

## 스티렌과 *p*- 및 *m*-메틸스티렌 공중합체와 폴리(비닐 메틸 에테르) 블렌드의 FTIR에 의한 상용성 연구

하 창 식 · 류 진 호\* · 조 원 제

부산대학교 고분자공학과 · \*산업과학기술연구소

(1992년 5월 6일 접수)

### Miscibility of Poly(vinyl methyl ether) and Styrene and *p*- or *m*-methylstyrene Copolymers by FTIR Spectroscopy

Chang Sik Ha, Jin Ho Ryou\*, and Won Jei Cho

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

\*Research Institute of Industrial Science & Technology, Pohang P. O. Box 135, Kyunghuk 790-600, Korea

(Received May 6, 1992)

**요 약 :** 저임계용액온도(LCST)를 보이는 범위 내에서의 styrene과 *p*- 및 *m*-메틸스티렌 공중합체와 poly(vinyl methyl ether)(PVME)와의 상용성을 FT-IR 분광 분석법에 의해 조사하였다. 본 연구를 위해 스티렌 유도체의 함량이 feed ratio로 10 및 20 wt. %가 되도록 중합시킨 공중합체를 사용하였다. Hsu's Criterion에 의해 PVME와의 상용성은 두 공중합체 모두 폴리스티렌보다는 나쁜 상용성을 보였으나, poly(styrene-co-*p*-methylstyrene)이 poly(styrene-co-*m*-methylstyrene) 보다 양호한 상용성을 보임을 알았다. 또한 공중합체내 스티렌유도체와 PVME의 함량이 증가할수록 상용성은 감소하였다. 이 결과는 광산란법과 fluorescence 분광 분석법에 의해서도 확인되었다.

**Abstract :** Miscibility of the blends of poly(vinyl methyl ether)(PVME) and copolymers of styrene and *p*- or *m*-methylstyrene showing LCST behavior was investigated by Fourier Transform Infrared (FTIR) spectroscopy. In this work, we synthesized poly(styrene-co-*p*-methylstyrene) and poly(styrene-co-*m*-methylstyrene) by radical polymerization, in which the component of styrene is 10 and 20 wt.%. The miscibility of the styrene/styrene derivative copolymers with PVME, based on the Hsu's criterion, was poorer than for polystyrene/PVME. However, poly(styrene-co-*p*-methylstyrene) showed better miscibility than poly(styrene-co-*m*-methylstyrene). The miscibility decreased with increasing compositions of styrene derivatives in the copolymers and PVME concentrations. This behavior is in good agreement with the results obtained by light scattering and fluorescence spectroscopy.

## INTRODUCTION

Fourier transform infrared (FTIR) spectroscopy has been recognized as a useful tool for elucidation of structure in the polymer sciences.<sup>1-4</sup> The position, intensity and shape of vibrational bands are useful in clarifying conformational and environmental changes of polymers in molecular level. When two polymers are completely miscible, there is a distinct chemical interaction between the two different polymers. This interaction leads to a considerable difference in spectrum between the homopolymer and blends. This spectroscopic difference can easily be detected by subtraction the contributions between both homopolymers and blends.<sup>5-9</sup>

Hsu and his co-workers<sup>3</sup> once reported on the definite spectral features sensitive to the miscibility of the blends of polystyrene (PS) and poly(vinyl methyl ether) (PVME) by using FTIR spectroscopy. They revealed 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 COCH<sub>3</sub> vibrations of PVME. The spectroscopic features can be regarded as a very useful and sensitive probe of specific interactions between styrenic copolymers and PVME as well as PS and PVME. We found that their suggestions could be also served as a definite "criterion" for the miscibility of PVME with poly(styrene-co-1-vinylnaphthalene).<sup>10</sup>

The purpose of this work is to investigate the miscibility of PVME and copolymers of styrene and styrene derivatives having similar structures by using FTIR spectroscopy. We synthesized a series of copolymers containing styrene as a major component in which another minor component is styrene derivative i.e., *p*-methylstyrene or *m*-methylstyrene. According to the equation of state theory, the miscibility is significantly affected by molecular weight (MW), molecular weight distribution (MWD), thermal expansion coefficient, etc. Thus, all-out efforts were made to synthesize the copolymers so that their molecular weight was not

exceeded 20,000 and the conversions were below 20% in order to avoid any artificial effect of molecular weight and molecular weight distribution.

Here we report the effect of chemical nature and compositions of comonomer components and the blend concentration on the miscibility of the blends in PVME and a series of styrene and styrene derivative copolymers.

