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# Polyurethane-polystyrene interpenetrating polymer networks synthesized in the presence of a common solvent

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## SUMMARY

Interpenetrating polymer networks (IPN's) of polyurethane and polystyrene were synthesized by simultaneous polymerization. The effect of compositional variation and the presence of a common solvent in the reaction medium on the rate of polymerization, the onset of phase separation, and the morphology of product were investigated. 1,4–Dioxane was selected as a common solvent by the swelling experiment. The rate of network formation in the early stage of polymerization process increased with increasing the polyurethane composition. When 1,4–dioxane was present in the reaction medium, the extent of reaction of both components at the onset of phase separation was higher than that of IPN's by bulk preparation. The morphology of final product was influenced by the extent of reaction at the onset of phase separation. The density, glass transition behavior, and thermal stability were also studied.

## INTRODUCTION

Interpenetrating polymer networks (IPN's) are defined as a mixture of two or more crosslinked polymer networks which have partial or total physical interlocking between them. IPN's can be obtained by latex blending, sequential polymerization, and simultaneous polymerization (1).

Like other multipolymer systems, IPN exhibits phase separation, which arises from the mutual incompatibility inherent in polymers. The interpenetration plays a significant role in enhancing the intermixing of the polymer components through physical interlocking which prohibits further phase separation when the polymerization is proceeded after gel point is reached (2).

The morphology of IPN's and their properties depend on several factors, viz. miscibility of the constituents, rate of the network formation, and chain mobility. Those factors are related to the process conditions, such as the synthesis temperature, synthesis pressure, and composition (3,4).

Recently, interest centered on the effect of composition, degree of cross–linking, synthesis temperature and pressure on the morphology, phase separation, and network formation behavior during the polymerization process (3–12).

Addition of a common solvent of the constituent polymers to the reaction mixture can be another factor enhancing the miscibility in IPN synthesis. The existence of small amount of solvent in the reaction mixture has direct and indirect effects on the onset point of phase separation, the rate of phase separation, and the rate of network formation. The onset point of phase separation moves toward higher conversion with increasing the amount of solvent due to the enhancement of miscibility, while the rate of phase separation increases due to low medium viscosity.

In this study, the effect of the presence of common solvent in the reaction medium on the phase separation and the network interlocking process during the simultaneous polymerization was analyzed.

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## EXPERIMENTAL

### Materials

Poly(tetramethylene ether) glycol (PTMG, molecular weight 1020), 1,4–butanediol (BD), and trimethylol propane (TMP) were degassed at 60 °C for about 5hr under vacuum. Styrene monomer was purified before use (13). 4,4'–diphenylmethane diisocyanate (MDI), divinyl benzene (DVB, 50% purity), and 2,2'–azobis isobutyronitrile (AIBN) were used without further purification. Solvents, such as 1,4–dioxane, were dried over Linde 4A molecular sieves before use.

### Synthesis

The isocyanate–terminated polyurethane prepolymer was prepared by reacting 1 equiv. of PTMG with 2 equiv. of MDI at 60 °C. The reaction was continued until the theoretical isocyanate contents was reached as determined by the di–n–butylamine method (14). A mixture of TMP and BD in 1:1 equivalent ratio was used as the crosslinking and chain extending agent for the polyurethane (PU) network and DVB was used as the crosslinking agent for the polystyrene (PS) network (2.8 wt%). IPN's of PU and PS were prepared by mixing PU prepolymer, BD/TMP mixture (amount adjusted to give total NCO/OH ratio as 1), styrene monomer, DVB, AIBN (1 wt% of PS component mixture), and common solvent (1,4–dioxane, 25 wt% of The PU/PS component mixture). The homogeneous mixture was charged in a glass plate mold and glass tubes, which then were degassed and sealed. The reaction mixture was polymerized at 60 °C for 72hr. Samples prepared were coded with a letter denoting the component (U for polyurethane, S for polystyrene and D for 1,4–dioxane) and a number denoting the weight percentage of the component.

### Measurements

Swelling experiment (15) was conducted. To select an appropriate common solvent, the solubility parameters ($\delta$) of polyurethane, polystyrene,and PU–PS IPN were measured by soaking a small rectangular specimens (ca. 0.1g) in fifteen different solvents with $\delta$ values ranging from 15.1 ($J^{1/2}cm^{3/2}$) (diethyl ether) to 24.3 ($J^{1/2}cm^{3/2}$) (acetonitrile). The swelling experiments were conducted at 25 °C until the equilibrium state was reached.

