Polymer(Korea). Published by the Polymer Society of Korea
Vol. 13, No. 8, 1989

Poly(1-vinyl naphthalene) 및 Poly(styrene-co-1-vinyl naphthalene)과 Poly(vinyl methyl ether)블렌드들의 상용성

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(1989년 3월 3일 접수)

Miscibility of the Blends of Poly(vinyl methyl ether) with Poly(1-vinyl naphthalene) and Poly(styrene-co-1-vinyl naphthalene)

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(Received March 3, 1989)

요 약 : 1-naphthyl ethanol의 탈수에 의해 합성된 1-vinyl naphthalene (1VN)을 CH_2Cl_2 속에서 촉매로 $TiCl_4$를 사용하여 −78℃에서 단독중합 하였으며 같은 조건에서 styrene과 양이온 공중합하였다. UV 분광법으로 공중합체들의 상대조성을 분석하였으며, 공중합체내의 styrene 무게 %는 각각 20, 49, 75이었다. poly(1-vinyl naphthalene) (P1VN) 과 poly (vinyl methyl ether) (PVME)의 블렌드는 trimethyl benzene (TMB)을 용매로, 그리고 poly(styrene-co-1-vinyl naphthalene) [P(S-co-1VN)]과 PVME의 블렌드는 TMB 와 benzene의 50/50 (v/v) 혼합 용매를 사용하여 필름으로 성형하였다. 이들 블렌드의 상용성은 optical clarity와 glass transition temperature (Tg) 특성 및 FT-IR 분광 분석법에 의하여 결정하였다. 중량평균 분자량이 5,400인 P1VN 과 PVME의 블렌드는 P1VN의 조성이 15~50 wt% 인 경우 상용하였으며, 65~85 wt%인 경우 불용하였다. 분자량이 11,500 및 21,000 인 P1VN 와 PVME의 블렌드들은 P1VN의 조성이 15 wt% 인 경우에만 상용하였으며 25~85 wt% 인 경우는 불용하였다. P(S-co-1VN)/PVME 블렌드들의 상용성은 공중합체내의 styrene 함량이 증가할수록 그리고 블렌드에서 PVME의 함량이 증가할수록 증가하였다.

Abstract : 1-vinyl naphthalene (1VN) synthesized by the dehydration of 1-naphthyl ethanol was copolymerized with styrene by $TiCl_4$ in CH_2Cl_2 at-78℃. It was identified by UV spectrophotometer that three kinds of poly(styrene-co-1-vinyl naphthalene) [P(S-co-1VN)] contained styrene of 20, 49 and 75 wt%, respectively. The blend films were cast from trimethyl benzene (TMB) in the poly(1-vinyl naphthalene) (P1VN)/

poly(vinyl methyl ether) (PVME) blend and the mixed solvent of TMB / benzene [50/50(v/v)] in the P(S-co-1VN) / PVME blends. The miscibility of these blends was determined by optical clarity, glass transition temperature (Tg) behaviour, and FT-IR spectroscopic analysis. The P1VN (5,400) / PVME blends in which the weight average molecular weight ($\overline{M}w$) of P1VN is 5,400 were miscible in the P1VN concentrations of 65 to 85 wt%. The P1VN / PVME blends in which the $\overline{M}w$ of P1VN are 11,500 and 21,000, however, were miscible in the P1VN concentration of only 15 wt% and were immiscible in the P1VN concentrations of 25 to 85 wt%. The miscibility of P(S-co-1VN) / PVME blends increased with increasing content of styrene in the copolymers and in concentration of PVME in the blend.

INTRODUCTION

Polymer blend has been extensively investigated because physical blending of polymers is economically much more attractive than synthesis of new homopolymers or copolymers as a material development approach. A limitation exists, however, in that the bulk properties of the blend depend largely on its miscibility which is rare phenomenon in mixing of the high molecular weight polymers.[1~3] Many experimental techniques such as calorimetry,[4~6] spectrophotometry,[7~11] light or neutron scatterg, [12,13]and fluorescence[14] have been used for the investigation of blend miscibility.

