

스티렌과 1- 및 2-비닐나프탈렌 공중합체와 폴리(비닐메틸에테르) 블렌드의 상용성

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(1992년 1월 6일 접수)

Miscibility of Blends Containing Copolymers of Styrene and 1- or 2-Vinylnaphthalene with Poly(Vinyl Methyl Ether)

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(Received January 6, 1992)

요약 : 스티렌과 1- 및 2-비닐나프탈렌 공중합체와 폴리(비닐메틸에테르) 블렌드의 상용성을 T_g 특성 및 형광 분광 분석법에 의하여 결정하였다. 스티렌과 1- 및 2-비닐나프탈렌 공중합체를 포함하는 공중합체를 라디칼 공중합으로 합성하였다. 이들 블렌드들의 상용성은 공중합체의 조성과 블렌드 조성에 크게 의존하였는데, 블렌드의 상용성은 공중합체내의 스티렌 함량이 증가될수록 그리고, 블렌드에서 PVME 함량이 증가될수록 증가되었다. 결론적으로는 스티렌과 2-비닐나프탈렌 공중합체가 스티렌과 1-비닐나프탈렌공중합체보다 PVME와 나은 상용성을 나타내었다.

Abstract : Miscibility of blends consisting of copolymers of styrene and 1- or 2-vinylnaphthalene [P(S-co-VN)] with poly(vinyl methyl ether) (PVME) were investigated in terms of the fluorescence spectroscopic analysis and the thermal behavior. For this work, the copolymers containing three different compositions were synthesized by radical polymerization. The fluorescence spectra together with the optical clarity and the glass transition temperature behavior of the blends indicated that the miscibility of poly(styrene-co-1-vinylnaphthalene) [P(S-co-1VN)] and poly(styrene-co-2-vinylnaphthalene) [P(S-co-2VN)] with PVME was largely affected by the composition of the copolymers and the blend concentration. The miscibility increased with increasing styrene composition and PVME contents. It was found that the miscibility of P(S-co-2VN) was better than P(S-co-1VN) with PVME.

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INTRODUCTION

Most pairs of polymers having long-chain structure are immiscible in each other because of their small entropy gain in the mixture. However, it has been reported that some polymer blends show unusual miscibility behavior when there is a specific interaction between the component polymers in the mixture. In last two decades, the miscibility of polymer blends has been one of the most important subjects in the polymer science.¹⁻⁹ Among the miscible polymer blends to show specific types of intermolecular interactions are the mixtures of polystyrene(PS) and poly(vinyl methyl ether) (PVME).¹⁰⁻¹⁸

Recently the blends of polystyrene(PS) and poly(vinyl methyl ether)(PVME) have attracted much interest because of their miscibility over a wide range of blend concentration, even though the miscibility of the two polymer blends was affected by several factors including solvent, temperature, molecular weight, and concentration. The miscibility of PVME with styrenic copolymers has been also extensively investigated; These literatures^{19,20} show that the miscibility and phase separation behavior are very dependent on the chemical nature of comonomer.

The blends of PVME with poly(1-vinylnaphthalene) or poly(2-vinylnaphthalene) were found to be immiscible over the whole concentration range of poly(vinylnaphthalene)s when cast from benzene, whereas PS was miscible with PVME over a wide range of concentrations in the same solvent.^{21,22} This is of interest because the results indicate that the molecular interactions of poly(vinylnaphthalene)s(PVN) and PS on PVME are significantly different despite of the similar molecular structure of PS and PVN.

In this work, we synthesized the copolymers of styrene and 1-vinylnaphthalene or 2-vinylnaphthalene [P(S-co-1VN) or P(S-co-2VN)] of three different compositions by radical polymerization. The blends of PVME and those copolymers were prepared by casting from benzene.

The miscibility of P(S-co-1VN)/PVME and P(S-co-2VN)/PVME blends were analyzed by the fluorescence spectroscopy together with conventional optical clarity and the glass transition temperature behavior of these blends.