The reaction kinetics in early stage of the individual network formation during the IPN synthesis was investigated as follows : For PU, the extent of reaction was determined by measuring the free NCO group through di–n–butylamine titration method. The measurement was performed while the fluidity of the reacting mixture was remained. For PS, the extent of reaction was measured by weighing the samples after stripping the unreacted styrene monomer under vacuum at 20 °C for 5 days.

The change of turbidity during the polymerization reaction was determined using the turbidimeter (HF model DRT–1000) connected to a recorder. The samples in glass tubes (ID 4mm) were inserted in the temperature controlled chamber, kept at 60 °C. The beginning of the phase separation was indicated at the point of the abrupt increase of the turbidity. It was assumed that the polymerization starts immediately after insertion of the sample into the chamber.

The morphology of the IPN's was observed using the transmission electron microscope (TEM) (JEOL model JEM–2000X). The sample preparation technique used was based on Kato's osmium tetraoxide staining technique (16) and Matsuo's two–step sectioning method (17).

The density at room temperature was obtained using the density gradient column.

The glass transition temperatures were determined using a duPont 982–9900 dynamic mechanical analyzer. The oscillation amplitude was 0.2mm. The scanning rate was 5 °C/min over a temperature range of –80 to 140°C. The glass transition temperature was noted as the peak of the loss modulus curve.

TGA thermograms were obtained using a Perkin–Elmer model TGA–II thermogravimetric analyzer. The sample weight was about 10mg, $N_2$ flow rate was $120cm^3/min$, and the heating rate was 40 °C/min.

## RESULTS AND DISCUSSION

Fig.1 shows the swelling coefficient Q versus $\delta$ for the U50S50 IPN and the component polymer networks. Q values were calculated from,

$$Q = \frac{m - m_0}{m_0} \times \frac{1}{d_s}$$

where m is the weight of the swollen sample, $m_0$ is the dry weight, and $d_s$ is the density of the swelling agent. From Fig.1, the solubility parameters of PU, PS network and U50S50 IPN were obtained as 21.7, 18.6, and 20.5 ($J^{1/2}\ cm^{3/2}$), respectively. From the solubility parameter values, 1,4–dioxane ($\delta$ value of 20.5) was selected as the common solvent for the IPN synthesis. The characteristics, such as the chemical stability (18) and boiling point of 1,4–dioxane (101 °C), also, were suitable for use in our experimental condition.

Fig.2 shows the second order plot of the PU formation during the IPN synthesis. The rate of PU formation increased with increasing PU composition. When 1,4–dioxane was present in the reaction medium, the rate of PU formation decreased in comparison with their corresponding IPN's through bulk preparation. The values of second order rate constant $k_{pu}$ are listed in Table 1. $k_{pu}$ was calculated by the usual expression :

$$k_{pu} = \frac{1}{t} \times \frac{x}{(NCO)_0\ (1-x)}$$

Where $(NCO)_0$ is the initial isocyanate concentration (mol/g), x is the fraction of conversion, and t is time (hr). The value of $k_{pu}$ slightly decreased with decreasing

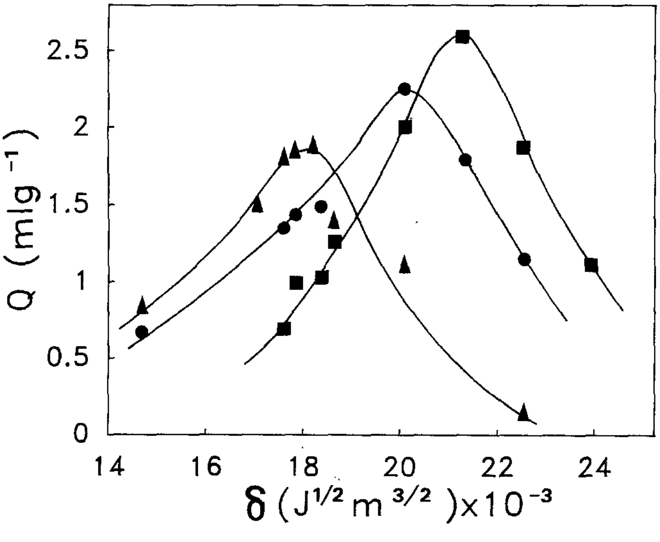

Figure 1. Swelling coefficients vs. solubility parameter plot for PU (■), PS (▲), and U50S50 IPN (●).