## EXPERIMENTAL

### Materials

Styrene (Junsei Chemical) and *p*-methylstyrene (Aldrich Chemical) were washed with 10% aqueous solution of NaOH to remove inhibitor, followed by washing with distilled water until it became neutral. After drying with CaCl<sub>2</sub> for two days, it was purified by distillation. *M*-methylstyrene (Fluka Chemical) was used without further purification. Azobisisobutyronitrile (AIBN) (Yakuri Pure Chemical) was purified by recrystallization from ethanol. Poly(vinyl methyl ether) (PVME) (Scientific Polymer Products) was purified by the same method as described elsewhere.<sup>11</sup>

### Syntheses of Polymers

Polystyrene (PS) was prepared in a polymerization tube by adding 3.0M styrene solution of toluene, with 1.0 wt.% AIBN. The tube was sealed after purging with nitrogen gas and polymerization was carried out at 60°C for 4 hrs.

Poly(styrene-co-*p*-methylstyrene) [P(S-co-*p*MeS)] and poly(styrene-co-*m*-methylstyrene) [P(S-co-*m*MeS)] were synthesized in weight ratios 90/10 and 80/20, respectively, by the same method as used for PS. Various reaction time was adjusted for each copolymer so that the polymer obtained has molecular weight below 20,000 and molecular weight distribution below 2.0 by controlling the conversion of monomer to polymer in the range below 20%.

Purification of the polymers was accomplished by reprecipitation in methanol from their toluene solutions followed by drying in a vacuum oven at room temperature. The characteristics of the poly-

**Table 1.** Characteristics of Polymers used in the Study

Sample	Wt. % of styrene		Conversion (%)	$\bar{M}_n^{(b)}$	$\bar{M}_w^{(b)}$	$\bar{M}_w/\bar{M}_n^{(b)}$	Source
	in feed	in copolymer <sup>a)</sup>					
PS	100		11.9	13,100	17,200	1.31	synthesized <sup>c)</sup>
PVME	0		—	46,500	99,000	2.13	Scientific Polym. Prod.
P(S9-co- <i>m</i> MeS1)	90	87.5	7.8	12,800	15,200	1.19	synthesized <sup>c)</sup>
P(S8-co- <i>m</i> MeS2)	80	76.5	7.3	12,200	15,600	1.28	synthesized <sup>c)</sup>
P(S9-co- <i>p</i> MeS1)	90	87.3	15.6	14,500	19,700	1.36	synthesized <sup>c)</sup>
P(S8-co- <i>p</i> MeS2)	80	78.5	15.8	13,700	19,400	1.42	synthesized <sup>c)</sup>

<sup>a)</sup> analyzed by <sup>1</sup>H-NMR.

<sup>b)</sup> measured by GPC.

<sup>c)</sup> synthesized by radical polymerization.

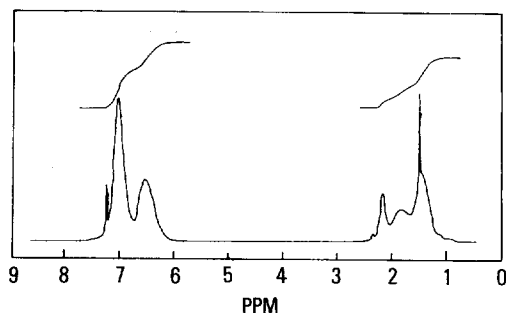
mers used in this study are given in Table 1.

The composition notation described in Table 1 and in the text are based on monomer feed ratios in copolymers throughout the article, unless otherwise noted. For instance, P(S8-co-*m*MeS2) denotes that the composition of the copolymer is 80 wt % of styrene and 20 wt % *m*-methylstyrene in monomer feed ratio, even though the copolymer contains slightly different comonomer compositions. The copolymer compositions were determined by <sup>1</sup>H-FT-NMR spectroscopy (JEOL-FX90Q, 90MHz). Fig. 1 shows a typical NMR spectrum of P(S8-co-*m*MeS2). The C-CH<sub>3</sub> protons appeared at 2.1 ppm, which are appeared in *m*-methylstyrene only, were used to determine the copolymer compositions.<sup>12</sup>

#### Measurement

**Optical Clarity** : The blends of PS as well as styrene/styrene derivative copolymers with PVME blends with various concentrations were prepared by casting from 5 wt % solutions in toluene. The blends were dried slowly in a petri dish at room temperature and then kept in a vacuum oven until they reached constant weight.

**Molecular Weight of Polymers** : Molecular weight of polymers were determined from GPC (Waters 244) with Ultrastyrigel 500 A-linear-columns. The measurement was conducted using the RI detector in THF at the flow rate of 1.0 ml/min at 28 °C. PS was used as a standard material for calibra-



**Fig. 1.** A typical <sup>1</sup>H-NMR spectra of P(S8-co-*m*MeS2) synthesized at 60°C for 4hrs.

tion.

**Light Scattering** : Details of light scattering experiment were described elsewhere.<sup>13,14</sup> A low-power 2mW He-Ne laser was used as a light source, and a photodiode (EG & G HAV-1000 with a sensitivity of  $7 \times 10^6$  V/W at  $R_f = 20$  M $\Omega$  for 6328Å wavelength) was used as the detector. All measurements were performed at a 90 degree scattered angle. Temperature was repeatedly cycled from about 50°C below the cloud point to about 30°C above it at a constant heating and cooling rate, 2 °C/min. Reproducibility of the cloud point on successive temperature cycles was fairly good.