Recently the blends of polystyrene (PS) and PVME have attracted much interest because they are miscible over a wide range of blend concentration, even though the miscibility of the two polymers was affected by several factors including solvent, temperature, molecular weight and concentration.[6, 15~17]

Lu et al.[8] reported the spectroscopic study of the PS / PVME blends using FT-IR and revealed that the definite spectral features are sensitive to the miscibility of the blends. They concluded that the vibrations most sensitive to change in molecular environment are the C−H out-of-plane vibration of phenyl ring in PS and the CO vibrations of PVME.

It is interesting to examine how the miscibility of P1VN / PVME blends is different with that of PS / PVME blends and how the miscibility of P(S-co-1VN) / PVME blends changes with the relative compositions of the copolymers. In this work, PIVN and P(S-co-1VN) were synthesized by cationic polymerization and the blends of these with PVME were examined by FT-IR together with such classical methods as the optical clarity and the Tg behaviour.

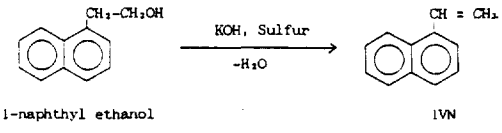
EXPERIMENTAL

Purification of Materials

Styrene (Junsei Chemical) was purified by standard procedure and azobisisobutyronitrile (AIBN) (Yakuri Pure Chemical) was purified by recrystallization from ethanol. PVME obtained from GAF(Garantrez M-574) was purified according to the literature.[17] $TiCl_4$ was purified by simple distillation after refluxing for three hours with copper powder before use. TMB and benzene used as blending solvents were dried using molecular sieve 4A.

Synthesis of 1VN

1VN monomer was synthesized by dehydration[18] of 1-naphthyl ethanol (Aldrich): 50g of 1-naphthyl ethanol with 2g of potassium hydroxide and 0.6g of sulfur was dehydrated in 100ml vacuum ditillation flask. The product, 1VN was distillled at 81℃ under 0.4mmHg



immediately on dehydration. It had a 63% yield of 1-naphthyl ethanol and it was identified by IR and NMR as shown in Figures 1 and 2.

Syntheses of Homopolymers and Copolymers

Polymerization was carried out in three neck flask equipped with mechanical stirrer, thermometer and Ar gas inlet. Homopolymers were obtained by cationic polymerization of a 0.45 mole styrene solution and a 0.25 mole 1VN soultion of CH_2Cl_2, respectively, at −78℃ for 10 minutes in the presence of $TiCl_4$, where its concentraction was 1.2×10^{-2}mole. Three kinds of P(S−co−1VN)were synthesized at 78/22, 55/45, and 29/71 ratios of styrene to 1VN by the same method as homopolymers, Purification of the polymers was accomplished by reprecipitation in methanol from their toluene solutions and they were dried in a vacuum oven until a constant weight was obtained. The conversions of monomer to polymer were 95% for PS and 74% for P1VN, and those for the copolymers ranged from 74 to 82%. The characteristics of the polymers synthesized are given in Tables 1 and 2.

Composition Analysis of the P(S-co-1VN)

The compositions of the copolymers were analyzed using Hitachi 220 ultraviolet spectrophotometer with 1.0 cm quartz cell. The UV spectra of copolymers were obtained in chloroform and 288 nm was selected as the characteristic wavelength for analysis because PS exhibited little absorbance at that wavelength. From the specific extinction coefficients of PS and P1VN at 288 nm, the following equation was obtained:

$$E_{co} = 38.05X + 0.03\ (1-X)$$

where X is the weight fraction of 1VN in the copolymers and E_{co} is the specific extinction

Table 1. Characteristics of Polymers Synthesized by the Cationic Polymerization

Sample[a]	Wt % of Styrene in Feed	Conversion (%)	Ext. Coefficient[b] at 288 nm (g/l)	Wt % of Styrene in Copolymer
PS	100	95	0.03	100
P(S75−co−1VN25)	78	76	9.54	75
P(S49−co−1VN51)	55	82	19.42	49
P(S20−co−1VN80)	29	74	30.54	20
P1VN	0	74	38.05	0

[a] The copolymers were named according to polymer composition analyzed by UV.
[b] Extinction coefficient is defined as the absorbance divided by concerntration.