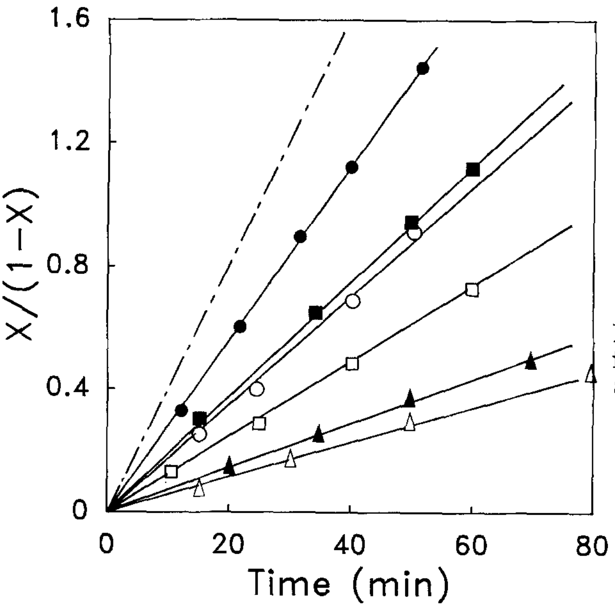

Figure 2. Second order plots for PU polymerization reaction at 60 °C.
●: U75S25, ○ : U75S25D,
■: U50S50, □ : U50S50D,
▲: U25S75, △ : U25S75D,
–·–: U100

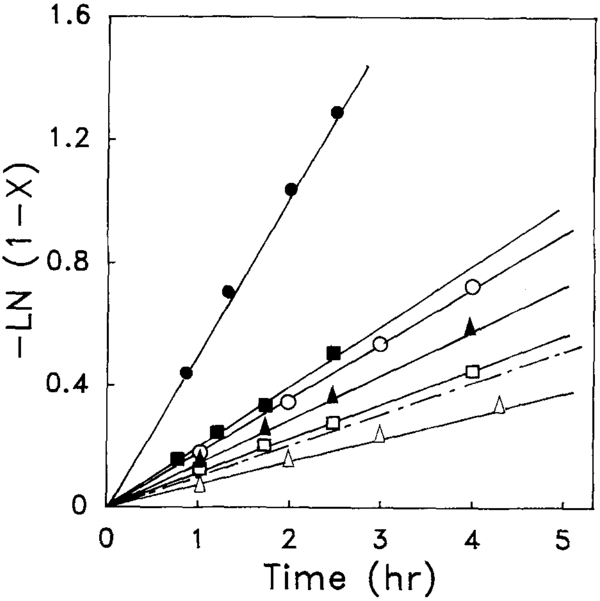

Figure 3. First order plots for PS polymerization reaction at 60 °C.
●: U75S25, ○ : U75S25D,
■: U50S50, □ : U50S50D,
▲: U25S75, △ : U25S75D,
–·–: S100

Table 1 : Rate Constants of PU and PS Formation during the IPN Synthesis and Time at the Onset of Phase Separation

| Composition | $k_{pu} \times 10^{-3}$<br>g mol$^{-1}$hr$^{-1}$ | $k_{ps} \times 10^{1}$<br>hr$^{-1}$ | t<br>min |
|---|---|---|---|
| U75S25 | 1.85 | 5.16 | 4.0 |
| U50S50 | 1.85 | 1.99 | 4.8 |
| U25S75 | 1.52 | 1.45 | 10.0 |
| U75S25D | 1.70 | 1.82 | 13.0 |
| U50S50D | 1.55 | 1.17 | 12.2 |
| U25S75D | 1.43 | 0.76 | 20.5 |

the PU composition, presumably because of the dilution effect of the reactant. Such a diminution has been discussed by S.R.Jin et al (19).

Fig.3 shows the first order plot for the PS formation during the IPN synthesis which satisfactorily described the kinetics of PS formation in the early stage of polymerization process. The rate of PS formation increased with increasing the PU composition, which indicated that the polymerization of PS was accelerated by high viscosity of the reaction medium with reduced termination reaction. When 1,4–dioxane was present in the reaction medium, the rate of PS formation was lower than that of their corresponding IPN's through bulk preparation. The values of first order rate constant $k_{ps}$ are listed in Table 1.