**FT-IR Spectroscopy** : IR spectra were obtained using an Analect FX-6160 FT-IR spectrophotometer. Blends with various concentrations were prepared by 3 wt % solutions in toluene. For the analyses, blend solutions of toluene were directly in-

jected into the liquid cell. Thirty-two scans at a resolution of  $2\text{cm}^{-1}$  were signal-averaged.

**Fluorescence Spectroscopy** : Fluorescence spectra were obtained using a KONTRON SFM25 spectrophotometer. The thin films of polymers were cast from 5 wt % toluene solution onto slide glasses at room temperature. The films were then dried under vacuum at  $55^\circ\text{C}$  for at least 72 hrs to ensure removal of the residual solvent.

The sample was excited at 260nm in a front-face arrangement to minimize self-absorption. Measured intensities at 278nm(monomer) and 312nm (excimer) showed no overlaps.

## RESULTS AND DISCUSSION

### Optical Clarity

All the styrene/styrene derivative copolymers as well as PS formed transparent films when blended with PVME. A brief review of the literatures indicates that the blends of PS and PVME show the miscibility over a wide range of blend concentrations, even though the miscibility of the two polymer was affected by several factors including solvent, temperature, molecular weight, and concentration.<sup>15-18</sup> From the standpoints of optical clarity, the blends cast in toluene shows miscibility over the whole concentration range examined in this study regardless of the chemical nature of styrene derivatives as a minor comonomer components. The literatures<sup>19-21</sup> show the same results as the fact that the PS/PVME blends cast in toluene show miscibility whereas the blends cast in chloroform or trichloroethane, etc. show phase separation.

### Phase Diagram

The observed cloud points of mixtures of PS with PVME is plotted in Fig. 2. The LCST behavior of PS/PVME blends is well known<sup>5,6,19,20</sup> The specific interaction between polystyrene and PVME, arising their compatibility, was reported to reside on the phenyl group of the styrene monomer and  $\text{COCH}_3$  of PVME.

Fig. 1 also illustrates the comparison in the

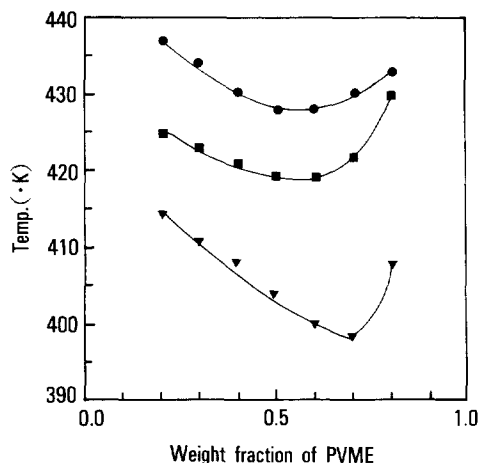


Fig. 2. Cloud points of mixtures containing PVME and one of the PS (●), P(S9-co-*p*MeS1) (■), and P(S9-co-*m*MeS1) (▼).

cloud points to the blends of PVME and one of the PS, P(S9-co-*m*MeS1), and P(S9-co-*p*MeS1). In this case, there is a clear indication of the effect in addition of *p*-methylstyrene or *m*-methylstyrene on the miscibility of PS/PVME blends. The copolymers are evidently less compatible with PVME than PS, and the cloud points of mixtures containing styrene/styrene derivative copolymer are shifted downward by about  $10^\circ\text{C}$  for the p(S9-co-*p*MeS1)/PVME mixtures and by more than  $30^\circ\text{C}$  for p(S9-co-*m*MeS1)/PVME mixtures. It is interesting to note that the cloud points of mixtures containing copolymer are shifted downward in the order  $\text{PS} > \text{p(S9-co-}i>p\text{MeS1)} > \text{p(S9-co-}i>m\text{MeS1)}$  with PVME, regardless of the copolymer concentrations, meaning that the miscibility of the styrene-containing copolymers and PVME blends becomes weaker in that order.