Table 2. The Molecular Weights, Tg's and Decomposition Temperature Range of PS, P(S−co−1VN), P1VN, and PVME

Sample	$\overline{M}_n$	$\overline{M}_w$	T_g(℃)	Decom. Temp. Range(℃)
PS	57,000	88,000	102	380−445
P(S75−co−1VN25)	32,100	51,000	115	360−430
P(S49−co−1VN51)	12,400	19,800	129	365−435
P(S20−co−1VN80)	5,700	11,000	146	370−435
P1VN(l)	2,700	5,400	153	380−455
P1VN(m)	5,900	11,500	154	385−460
P1VN(h)	12,800	21,000	154	385−460
PVME	45,000	−	−23	−

coefficient of the copolymers. The compositions of the copolymers were calculated from the above equation using the specific extinction coefficient of each copolymer and were listed in Table 1.

Molecular Weight Measurements

The molecular weights of PS, P1VN and P(S-co-1VN) in Table 2 were determined by gel permeation chromatography (GPC) (Waters 244). The measurements were conducted in toluene. The apparatus was calibrated with PS standard.

P1VN was separated into three parts different in molecular weight by fractionation. Ethanol was dropped in the toluene solution of P1VN. When the solution was reached at the cloud point, it was heated to 40℃ to be clear. And then it was kept at room temperature. The solution of P1VN with the low molecular weight was decanted off from the precipitate. Fractionation was repeated according to the same method.

Preparation of Blends

The P1VN / PVME blends with various concentrations were prepared by casting from 3% (by weight) solution in TMB and the P(S-co-1VN) / PVME blends were also prepared in a mixture of benzene / TMB [50 / 50(v / v)]. The blends were dried slowly in a Petridish at room temperature and then kept under a vacuum until they reached constant weight. They were used for the optical clarity test and the thermal analysis. For the FT-IR analysis, the blended samples were cast directly on the KBr plate.

Measurements of DSC and FT-IR

Differential scanning calorimetry (DSC) was conducted using a Perkin-Elmer DSC-4 apparatus calibrated with pure indium as standard. The powdered polymers synthesized and the blend films prepared were pressed into aluminum pan after weighed. In order to avoid the thermal history from the samples packed in the aluminum pan and to eliminate any small traces of solvent, polymer samples were heated to 170℃ at the heating rate of 40℃ / min, maintained at 170℃ for 5 min, and then quenched at the rate of 320℃ / min to −70℃. For measurements, samples were heated again at the heating rate of 10℃ / min. The blend samples were cooled to −70℃ and then were measured at the heating rate of 10℃ / min to 170℃. All the reported Tg's were recorded at the half-height of the heat capacity jump. Themogravimetric analysis (TGA) was also performed using a Perkin-Elmer Thermogravimetric Analyzer.

Infrared spectra were obtained using a Digilab-45 FT-IR spectrophotometer. The thin films of P1VN, P(S-co-1VN), and blend samples were prepared by directly casting onto potassium bromide disk from 1% soultion of TMB or TMB / benzene (50 / 50) mixture. The solvent was removed by drying in a vacuum oven at room temperature for 2 weeks. The thickness of the films was in the range of 2~3 μm. Thirty-two scans at a resolution of 2cm^{-1} were signal-averaged.