Fig.4 shows the extent of reaction at the time phase separation occurred. The beginning of phase separation occurred at the very early stage of polymerization

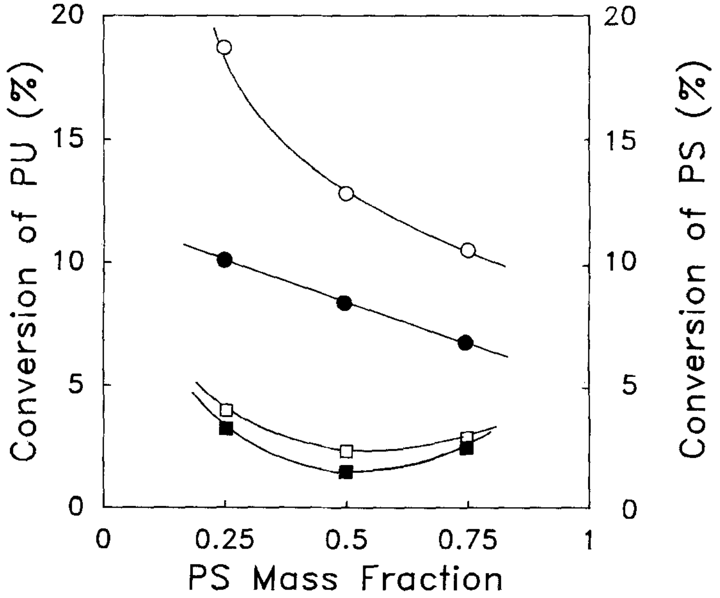

Figure 4. Conversion at the onset of phase separation vs. composition for IPN synthesis at 60 °C : ●,■; Conversion of PU and PS synthesized through bulk polymerization, ○,□; Conversion of PU and PS synthesized in the presence of 1,4–dioxane.

process due to the high incompatibility between PU and PS (Table 1). The conversion of PU at the onset of phase separation decreased with increasing the PS composition. It is probably connected with the rate of PU formation. When the rate of PU polymerization is fast, the conversion of PU at the onset point is high since PU oligomers are soluble in styrene monomer. However when both polymerization rates are similar, the conversion at the onset point of both PU and PS becomes closer to each other. The conversion of PS at the onset of phase separation in the U50S50 IPN was relatively low compared with other compositions, reflecting the lowest mutual compatibility of the component polymers in this composition. The solvent effects are also shown by the increased conversion at onset point.

The morphology via transmission electron microscopy of the IPN's synthesized in this study is shown in Fig.5. The PU phase was stained by osmium tetraoxide and appeared black and the unstained PS phase appeared white in the micrographs.In these IPN's, the distinctly dispersed and spherical PS domains were

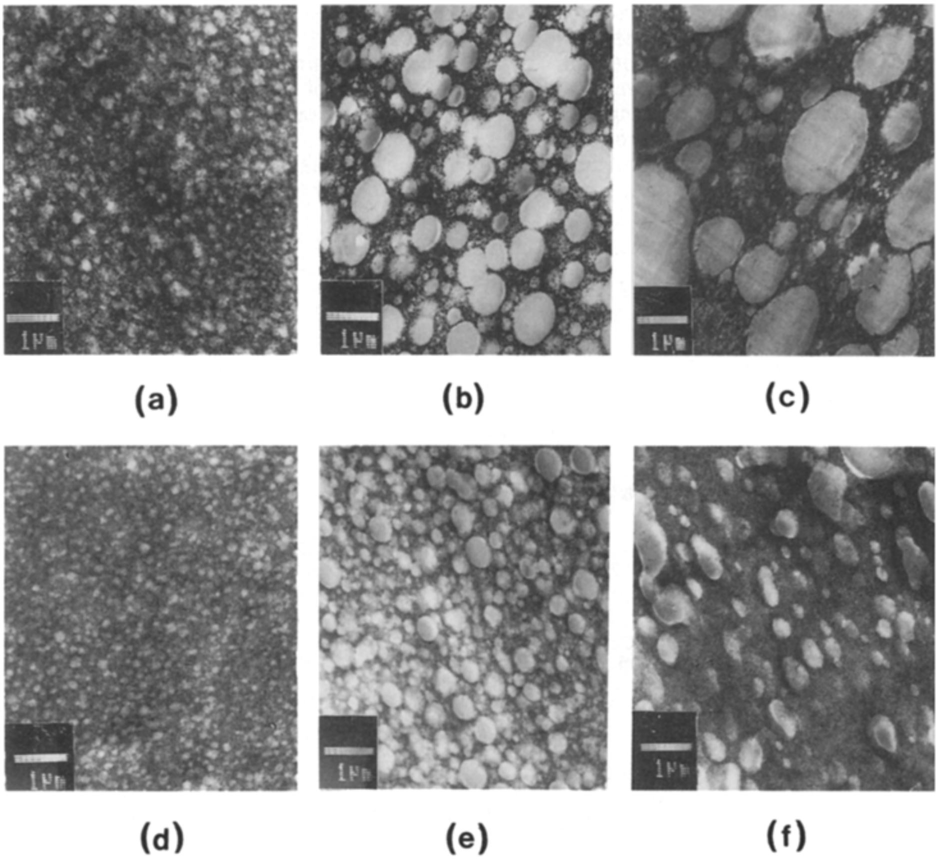

Figure 5. Electron micrographs of IPN's.
(a): U75S25 (b): U50S50 (c): U25S75
(d): U75S25D (e): U50S50D (f): U25S75D