Fig. 3 shows the cloud points of the mixtures of P(S-co-*m*MeS) and PVME of two compositions of 90 % and 80 % styrene [P(S9-co-*m*MeS1) and P(S8-co-*m*MeS2), respectively] and PVME. It clearly shows that the mixtures become less miscible as the composition of *m*-methylstyrene in the copolymer increases. The same trend in the light scattering results was observed for the blends of PVME

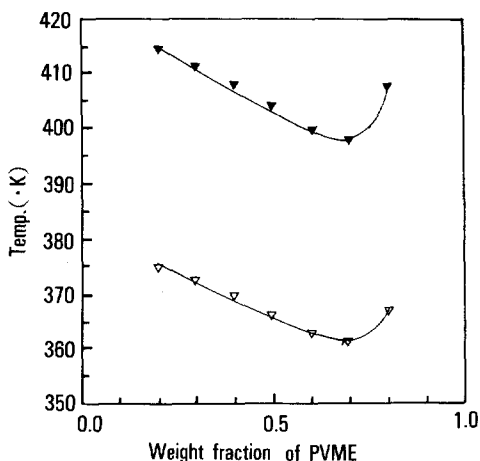


Fig. 3. Cloud points of mixtures containing PVME and one of the P(S9-co-*m*MeS1) (▼) and P(S8-co-*m*MeS2) (▽).

with copolymers of styrene and *p*-methylstyrene of the same compositions.

#### FTIR Spectra

Hsu and co-workers<sup>3</sup> reported on the FTIR study of PS/PVME blends that PVME has a strong doublet at 1085 and 1107 cm<sup>-1</sup> with a shoulder at 1132 cm<sup>-1</sup> and the relative intensity of this doublet varies considerably when the blend sample is cooled or heated. In addition, 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<sup>-1</sup> peak was greater than that of the 1107 cm<sup>-1</sup> peak for the miscible blend (We called it "Hsu's criterion."). They also reported that another peak sensitive to miscibility in the PS/PVME blends is that of 698 cm<sup>-1</sup> which is generally assigned to the C-H out-of-plane bending vibration of phenyl ring in PS.

Our results investigated by FTIR showed a similar tendency in the variation of the relative intensity of a doublet in 1100 cm<sup>-1</sup>, except that the peak height ratio of 1108 cm<sup>-1</sup> component to 1080 cm<sup>-1</sup> one ( $A_{1108\text{cm}^{-1}}/A_{1080\text{cm}^{-1}}$ ) in this study is much larger than similar peak height ratio of  $A_{1107\text{cm}^{-1}}/A_{1085\text{cm}^{-1}}$  for the PS/PVME systems of Hsu, et al.<sup>3</sup> The difference may be due to the different experimental methods to obtain FTIR spectra: a

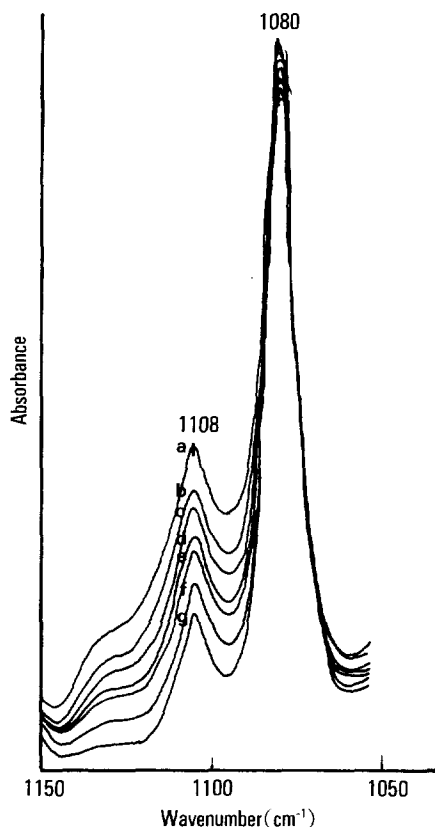
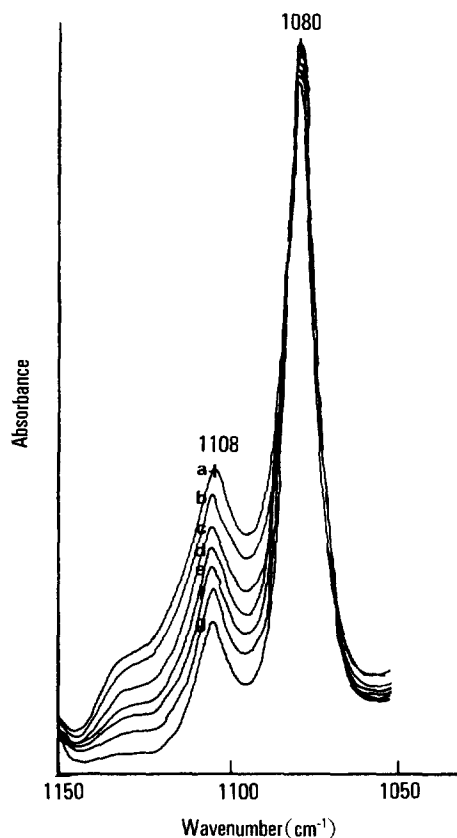


Fig. 4. Relative Intensity of the doublet of the 1100 cm<sup>-1</sup> region for P(S9-co-*p*MeS1)/PVME Blend: (a) 20, (b) 30, (c) 40, (d) 50, (e) 60, (f) 70, and (g) 80 wt. % P(S9-co-*p*MeS1).