RESULTS AND DISCUSSION

Identification of 1VN

IR spectrum of 1VN in Fig. 1 doesn't show aliphatic CH peak to the right of 3000 cm^{-1} and OH peak (3200~3500 cm^{-1}) differently with that of 1-naphthyl ethanol. Instead it shows a new peak of vinylic carbon double bond at 1615 cm^{-1}. Proton NMR spectrum of 1VN in Fig. 2 shows H_a at 5.35 ppm, H_b at

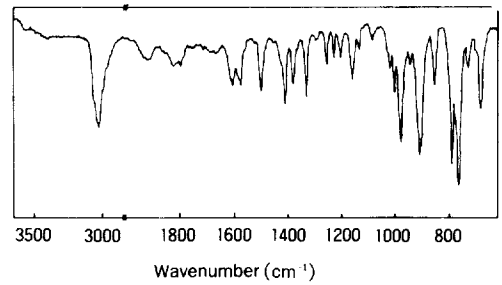


Fig. 1. Infrared spectrum of 1−vinyl naphthalene.

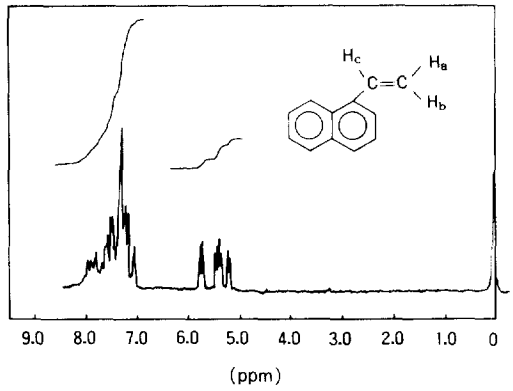


Fig. 2. Proton NMR spectrum of 1-vinyl naphthalene.

570 ppm, H_c at 7.35 ppm, and naphthalenic protons at 7.2~8.2 ppm. J_{ab}, coupling constant between H_a and H_b is 2 Hz, J_{ac} is 11 H_z and J_{bc} is 17 H_z.

Composition and Molecular Weight of Copolymers

The relative composition of 1VN to styrene in cationically polymerized copolymers analysed by UV spectrophotometer is shown by the plot of styrene weight % in copolymers against that in the monomer feed in Fig.3, along with that in radically polymerized copolymers. Although the relative reactivity of 1VN to styrene in the radical polymerization is known to be large,[19] the relative reactivity of 1VN to styrene in our work is also large in the cationic polymerization as well as the radical polymerization.

The molecular weights of the copolymers, P1VN and PVME are listed in Table 2. It is seen that the molecular weights of the separated P1VN are considerably different and, the molecular weighr in the copolymers decreases with increasing content of 1VN. The latter may be ascribed to the fact that the rate of chain transfer of 1VN is larger than that of styrene during polymerization, even though the relative reactivity of 1VN is reported to be lager than that of styrene in literatures.[18,19]

Thermal Properties of Copolymers

The DSC thermograms of the copolymers are shown in Fig. 4. The Tg increases with

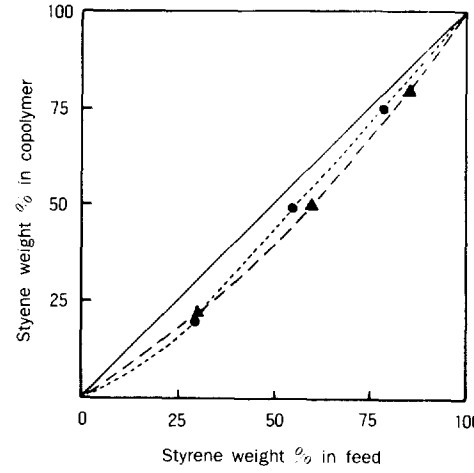


Fig. 3. Plots of styrene weight % in copolymer vs styrene weight % in the monomer feed for the cationic (●) and radical (▲) copolymerizations of styrene and 1VN.