EXPERIMENTAL

Materials

Styrene(Junsei Chemical) was washed with 10 % aqueous solution of NaOH to remove inhibitor and followed by washing with distilled water until it became neutral. After drying with CaCl₂ for two days, it was purified by distillation. Azobisisobutyronitrile (AIBN) (Yakuri Pure Chemical) was purified by recrystallization from ethanol. 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. 1-Vinylnaphthalene(1VN) monomer was synthesized by dehydration of 1-naphthyl ethanol(Aldrich Chemical); 25g of 1-naphthyl ethanol with 1 g of potassium hydroxide and 0.3 g of sulfur in 50 ml distillation flask was dehydrated and the product 1VN was distilled at 81°C under 0.4 mmHg. It had a 63% yield of 1-naphthyl ethanol. 2-Vinylnaphthalene(2VN) (Aldrich Chemical) was purified by the same procedure as AIBN. Poly(vinyl methyl ether) (PVME) (Scientific Polymer Products) was reprecipitated twice from toluene into n-haptane and dried in vacuum before use. Toluene(Junsei Chemical) was fractionally distilled after refluxing with P₂O₅ for 5 days.

Syntheses of Polymers and Copolymers

PS, P1VN and P2VN were prepared in the polymerization tubes putting a 4.4 mol styrene solution and a 3.0 mol 1VN or 2VN solution of toluene, respectively, with 1.0 wt.% AIBN of monomers. The tubes were sealed after charging with nitrogen gas and polymerization was carried out at 70°C for 72 hr. Three kinds of P(S-co-VN) were synthesized at the weight ratios (styrene/vinylnaphthalene (VN) of 85/15, 60/40, and 30/70 in monomer feed by the same method as that of PS, P1VN or P2VN

homopolymer. Purification of the polymers was accomplished by reprecipitation in methanol from their toluene solutions and then drying in a vacuum oven until kept at a constant weight. The characteristics of the polymers synthesized are given in Tables 1, 2 and 3.

Preparation of Blends

The films of P(S-co-VN)/PVME blends with various concentrations were prepared by casting from 3% (by weight) solutions in benzene. The films were dried slowly in a Petri dish at room temperature and then kept under a vacuum until they reached constant weight. The films were used for the optical clarity test and the thermal analysis. For the fluorescence analyses, films were prepared separately.

Copolymer Composition

The copolymer composition was analyzed using UV spectrophotometer (UVIKON 860) with 1.0 cm quartz cell. All measurements were made using polymer solution dissolved in chloroform. Attention was especially given to the exact weighing of polymers and preventing the evaporation of solvent. The absorbances of the mixtures of PS and P1VN were recorded at 288 nm, and the mixtures of PS and P2VN solutions were recorded at 278 nm in order to calibrate the absorbance to the concentration of poly(vinylnaphthalene). The absorbances of copolymers for analysis were then measured.

Molecular Weight

The molecular weights of PS, P1VN, P2VN, P(S-co-1VN) and P(S-co-2VN) were determined by gel permeation chromatography (GPC) (Waters, Water 244) with Ultrastyrigel 500 Å-linear-columns. The measurement was conducted in THF at 28°C. The apparatus was calibrated with PS standards.

Thermal Analysis

Glass transition temperatures(Tg's) were measured from a differential scanning calorimetry (Perkin-Elmer DSC-7500) calibrated with pure indium as standard. The polymer samples synthesized and the blend films were weighed and pressed into aluminum pan. In order to avoid the ther-

mal history from the samples packed in the aluminum pan and to eliminate any small traces of solvent, samples were heated to 443 K at the heating rate of 40°C/min, maintained at 443 K for 5 min, and then quenched at the rate of 80°C/min to 203 K. For measurements, samples were heated again at the heating rate of 10°C/min. All the reported glass transition temperatures (Tg's) were recorded at the half-height of the heat capacity jump.

Fluorescence Spectroscopy

Fluorescence spectra were obtained using a KONTRON SFM25 spectrophotometer. The thin films of polymers were prepared by casting from 5 wt.% toluene solution onto slide glasses at room temperature. The films were then dried under vacuum at 55°C for at least 72hrs to ensure removal of the castig solvent. No evidence of residual solvent was found from the fluorescence spectra of neat PVME films prepared under identical conditions.