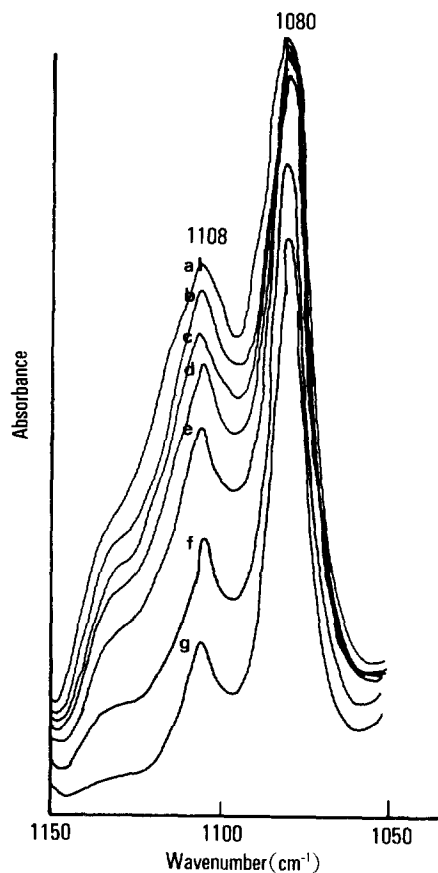
solvent-casted KBr film was used in their work of Hsu et al.,<sup>3</sup> whereas a direct blend solution of toluene was used in this work. The larger peak height ratio may be caused by solvent effect. It was assumed, however, that the different peak height ratio has no significant meaning to define the miscibility of styrene-containing copolymer with PVME, since the FTIR experiments in this work were carried out under the same conditions for all the blend samples. In fact, our light scattering and fluorescence spectral studies will prove the assumption to be valid, which will be discussed later.

The FTIR spectra in the 1100 cm<sup>-1</sup> region are presented in Fig. 4~6 for the blends of PVME and



**Fig. 5.** Relative Intensity of the doublet of the  $1100\text{ cm}^{-1}$  region for P(S8-co-*p*MeS2)/PVME Blend. ; (a) 20, (b) 30, (c) 40, (d) 50, (e) 60, (f) 70, and (g) 80 wt. % P(S8-co-*p*MeS2).

one of the P(S9-co-*p*MeS1), P(S8-co-*p*MeS2), and P(S8-co-*m*MeS2), respectively, as a function of increasing PVME concentration. In all cases, the spectra show that the  $1080\text{ cm}^{-1}$  component is dominant over the  $1108\text{ cm}^{-1}$  component and the relative intensity of  $1108\text{ cm}^{-1}$  band increases as the PVME concentration increases in the blends. More interesting feature of the doublet of  $1100\text{ cm}^{-1}$  region is shown in P(S-co-*m*MeS)/PVME blends, as shown in Fig. 6. In contrast to Figs. 4 and 5, there is a remarkable increase and decrease in the absorbance at  $1108\text{ cm}^{-1}$  and at  $1080\text{ cm}^{-1}$ , respectively, as PVME concentration increases. Careful inspections of Fig. 4 through Fig. 6 show that the re-



**Fig. 6.** Relative Intensity of the doublet of the  $1100\text{ cm}^{-1}$  region for P(S8-co-*m*MeS2)/PVME Blend. ; (a) 20, (b) 30, (c) 40, (d) 50, (e) 60, (f) 70, and (g) 80 wt. % P(S8-co-*m*MeS2).

lative intensity of  $1080\text{ cm}^{-1}$  did not change significantly compared to that of  $1108\text{ cm}^{-1}$  for the blends of PVME with *p*-methylstyrene containing copolymer. However, the ratio of the intensity of the doublet bands decreased remarkably as the PVME concentration increased in the blends of PVME with *m*-methylstyrene containing copolymer. Taking account the Hsu's criterion into consideration that the intensity of  $1080\text{ cm}^{-1}$  band is greater than that of  $1108\text{ cm}^{-1}$  for miscible blends and that the reverse corresponds to immiscible blends, the FTIR results for the P(S8-co-*m*MeS2)/PVME blends imply that the miscibility became weak as

the 20 wt.% of *m*-methylstyrene is included in the copolymer. Similar results were obtained in the case of the P(S9-co-*m*MeS1)/PVME blends.

From the figures mentioned above, it is evident that the FTIR spectral features are sensitive to the miscibility of blends of PVME with styrene/styrene derivative copolymers, as shown in the system of Hsu et al. The different FTIR spectra suggest that the miscibility of P(S-co-*m*MeS) with PVME would be much poorer than that of P(S-co-*p*MeS) with PVME, when the composition of styrene derivative is the same. The fact implies that the miscibility of the blends is considerably affected in a certain manner by the chemical nature of the styrene derivative in the copolymers. At this moment, *m*-methylstyrene unit in the copolymers shows stronger influence on the miscibility with PVME than *p*-methylstyrene one in the copolymers when the copolymers of those styrene derivatives and styrene are blended with PVME. The speculation is well proved when the relative intensities of the doublet of 1100  $\text{cm}^{-1}$  region for the blends of PVME and any of the copolymers are

compared, as shown in Figs. 7 and 8.