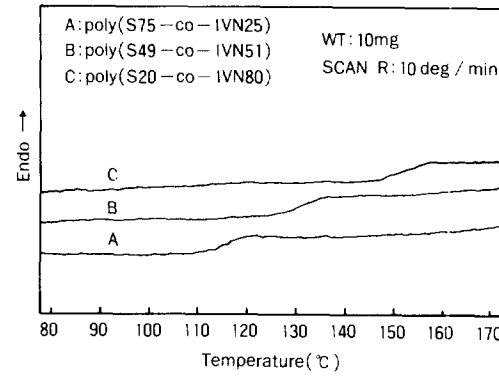


Fig. 4. DSC thermograms of three copolymers synthesized by cationic polymerization.

increasing composition of 1VN in the copolymers because of the rigidity of 1VN molecule. It is also shown in Table 2 that the decomposition temperatures of PS, P1VN, and their copolymers are over 360~460℃ range regardless of relative compositions in case of copolymers.

Optical Clarity and Tg Behaviour

The optical clarity of P1VN/PVME blends is summarized along with Tg behaviour in Table 3. It was obvious from the preliminary observations by optical clarity that the miscibility of P1VN/PVME blends cast from TMB

Table 3. Effect of the Molecular Weight of P1VN on Miscibility Based on the Optical Clarity, Tg, and FT−IR Characteristics in the P1VN / PVME Blends

Polymer	P1VN wt % in Blends	Optical Clarity	Tg (℃)	Naphthyl Peak(cm^{-1})	Miscibility
P1VN (5,400)	15	Clear	−17	778.3	M
	25	Clear	−15	777.8	M
	35	Clear	−14	777.3	M
	50	Clear	−13	776.8	M
	65	Clear	−15, 150	776.3	IM
	75	Clear	−15, 151	775.4	IM
	85	Clear	−15, 151	775.0	IM
P1VN (11,500)	15	Clear	−17	·	M
	25	Hazy	−17, 151	·	IM
	35	Hazy	−18, 152	·	IM
	50	Hazy	−18, 153	·	IM
	65	Hazy	−19, 154	·	IM
	75	Hazy	−19, 154	·	IM
	85	Hazy	−18, 152	·	IM
P1VN (21,000)	15	Clear	−17	778.3	M
	25	Hazy	−18, 152	777.0	IM
	35	Hazy	−19, 153	776.3	IM
	50	Hazy	−19, 154	776.0	IM
	65	Hazy	−20, 154	775.4	IM
	75	Hazy	−20, 154	775.0	IM
	85	Hazy	−19, 152	774.4	IM

is better than that of the blends cast from such solvents as benzene, toluene, xylene, and CH_2Cl_2. The blend was determined as miscible when it not only is optically clear but also has single Tg.

The weight average molecular weights ($\overline{M}w$) of P1VN separated by fractionation were 5,400, 11,500, and 21,000, respectively. The miscibility of P1VN / PVME blends cast from TMB at room temperature was strongly influenced by the molecular weight of P1VN. The P1VN (5,400) / PVME blends were optically clear over all the blend concentrations. But the blends of P1VN (11,500) and P1VN (21,000) with PVME were phase-separated over almost all blend concentrations, as shown in Table 3. Moreover, the optical clarity of these blends was largely influenced by the temperature at which the blend solution gelled into the film. The optical clarities of the P1VN (21,000) / PVME (50 / 50) blends evaporated from 5, 15, 25 and 35℃ were clear, a little hazy, hazy and very hazy, respectively. The such sensitivity in optical clarity of P1VN / PVME blend to small difference of temperature may be due to the fact that a lower critical soultion temperature (LCST) of this blend is around room temperature. It is well known that because of a decrease in miscibility with increasing temperature, PS / PVME blend exhibits LCST in the range of 97 to 130℃, depending on the molecular weights of the two components.[6,20] And the rate of solvent evaporation which is related to the temperature of evaporation might be another factor. Rapid drying in high temperature yields hazy films while slow drying produces clear film with extremely finely dispersed domains.

