).
2. F. Amrani, J. M. Hung, and H. Morawetz, *Macromolecules*, **13**, 649 (1980).
3. F. Amrani, J. M. Hung, and H. Morawetz, *Macromolecules*, **13**, 969 (1980).
4. S. N. Semark and C. W. Frank, *Can. J. Chem.*, **63**, 1328 (1985).
5. C. W. Frank and W. C. Zin, In "Photophysics of Polymer"; C. E. Hoyle and J. M. Torkelson Eds., ACS Symp. Ser. 358, ACS, Washington, DC (1987), Chap. 3.
6. R. G. Gelles and C. W. Frank, *Macromolecules*, **16**, 1448 (1983).
7. G. D. Jones, *Ind. Eng. Chem*, **44**, 2686 (1952).
8. H. W. Gibson and F. C. Bailey, *Macromolecules*, **9**, 688 (1976).
9. M. E. Tate and C. T. Bishop, *Can. J. Chem.*, **41**, 1800 (1963).
10. S. J. Cristol, J. W. Ragsdall, and J. S. Meck, *J. Am. Chem. Soc.*, **71**, 1863 (1949).
11. F. Mikes, H. Morawetz, and K. S. Dennis, *Macromolecules*, **13**, 969 (1980).
12. R. J. Roe and W. C. Zin, *Macromolecules*, **13**, 1221 (1980).
13. T. Nishi and T. K. Kwei, *Polymer*, **16**, 285 (1975).
14. A. Robard and D. Patterson, *Macromolecules*, **10**, 1021 (1977).