Fig. 7 illustrates the comparison in the relative intensity of the doublet of 1100  $\text{cm}^{-1}$  region for the blends of PVME and one of the P(S9-co-*m*MeS1) and P(S9-co-*p*MeS1). In this figure, the copolymer concentration in the blends are 30, 50 and 70 wt.%. The figures show clearly that the intensity at 1108  $\text{cm}^{-1}$  component relative to that of 1080  $\text{cm}^{-1}$  one is larger in case of P(S9-co-*m*MeS1)/PVME blends than in P(S9-co-*m*MeS1)/PVME blends regardless of the copolymer(or PVME) concentrations. Comparison of the figures also shows that the relative intensity of 1108  $\text{cm}^{-1}$  component increased as the copolymer concentration is decreased(PVME concentration is increased) regardless of the copolymer types.

The similar trend in FTIR results was observed for the blends of PVME with copolymers of styrene and styrene derivative of 80/20 composition by weight in feed ratio, as shown in Fig. 8. Fig. 8 shows the relative intensity of the doublet of 1100  $\text{cm}^{-1}$  region for the blends of PVME and one of the P(S8-co-*m*MeS2) and P(S8-co-*p*MeS2). Accord-

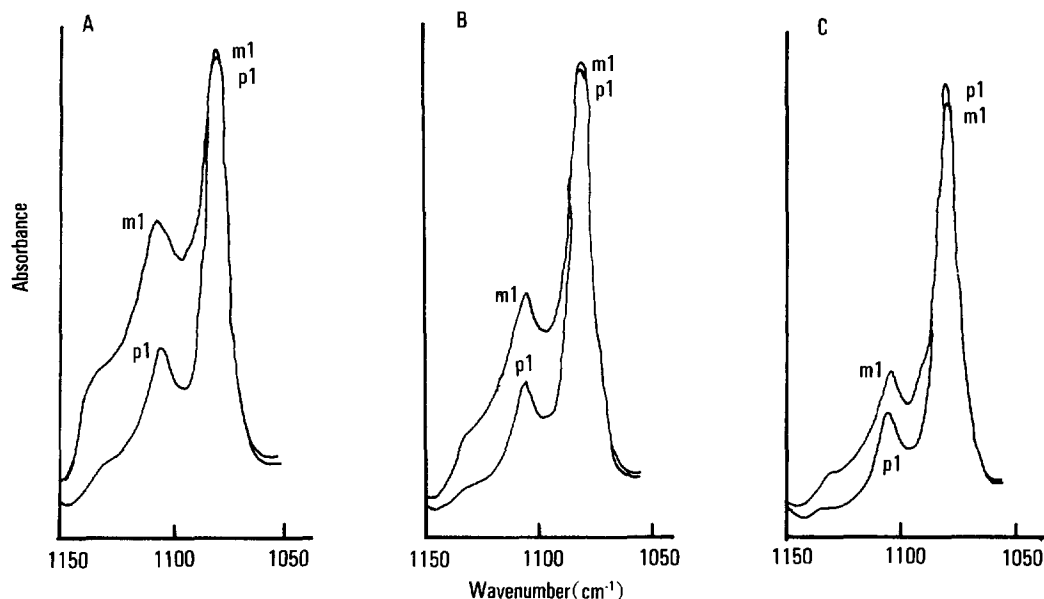


Fig. 7. Relative Intensity of the doublet of the 1100  $\text{cm}^{-1}$  region for PVME and one of the P(S9-co-*p*MeS1)(*p*1) and P(S9-co-*m*MeS1)(*m*1). Copolymer wt. % in blends (A) 30 ; (B) 50 ; (C) 70.