The sample was excited at 290nm in a front-face arrangement to minimize self-absorption. Simple fluorescence intensities were measured at 313 nm (monomer) and 370 nm(excimer), where there was no overlap of excimer and monomer bands.

RESULTS AND DISCUSSION

Analysis of Copolymer Composition

The spectra of PS, P1VN and P2VN in chloroform are shown in Figure 1. The characteristic wavelength 278 nm or 288 nm were selected for composition analysis because PS scarcely absorbs the light of the wavelength. Then, the calibration curve can be obtained from the absorbances of the solution mixtures of PS/P1VN, and PS/P2VN with given weight fractions at 288 nm, and 278 nm, respectively. Figure 2 shows the results, exhibiting that the absorbance of the mixtures of PS/P1VN and PS/P2VN are directly proportional to the weight fraction of Poly(vinylnaphthalene)s. From the specific extinction coefficients of PS/P1VN at 288 nm, and PS/P2VN at 278 nm, respectively. Equation 1 and 2 were obtained :

Table 1. Extinction Coefficient and Styrene wt.% in the Poly(Styrene-co-1-Vinylnaphthalene) Copolymers

Sample ^{a)}	Wt% of styrene in feed	Ext. Coefficient at 288 nm (g/l) ^{b)}	Wt% of styrene in copolymer
PS	100	0.35	100
P(S76-co-1VN24)	85	9.31	76
P(S47-co-1VN53)	60	19.73	47
P(S20-co-1VN80)	30	29.70	20
P1VN	0	37.03	0

^{a)} The samples were named according to copolymer composition analyzed by UV.

^{b)} Extinction coefficient is defined as the absorbance divided by concentration

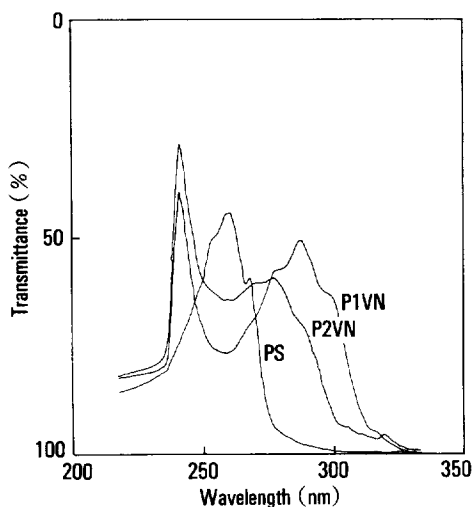


Fig. 1. UV spectra of PS(40mg/100ml), P1VN(4mg/100ml) and P2VN(4mg/100ml) in chloroform.

$$E_{co}^* = 37.03X_1 + 0.35(1 - X_1) \quad (1)$$

$$E_{co}^* = 30.37X_2 + 0.69(1 - X_2) \quad (2)$$

where X_1 is the weight fraction of 1VN in the copolymers and X_2 is the weight fraction of 2VN in the copolymers, E_{co}^* is the specific extinction coefficient of the copolymers. The compositions of the copolymers were calculated from eq.1 or 2 using the specific extinction coefficient of each copolymer and were listed in Tables 1 and 2.

Table 2. Extinction Coefficient and Styrene wt.% in the Poly(Styrene-co-2-Vinylnaphthalene) Copolymers

Sample ^{a)}	Wt% of styrene in feed	Ext. Coefficient at 278 nm (g/l) ^{b)}	Wt% of styrene in copolymer
PS	100	0.69	100
P(S84-co-2VN16)	85	5.38	84
P(S51-co-2VN49)	60	15.23	51
P(S21-co-2VN79)	30	24.25	21
P2VN	0	30.37	0

^{a)} The samples were named according to copolymer composition analyzed by UV.