The P1VN (5,400) / PVME blends in which the $\overline{M}w$ of P1VN is 5,400 were miscible in the P1VN concentrations of 15 to 50wt% and were immiscible in the P1VN concentration of 65 to 85wt% since they exhibited two Tg's differently with their optical clarity as shown in Table 3. The P1VN / PVME blends in which the $\overline{M}w$ of P1VN are 11,500 and 21,000 were miscible in the P1VN concentration of 15wt%, and were immiscible in the P1VN concentrations of 25 to 85 wt% since they exhibited two Tg's as shown in Table 3.

It can be concluded from optical clarity and Tg behaviour that the miscibility of the P1 VN / PVME blends is sensitive to the $\overline{M}w$ of P1VN and that these blends are nearly immiscible with the exception of the P1VN (5,400) / PVME blends, where P1VN is a low molecular weight polymer.

The optical clarity and the Tg's of the P (S-co-1VN) / PVME blends are summarized in Table 4. Though there is some disagreement between optical clarity and Tg behaviour around the boudary region of miscibility, the copolymer having higher styrene content shows better miscibility with PVME. Miscibility trend of these blends is similar to that of our previous work performed with P(S-co-1VN) synthesized by the radical polymerization.[21]

Fig. 5 shows the plot of the glass transition temperatures of the blends against the weight fraction of the copolymers. In each figure the block drawn with the broken line is the immiscibility window which shows two separated Tg's within the blend concentration ranges. It is shown that the window becomes broader with

Table 4. Miscibility Based on the Optical Clarity and the T_g for the P(S−co−1VN) / PVME Blends Cast from Benzene / TMB (50 / 50)

Copolymer	Wt % of Copolymer in Blends	Optical Clarity	T_g (℃)	Miscibility
P(S75−co−1VN25)	15	Clear	−18	M
	25	Clear	−16	M
	35	Clear	−11	M
	50	Clear	− 7	M
	65	Clear	−16, 118	IM
	75	Trans[a]	−13, 118	IM
	85	Clear	70	M
P(S49−co−1VN51)	15	Clear	−15	M
	25	Clear	−13	M
	35	Clear	−12	M
	50	Trans[a]	− 9, 129	IM
	65	Hazy	−11, 130	IM
	75	Hazy	− 8, 130	IM
	85	Clear	92	M
P(S20−co−1VN80)	15	Clear	−17	M
	25	Clear	−15	M
	35	Trans[a]	−16, 148	IM
	50	Hazy	−16, 148	IM
	65	Hazy	−17, 149	IM
	75	Hazy	−17, 149	IM
	85	Trans[a]	−16, 114	IM

[a]Translucent

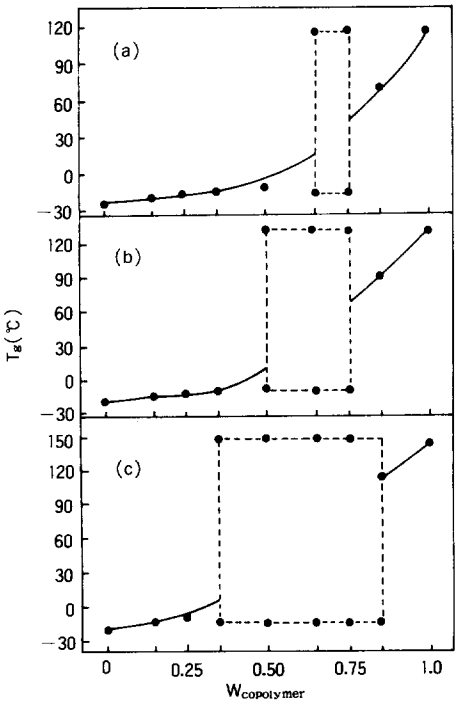


Fig. 5. Glass transition temperature vs the weight fractioin of copolymer in P(S75-co-1VN25) / PVME blends (a), P(S49-co-1VN51) / PVME blend (b), and P(S20-co-1VN80) / PVME blends (c).

increasing content of 1VN in the copolymers and the blends of the copolymer rich concentration have a trend to be immiscible.