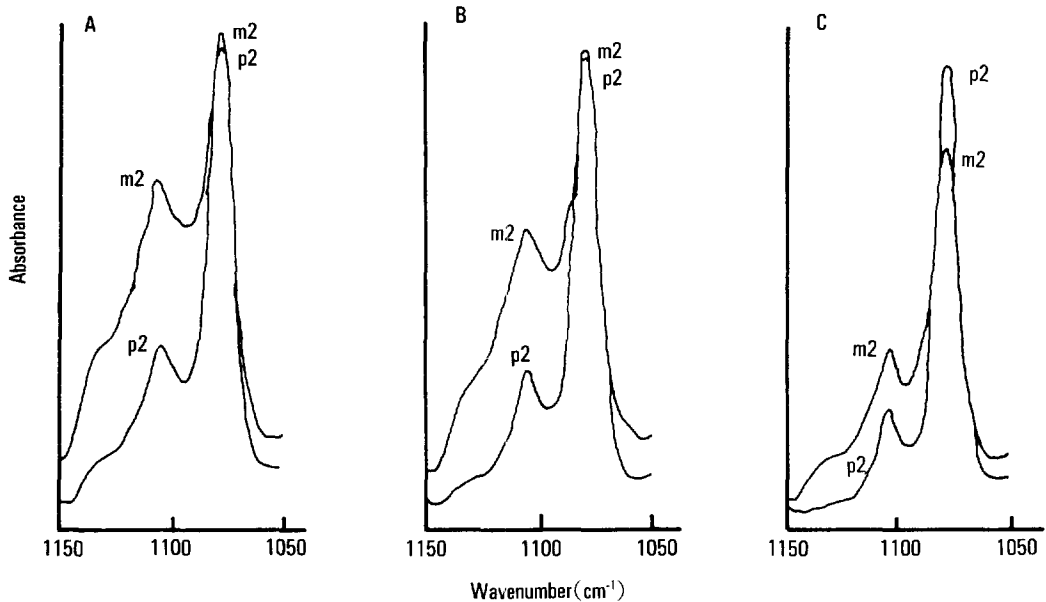


Fig. 8. Relative Intensity of the doublet of the  $1100\text{ cm}^{-1}$  region for the blends of PVME and one of the P(S8-co-*p*MeS2) (*p*2) and P(S8-co-*m*MeS2) (*m*2). Copolymer wt. % in blends (A) 30 ; (B) 50 ; (C) 70.

ding to the Hsu's criterion, the miscibility decreased with increasing PVME concentrations while the miscibility of the copolymers with PVME become weaker in case of P(S8-co-*m*MeS2) than in P(S8-co-*p*MeS2).

We tested the specific absorptions in PS in order to find the potential sensitivity to miscibility of the styrene/styrene derivative copolymer/PVME blends. Hsu et al.<sup>3</sup> also insisted that the band assigned to the CH out-of-plane bending vibration around  $700\text{ cm}^{-1}$  is also sensitive to the miscibility of PS/PVME blends. However, we were not able to obtain any significant informations from the  $700\text{ cm}^{-1}$  component for all the blends tested in this study.

#### Fluorescence Spectra

It is now recognized that the observed miscibility is strongly dependent upon the technique used ; a polymer blend may be miscible using one particular method while be immiscible using another sensitive method, simply due to the fact that the size of the phases is below the resolution limit of the first technique.<sup>22</sup>

Fluorescence spectroscopy is one of the new and more sensitive techniques in using the miscibility study of polymer blends. It exhibits a high sensitivity to detect small-scale heterogeneities and has the ability to analyze small concentrations of one component.<sup>23~27</sup> Although the application of this technique is restricted to the systems such as aromatic vinyl homo- and copolymers or aromatic polyester, it has been proved by many investigators that excimer fluorescence may provide detailed molecular information on intermolecular aggregation phenomena associated with phase separation in immiscible blends.<sup>23</sup> In our previous work,<sup>11</sup> we reported that the excimer fluorescence technique was successfully applicable to determine the miscibility behavior of poly(vinyl methyl ether) (PVME) with poly(styrene-co-1-vinylnaphthalene) or poly(styrene-co-2-vinylnaphthalene).

In Fig. 9, the emission intensity ratio of excimer to monomer,  $I_D/I_M$ , measured at their maximum emission wavelength is plotted as a function of copolymers weight for the blends containing PVME and one of the PS, P(S8-co-*p*MeS2), and P(S8-co-



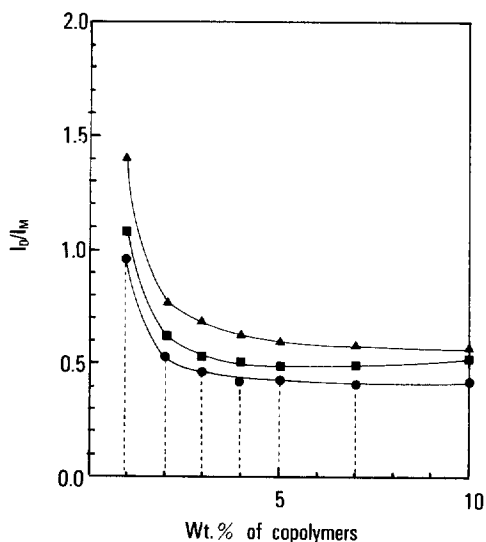


Fig. 9. Ratio of excimer to monomer fluorescence intensities of blends containing PVME and one of the PS(●), P(S8-co-*p*MeS2) (■) and P(S8-co-*m*MeS2) (▲).