^{b)} Extinction coefficient is defined as the absorbance divided by concentration

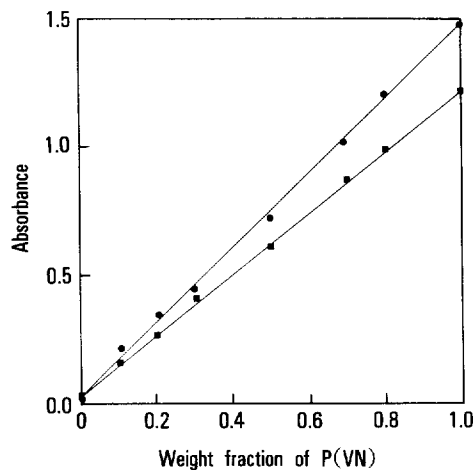


Fig. 2. Calibration curve for the composition analysis of copolymer : Absorbance is obtained from mixtures of PS/P1VN(●) at 288nm and PS/P2VN(■) at 278 nm.

Molecular Weight of Polymers

The molecular weights of the copolymers, PS, P1VN, P2VN and PVME are listed in Table 3. The molecular weights of the polymers synthesized were below 20,000.

Optical Clarity and T_g Behavior

The optical clarity and the T_g 's of the P(S-co-1VN)/PVME blends and P(S-co-2VN)/PVME blends are summarized in Tables 4 and 5. In these tables, the criterion for miscibility is the existence

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Table 3. Characteristics of Polymers Used in the Study

Sample	Wt% of in feed	styrene in copolymer ^{a)}	M_n	M_w	M_w/M_n ^{b)}	Source
PS	100	100	13,100	17,200	1.31	synthesized ^{c)}
PVME	0	—	46,500	99,000	2.13	Scientific Polym. Prod.
P(S76-co-1VN24)	85	76	7,300	18,900	2.59	synthesized
P(S47-co-1VN53)	60	47	8,500	19,500	2.29	synthesized
P(S20-co-1VN80)	30	20	5,800	15,400	2.66	synthesized
PIVN	0	0	5,100	14,600	2.86	synthesized
P(S84-co-2VN16)	85	84	6,700	18,800	2.81	synthesized
P(S51-co-2VN49)	60	51	5,300	11,500	2.17	synthesized
P(S21-co-2VN79)	30	21	5,300	13,100	2.47	synthesized
P2VN	0	0	3,650	12,250	3.36	synthesized

^{a)} analyzed by UV.

^{b)} GPC

^{c)} synthesized by the radical polymerization

Table 4. Miscibility Based on the Optical Clarity and the Glass Transition Temperature for the P(S-co-1VN)/PVME Blends

Copolymer	Wt% of copolymer in the Blends	Optical clarity	T_g (°C)	Miscibility
P(S76-co-1VN24)	15	Clear	-17	M
	25	Clear	-15	M
	35	Clear	-12	M
	50	Clear	-10	M
	65	Clear	-17, 120	IM
	75	Clear	-16, 120	IM
	85	Clear	-16, 120	IM
P(S47-co-1VN53)	15	Clear	-17	M
	25	Clear	-15	M
	35	Clear	-13	M
	50	Clear	-12	M
	65	Trans ^{a)}	-17, 132	IM
	75	Hazy	-18, 132	IM
	85	Trans ^{a)}	-16, 90	IM
P(S20-co-1VN80)	15	Clear	-17	M
	25	Clear	-16	M
	35	Hazy	-15, 149	IM
	50	Hazy	-16, 149	IM
	65	Hazy	-16, 150	IM
	75	Hazy	-16, 150	IM
	85	Trans ^{a)}	-17, 115	IM

^{a)} Translucent

Table 5. Miscibility Based on the Optical Clarity and the Glass Transition Temperature for the P(S-co-2VN)/PVME Blends