FT-IR Spectroscopy

Many workers have been using FT-IR spectroscopy to study polymer blends,[9,10,22] because the position, intensity, and shape of vibrational peaks are useful in clarifying conformational and environmental changes of polymers at the molecular level. According to thermodynamic theory, there should be a favorable specific interaction between two polymers in order that the polymer blends are miscible. This interaction leads to a considerable difference between the spectrum of a pure polymer and that of the polymer in the blend. This spectroscopic difference can easily be detected by subtracting the contributions of both homopolymers from the spectrum of blended polymer.

Hsu and co-workers[8] reported on the PS / PVME blends that PVME has a strong doublet at 1085 and 1107 cm^{-1} peak was greater than that of the 1107 cm^{-1} with a shoulder at 1132 cm^{-1} and the relative intensity of this doublet vaires considerably when the blend sample is cooled or heated. Thus, they concluded that the relative intensity of this doublet was sensitive to the miscibility of the PS / PVME blends, indicating that the intensity of the 1085 cm^{-1} peak was greater than that of the 1107 cm^{-1} peak for the miscible blend.

They also reported that there is another 698 cm^{-1} peak sensitive to miscibility in the PS / PVME blends which is generally assigned to the C−H out-of-plane bending vibration of phenyl ring in PS.

The infrared spectrum of P1VN has 774.4 cm^{-1} peak due to the CH out-of-plane bending of naphthyl ring. The wavenumbers of this peak in the P1VN / PVME blends are summarized in Table 5, along with the shape of the doublet of 1100 cm^{-1} region due to the CO vibration of PVME. Frequency shift increases with increasing PVME concentration in both P1VN (5,400) / PVME and P1VN(21,000) / PVME blends. But the frequency shifts in the former system of low molecular weight are larger than those in the latter system of high molecular weight. Such a difference of frequency shift between two blend systems is supposed to be due to the steric hindrance of rigid bulky naphthyl ring on mixing of the high molecular weight P1VN with PVME. The frequency shift of naphthyl ring is plotted as a function of PVME concentration in the blend in Fig. 6. The shift increases nearly proportionately with increasing PVME concentration. This means that one naphthyl ring interacts with more than one CO groups.

As the P1VN concentration in the blend increases, the intensity of 1107 cm^{-1} peak increases more and more, as shown in Table 5. In the P1VN (21,000) / PVME blends where

Table 5. Relative Intensity of the Doublet of the 1100cm^{-1} Region and Wavenumbers of Naphthyl Peaks for the P1VN(5,400) / PVME and P1VN(21,000) / PVME Blends

P1VN Wt % in Blends	P1VN(5,400 / PVME Blend		P1VN(21,000) / PVME Blend	
	Band Shape 1107,1085cm^{-1}	Naphthyl Peak (cm^{-1})	Band Shape 1107,1085cm^{-1}	Naphthyl Peak (cm^{-1})
PVME				
15		778.3		778.2
25		777.8		777.3
35		777.3		776.3
50		776.7		776.0
65		776.3		775.4
75		775.4		774.9
85		775.4		774.4

Table 6. Phenyl and Naphthyl IR Peaks of the P(S−co−1VN) / PVME Blends

Copolymer	Wt % of copolymer in Blends	Measured Ring Frequency (cm^{-1})		Miscibility
		Phenyl,	Naphthyl	
P(S75−co−1VN25)	15	701.1	789.8	M
	25	701.0	783.7	M
	35	701.0	781.5	M
	50	700.8	779.8	M
	65	700.8	777.9	IM
	75	700.8	776.9	IM
	85	700.3	775.8	M
	100	699.1	773.0	−
P(S49−co−1VN51)	15	701.6	782.8	M
	25	701.6	781.2	M
	35	701.6	779.8	M
	50	701.2	778.0	IM
	65	701.0	777.6	IM
	75	700.5	776.8	IM
	85	700.4	776.2	M
	100	700.0	774.0	−
P(S20−co−1VN80)	15	702.4	781.2	M
	25	702.4	779.5	M
	35	702.4	778.6	IM
	50	702.4	778.0	IM
	65	702.0	777.3	IM
	75	701.6	776.8	IM
	85	701.3	776.3	IM
	100	700.9	775.5	−