Table 2 : Density and Glass Transition Temperature (Tg)

| Composition | Density (g/cm³) Actual | Density (g/cm³) Calcd.[a] | Tg (°K) Low Tg | Tg (°K) High Tg |
|---|---|---|---|---|
| U100 | 1.0998 | | 248 | |
| S100 | 1.0525 | | | 385 |
| U75S25 | 1.0906 | 1.0880 | 253 | 349 |
| U50S50 | 1.0782 | 1.0762 | 248 | 364 |
| U25S75 | 1.0650 | 1.0643 | 248 | 366 |
| U75S25D | 1.0917 | 1.0880 | — | 337 |
| U50S50D | 1.0788 | 1.0762 | 246 | 360 |
| U25S75D | 1.0668 | 1.0643 | 248 | 352 |

[a] Based on the volume additivity of the components.

observed since the PU network was formed first with faster rate of polymerization. The PS domain size decreased with increasing the PU composition due to the combined effect of the increased rate of network formation and the increased medium viscosity. When 1.4–dioxane was present in the reaction medium,the PS domain size became more uniform and reduced in size when compared with their corresponding IPN's prepared through bulk preparation. The presence of 1.4– dioxane in the reaction medium during the polymerization process increased the compatibility of the component polymers and raised the conversion at the onset of phase separation. Thus the phase separation proceeded at the later stage of reaction.

The densities and the glass transition temperatures (Tg's) of the IPN's are listed in Table 2. The IPN's all show slightly increased densities over the calculated densities based on the volume additivity of the component polymers. In contrast to

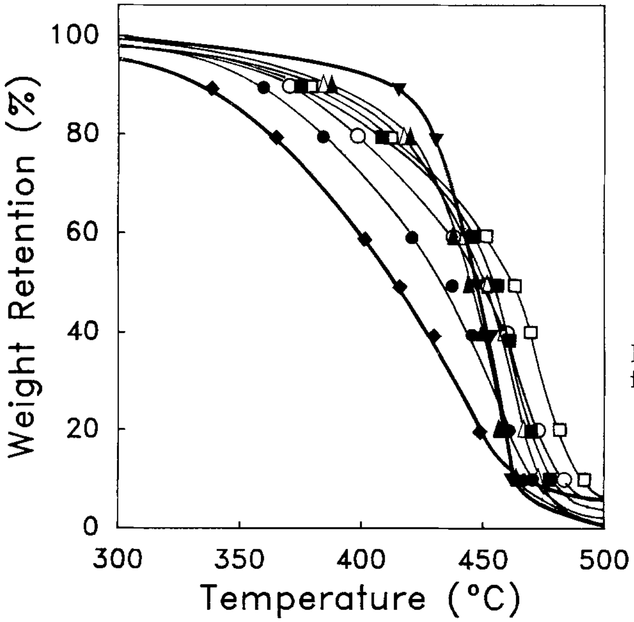

Figure 6. TGA thermograms for IPN's.
● : U75S25, ○ : U75S25D,
■ : U50S50, □ : U50S50D,
▲ : U25S75, △ : U25S75D,
◆ : U100,
▼ : S100

the previous studies (7,20), these increases are relatively small, but still show the presence of the physically intermixed (interlocked) phase boundaries since the polyurethane and polystyrene show negative volume change of mixing (7).

The glass transition behavior also indicates intermixed phases present in both component networks due to interpenetration. The shifts of the Tg's of the PU–dominant phases (low Tg) are not observed except in the U75S25 IPN. However,the Tg's of the PS–dominant phases (high Tg) shifted to lower temperature with intermixing of polyurethane networks. The presence of the common solvent enhanced the interpenetration by delaying the onset of phase separation during polymerization. Thus the Tg's of PS–dominant phases were lower when the IPN's synthesized in the presence of common solvent.

The thermogravimetric analysis results are shown in Fig.6. The enhancement of the thermal stability of PU–PMMA (21) and PU–PS IPN's (3,22) was reported, and it was presumed that the unzipped MMA or styrene monomer acted as the radical scavenger for the radicals produced from the PU degradation. The enhancement of the thermal stability became more prominent when the degree of interpenetration increased by the presence of the intermixed layer of PU and PS component. The IPN's synthesized in the presence of common solvent all showed increased thermal stability due to the higher degree of interpenetration.

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