Copolymer	Wt% of copolymer in the Blends	Optical clarity	T _g (°C)	Miscibility
P(S84-co-2VN16)	15	Clear	-24	M
	25	Clear	-24	M
	35	Clear	-23	M
	50	Clear	-19	M
	65	Clear	-15	M
	75	Clear	-10	M
	85	Clear	-9	M
P(S51-co-2VN49)	15	Clear	-24	M
	25	Clear	-24	M
	35	Clear	-22	M
	50	Clear	-21	M
	65	Clear	-19	M
	75	Clear	-16	M
	85	Clear	-12	M
P(S21-co-2VN79)	15	Clear	-24	M
	25	Clear	-24	M
	35	Clear	-23	M
	50	Trans ^{a)}	-22, 122	IM
	65	Hazy	-19, 122	IM
	75	Hazy	-19, 123	IM
	85	Hazy	-18, 120	IM

^{a)} Translucent

of a single T_g on DSC thermogram as well as optical clarity of the blend films. For instance, the P(S76-co-1VN24)/PVME blends are observed to be miscible only up to 50 wt.% of the copolymer concentration, even though the blends are observed to be optically clear(at a room temperature) over all the composition ranges examined in the study. In order to interpret accurately the results of different optical clarity and glass transition temperature behaviors, more thorough studies should be made to reveal the phase behavior of the blends by using the light scattering technique.

According to Table 4, the P(S47-co-1VN53)/PVME blends are miscible up to 50 wt.% of the copolymer concentration while most of the P(S20-co-1VN80)/PVME blends are immiscible over the broad concentration range except below 25 wt.% of

the copolymer concentration.

Table 5 shows that the P(S21-co-2VN79)/PVME blends are miscible only below 35 wt.% of the copolymer concentration. The P(S49-co-2VN51)/PVME and P(S84-co-2VN16)/PVME blends are, however, miscible over all the copolymer concentration ranges.

In Figure 3 or 4, the glass transition temperatures of the blends are shown at different copolymer compositions and blend concentrations by weight, in which block drawn with the broken line is the immiscibility window which shows two separated T_g's within the blend concentration ranges. As expected, the copolymer of higher styrene content shows better miscibility with PVME. It was revealed that the blends of PVME with poly(vinylnaphthalene)s [P1VN or P2VN]

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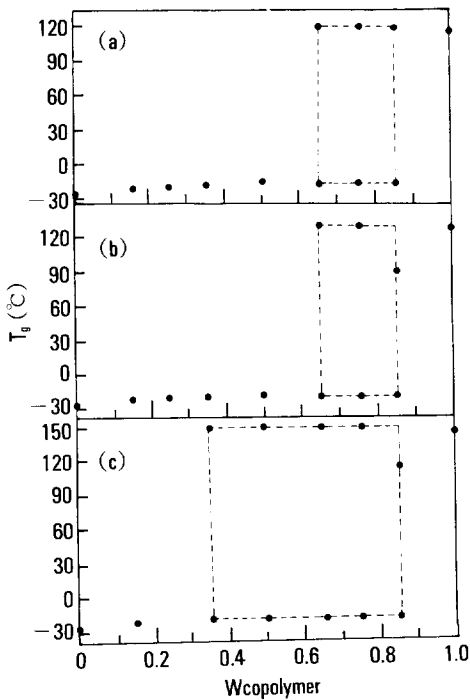


Fig. 3. Glass transition temperatures vs. the weight fraction of copolymer in P(S76-co-1VN24)/PVME blends (a), P(S47-co-1VN53)/PVME blends (b) and P(S20-co-1VN80)/PVME blends (c).

are immiscible whereas the PS/PVME blends are miscible over all the concentration ranges. This can be assumed that the molecular interaction between PS and PVME is larger than that between P1VN and PVME or P2VN and PVME.

Fluorescence Spectroscopy

Many experimental techniques have been developed for the characterization of polymer miscibility.^{3,23} One fundamental question that remains is the scale over which the blend components are mixed. It is now recognized that the measured miscibility is strongly dependent upon the technique used ; a polymer blend can be miscible using one particular method but phase-separated using another more sensitive method, simply due to the fact that the size of the phases is below the resolution limit of the first technique. In other case, the difference in T_g between the two polymers is smaller