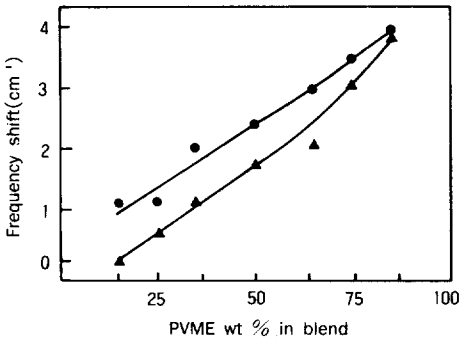


Fig. 6. The differences of naphthyl ring frequencies of P1VN (5,400) (●) and P1VN (21,000) (▲) from them in the individual blends with PVME, expressed as the PVME weight % in the blends.

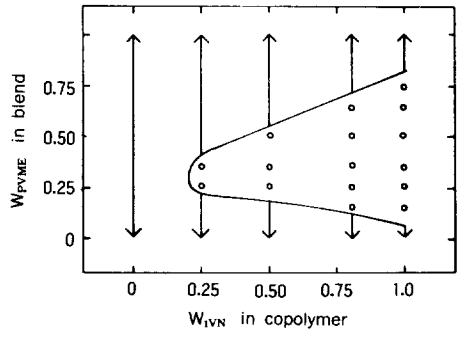


Fig. 7. The miscibility trend of the blends of PVME with P1VN and P(S−co−1VN). The blends are immiscible at the composition region (marked circle) within the curvature.

the P1VN concentration is from 30 to 85 wt %, the intensity of 1107 cm^{-1} peak of the doublet is same or rather strong.

Though the relative intensity of the doublet is not a decisive factor for the determination of the miscibility of this blend, it should be noted that the relative intensity of the 1100 cm^{-1} doublet has a considerable relation to the blend miscibility.

The individual infrared Peaks due to phenyl and naphthyl rings in the P(S-co-1VN) / PVME blends are summarized in Table 6. The careful inspection of Table 6 shows that the frequency shifts increase with increasing content of styrene in the copolymers and with increasing concentration of PVME in the blend, and that the difference of phenyl ring is nearly constantly small, whereas that of naphthyl ring can increases continuously with increasing PVME concentration. This means that there is a molecular interaction between the naphthyl ring of 1VN and CO group of PVME and one naphthyl ring interact with more than one CO groups.

It is supposed that these interactions are hydrogen bonding and / or dipole-dipole interaction between the CO group and the C−H group in aromatic rings, and that a degree of these interactions according to peak shift increases with increasing styrene content in copolymers and with increasing PVME concentration in the blend increases. The miscibility in this blend system increases with a degree of shift and this is in good accordance with the result of miscibility by optical clarity and Tg behaviour.

From the results on the P1VN / PVME and P(S-co-1VN) / PVME blends along with the result reported on the PS / PVME blends, the miscibilities of a series of these blend system are summarized as shown in Fig.7.

CONCLUSIONS

1. The miscibilities of P1VN / PVME blends were sensitive to the $\overline{M}w$ of P1VN.
2. The P1VN (5,400) / PVME blends were miscible in the P1VN concentrations of 15 to 50 wt %, whereas were immiscible in the P1VN concentrations of 65 to 85 wt %.
3. The P1VN (11,500) / PVME and P1VN (21,000) / PVME blends were immiscible with the exception of the P1VN concentration of 15 wt %.
4. The miscibility of P(S-co-1VN) / PVME blend increased with increasing content of styrene in copolymers and with increasing concentration of PVME in blends.

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