*m*MeS2). In these plots, smooth curves have been drawn through the data and the  $I_D/I_M$  values were given in the order of P(S8-co-*m*MeS2) > P(S8-co-*p*MeS2) > PS regardless of the PVME concentrations. The ratio of excimer to monomer intensity,  $I_D/I_M$ , at given casting and measuring temperatures should be a qualitative measure of interaction. The smaller  $I_D/I_M$  ratio corresponds to larger interaction. The result was in accordance with the FT-IR spectra, which exhibits that the miscibility of the copolymers with PVME became weaker in the order PS > P(S8-co-*p*MeS2) > P(S8-co-*m*MeS2). However, the effect of comonomer composition on the fluorescence spectra was not clearly shown.

### CONCLUDING REMARKS

FTIR spectroscopic studies were carried out on the miscibility of copolymers of styrene and *p*- or *m*-methylstyrene with PVME. The miscibility of the styrene/styrene derivative copolymers and PVME was discussed in terms of the "Hsu's criterion" to determine the miscibility of the blends. The doublet band around  $1100\text{ cm}^{-1}$  associated

with  $\text{COCH}_3$  in PVME on FTIR spectra is used as a potentially useful means of defining miscibility of the blends. We observed that the miscibility of the copolymers of styrene and *p*-methylstyrene showed better with PVME than with copolymers of styrene and *m*-methylstyrene, although the introduction of styrene derivatives decreased the miscibility of polystyrene with PVME. The miscibility of the copolymers of styrene and styrene derivative with PVME decreased with increasing compositions of styrene derivatives in copolymers and increasing PVME concentration.

This behavior was confirmed by fluorescence spectra as well as their phase diagrams by light scattering.

**Acknowledgements** : The work is supported by the Korea Science and Engineering Foundation (Grant #901-1005-004-2). We are grateful to Prof. R. J. Roe, University of Cincinnati, U. S. A., for his helpful discussions for this subject. Our thanks are also attributed to the Korea Petrochemical Co. for the experimental aids in FTIR spectroscopies.

### REFERENCES

1. M. M. Coleman and D. F. Varnell, *Macromolecules*, **13**, 1403 (1980).
2. D. F. Varness, J. R. Runt, and M. M. Coleman, *Macromolecules*, **14**, 1350 (1981).
3. F. J. Lu, E. Benedetti, and S. L. Hsu, *Macromolecules*, **16**(9), 1525 (1983).
4. D. F. Varnell and M. M. Coleman, *Polymer*, **22**, 1324 (1981).
5. G. Guerra, S. J. Choe, D. J. William, F. E. Karasz, and W. J. MacKnight, *Macromolecules*, **21**, 231 (1988).
6. D. Garcia, *J. Polym. Sci., Polym. Phys. Ed.*, **22**, 107 (1984).
7. J. Y. Lee, P. C. Painter, and M. M. Coleman, *Polymer Preprints*, **29**, 1, 313 (1988).
8. C. Qin, A. T. N. Pires, and L. A. Belfiore, *Macromolecules*, **24**, 666, (1991).

9. J. Y. Lee, P. C. Painter, and M. M. Coleman, *Macromolecules*, **21**, 346 (1988).
10. D. P. Kang, C. S. Ha, and W. J. Cho, *J. Polym. Sci., Polym. Chem.*, **27**, 1401 (1989).
11. J. H. Ryou, H. D. Kim, D. S. Lim, C. S. Ha, and W. J. Cho, *Polymer(Korea)*, **16**, 2, 322 (1992).
12. J. H. Ryou, M. S. Thesis, Pusan National University, Pusan, Korea (1992).
13. R. J. Roe and W. C. Zin, *Macromolecules*, **13**, 1221 (1980).
14. C. S. Ha, W. J. Cho, and R. J. Roe, *Polymer(Korea)*, **14**, 4, 322 (1990).
15. M. Bank, J. Leffingwell, and C. Thies, *Macromolecules*, **4**, 43 (1971).
16. R. G. Gelles and C. W. Frank, *Macromolecules*, **15**, 741 (1982).
17. T. Nishi and T. K. Kwei, *Polymer*, **16**, 285, (1975).
18. J. L. Harary, *Polymer*, **25**, 956 (1984).
19. T. K. Kwei, T. Nishi, and R. F. Roberts, *Macromolecules*, **7**, 667 (1974).
20. T. Nishi, T. T. Wang, and T. K. Kwei, *Macromolecules*, **8**, 227 (1975).
21. D. D. Davis and T. K. Kwei, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 2337 (1980).
22. S. Krause, *Chemtracts-Macromol. Chem.*, **2**, 367 (1991).
23. D. P. Kang and W. J. Cho, *Polymer(Korea)*, **10**, 3, 191 (1986).
24. S. Reich and Y. Cohen, *J. Polym. Sci., Polym. Phys. Ed.*, **19**, 1255 (1981).
25. S. N. Semerak and C. W. Frank, *Macromolecules*, **14**, 443 (1981).
26. R. Gelles and C. W. Frank, *Macromolecules*, **15**, 1486 (1982).
27. R. Gelles and C. W. Frank, *Macromolecules*, **16**, 1448 (1983).