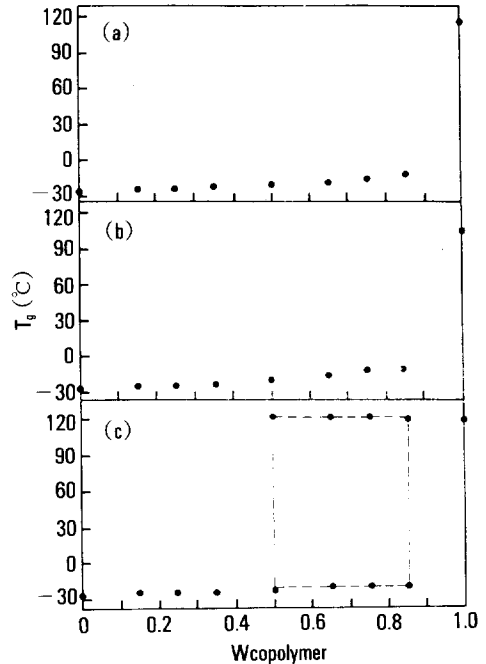


Fig. 4. Glass transition temperatures vs. the weight fraction of copolymer in P(S84-co-2VN16)/PVME blends (a), P(S51-co-2VN49)/PVME blends (b) and P(S21-co-2VN79)/PVME blends (c).

than 30°C and cannot be resolved by DSC.

Therefore, there is a need to develop new and more sensitive techniques to study the miscibility of polymer blends. Fluorescence spectroscopy^{24~34} is one of them. It exhibits a high sensitivity to detect small-scale heterogeneities and has the ability to analyze small concentrations of one component.

In Figure 5, I_D/I_M is plotted as a function of copolymers weight for the blends containing PVME and one of the P2VN, P(S76-co-1VN24), P(S47-co-1VN53) and P(S20-co-1VN80). In Figure 6, I_D/I_M is plotted as a function of copolymers weight for the blends containing PVME and one of the P2VN, P(S84-co-2VN16), P(S51-co-2VN49) and P(S21-co-2VN79). In these plots, smooth curves have been drawn through the data and I_D/I_M increase with increasing composition of vinylnaphthalene in the copolymers and with increasing concentration of copolymer (decreasing concentration of PVME)

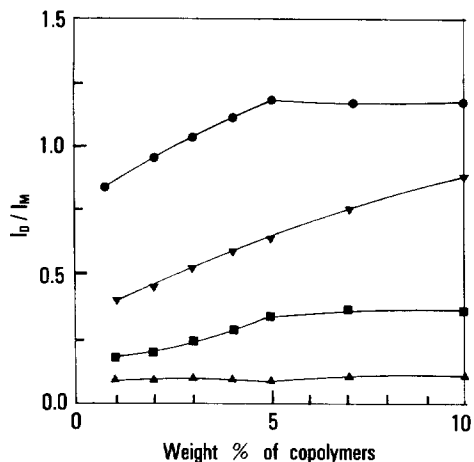


Fig. 5. Ratio of excimer to monomer fluorescence intensities of blends containing PVME and one of the P1VN(●), P(S76-co-1VN24)(▲), P(S53-co-1VN47)(■), P(S20-co-1VN80)(▼).

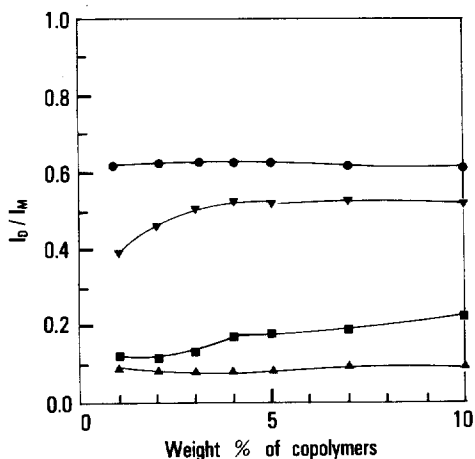


Fig. 6. Ratio of excimer to monomer fluorescence intensities of blends containing PVME and one of the P2VN(●), P(S84-co-2VN16)(▲), P(S51-co-2VN49)(■), P(S21-co-2VN79)(▼).

in the blends. The ratio of excimer to monomer intensity, I_D/I_M , at a given temperature and for the same casting temperature should be a qualitative measure of interaction. The minimum I_D/I_M ratio, corresponding to a maximum interaction. These measurements indicate clearly the I_D/I_M ratio is dependent upon the enthalpic interactions between

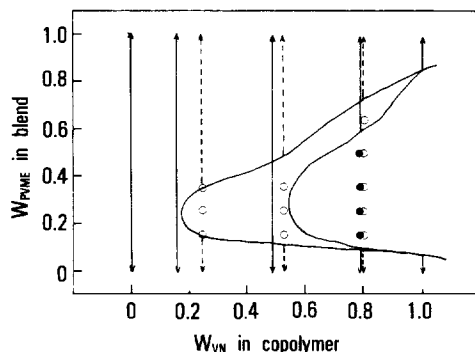


Fig. 7. The miscibility trend of P(S-co-1VN)/PVME blends and P(S-co-2VN)/PVME blends determined from optical clarity, T_g behavior, and fluorescence spectroscopy. The blends are immiscible at the composition region within the curvature: ○ and --- for P(S-co-1VN)/PVME blends, ● and — for P(S-co-2VN)/PVME blends.

styrene and vinylnaphthalene. The result means that the copolymers having higher concentration of vinylnaphthalene unit show poorer miscibility with PVME.

Careful inspections of Figures 5 and 6 imply that the P(S-co-1VN)/PVME blends have higher I_D/I_M ratio than the P(S-co-2VN)/PVME blends over all the blend concentration ranges. The result is closely related to the fact that the P(S-co-2VN) shows better miscibility with PVME than P(S-co-1VN) from the optical clarity and glass transition temperature behavior of the blends.

As a consequence, we can draw a miscibility map of the blends of PVME and P(S-co-VN) from the optical clarity, the T_g behavior, and fluorescence spectra. Figure 7 shows the miscibility map of P(S-co-1VN)/PVME and P(S-co-2VN)/PVME blends. Here, the abscissa and ordinate represent the compositions of the respective copolymers and PVME concentrations in weight fraction respectively. The circles denote immiscible blends. The boundaries between domains of miscibility and immiscibility are expressed by envelope for all the blend systems of the work.

It is clear that the miscibility in P(S-co-1VN)/PVME blends and P(S-co-2VN)/PVME blends are

considerably affected by the copolymer composition and the blend concentration and that the blends become more miscible as the composition of styrene increases in the copolymers. The exact reason why the P(S-co-2VN) shows better miscibility with PVME than P(S-co-1VN) is not clear at present. Further studies on this subject should be made to reveal the accurate interactions between PVME and styrene or vinylnaphthalenes.

CONCLUSIONS

In this work, the fluorescence spectroscopic analysis and the thermal behavior of the blends of styrene/vinylnaphthalene copolymers [P(S-co-1VN) or P(S-co-2VN)] and poly(vinyl methyl ether)(PVME) were investigated. The copolymers containing three different compositions were synthesized by radical polymerization. The blend films of the P(S-co-1VN) or P(S-co-2VN) and PVME were cast from benzene. It was found that the blends of PVME with P(S-co-1VN) of 76 wt.% styrene and 24 wt.% 1-vinylnaphthalene(1VN) show miscibility below 50 wt.% of the copolymer concentration and the concentration range to show miscibility becomes wider as the composition of 1VN decreased in the copolymers. The blends of PVME with P(S-co-2VN) of 21 wt.% styrene and 79 wt.% 2-vinylnaphthalene (2VN) show miscibility below 35 wt.% of the copolymer concentration and the concentration range to show miscibility becomes wider as the composition of 2VN decreased in the copolymers. In conclusion, the miscibility of P(S-co-2VN) was better than P(S-co-1VN) with PVME.

Acknowledgements : The authors wish to express their sincere thanks to the Korea Science and Engineering Foundation for their financial support. They also thank to Mr. Wan Kyu Lee and Ms. Mi Ja Lim of Hannam Chem. Corp. for their experimental assistances to measure DSC.

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