Reaction kinetics of polyurethane/polystyrene interpenetrating polymer networks by infra-red spectroscopy

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The reaction kinetics of simultaneous interpenetrating networks (SIN) composed of polyurethane (PU) and polystyrene (PSt) were studied by infra-red spectroscopy. The effects of synthesis temperature, polyurethane/polystyrene composition, catalyst concentration, initiator concentration and amount of added divinylbenzene on the synthesis of the IPN were investigated. It was found that all of the components in the PU/PSt IPN system follow the Beer–Lambert law. The isocyanate, NCO, absorption band at 2280 cm^{-1} and the C=C peak at 1645 cm^{-1} show a gradual decrease as the respective polymerizations proceed, and can be used to monitor the extent of reaction. The kinetic results obtained by spectroscopic analysis were in reasonable agreement with those obtained by chemical titration. It was found that the reactions of different components in the IPN followed their normal distinct reaction mechanisms and there was no interference between their reaction mechanisms. Increasing the PU/PSt proportion enhanced the rate of formation of PU and lessened the rate of formation of PSt. Changing the concentration of OcSn (AIBN) had an effect on the rate of formation of PU (PSt) and no effect on the rate of formation of PSt (PU). The rate of disappearance of double bonds in the IPN was increased by introducing a crosslinking agent for polystyrene, DVB. A theory for the cage effect of the PU network is proposed.

(Keywords: interpenetrating polymer networks; polyurethane; polystyrene)

INTRODUCTION

Interpenetrating polymer networks (IPNs) are a new class of polymer–polymer blend material differing from chemical copolymers and mechanical blends. Such systems involve intertwined networks of two polymers prepared by the polymerization of a monomer in the presence of another polymer. The networks are permanent and interlocking, and can be formed by entanglement between crosslinked bonds of different components. The morphology of IPN is fixed as soon as all the chemical reactions take place. It is not changed by exerting external stress or temperature. The development of IPNs is an important area of polymer technology that is challenging and economically rewarding.

Although many papers about IPNs have been published, most of them describe studies of morphology, mechanical properties, and thermal behaviour[1–7]. Studies of reaction kinetics of IPNs have started only recently[8]. The effect of reaction kinetics on the morphology and properties of IPNs is enormous, and merits detailed study.

Polymerization kinetics of an IPN, which is a multicomponent system, are far more complicated than those of a single polymer. The chemical reactions, which may influence each other, are further complicated by physical changes such as gelation, viscosity, volume and phase separation occurring during the process. An IPN is usually an insoluble solid, so many of the methods widely used for kinetic studies of polymerization reactions cannot be effectively applied to this type of system. In this paper it is demonstrated that infra-red spectroscopy is an appropriate method for studying reaction kinetics in IPNs.

The infra-red spectroscopic method requires that absorption peaks of reactants in the system follow the Beer–Lambert law. Specific absorption peaks of reactants are chosen and monitored during the reaction process. In this way the whole synthetic procedure for an IPN may be traced from its onset to complete conversion. So far very few papers have emerged in the literature concerning this approach to the study of IPN reaction kinetics, but as this work neared completion, Meyer[9] described a quantitative study of polyurethane/poly(methyl methacrylate) IPN by Fourier transform infrared spectroscopy. No systematic kinetic data were reported.

In this paper the reaction kinetics of PU/PSt IPN studied by infra-red spectroscopy are described. The effects of composition, temperature, catalyst concentration, initiator concentration, and amount of divinylbenzene on PU/PSt IPN synthesis were investigated. The aim of this research is to establish kinetics parameters which can be used in the reaction injection moulding (RIM) process.

EXPERIMENTAL

Materials

Polyol (Voranol 3010), $M_n = 3100$, OH no. = 55.1, $F_n = 2.23$, was supplied by Dow Chemical Corp. Di-

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isocyanate (TDI) was supplied by Olin. Chemical Corp. Stannous octoate (OcSn) was supplied by M. T. Corp. Styrene (St), purity >98%, was supplied by Shanghai Reagent Factory. Divinylbenzene (DVB) was supplied by Shanghai GaoQiao Factory of Chemical Industry. Azobisisobutyronitrile (AIBN) was supplied by XiAn Chemical Reagent Factory.

Styrene (St) and divinylbenzene (DVB) were washed with 5% aqueous potassium hydroxide solution, followed by distilled water, dried over anhydrous calcium chloride and distilled under vacuum before use. AIBN was dissolved in trichloromethane, then the solution was filtered and the trichloromethane evaporated.

Instrumentation and experimental procedure

An SP-200 infra-red spectrometer was employed to follow the reaction course for all studies. Precisely calculated amounts of the various reagents were mixed and stirred thoroughly. The blend was injected in a sample cell formed by two KBr windows separated by a PVF gasket (about 20 μm). The cell was placed in a thermostat (±1°C) and the absorption peaks were analysed at different times.

RESULTS AND DISCUSSION

The Beer–Lambert law can be expressed as follows:

$$A = abc \qquad (1)$$

where A is the absorbance, a is the molar extinction coefficient, b is the thickness of the test sample, and c is the concentration of the absorbing molecule.

Absorption peaks at 2280 and 1645 cm^{-1} were chosen for NCO (PU) and C=C (PSt), respectively. Both peaks showed a gradual decrease as the respective polymerizations proceeded (*Figure 1*) and for both peaks the Beer–Lambert law was valid (*Figure 2*). This meant that the absorption bands at 1645 and 2280 cm^{-1} could be followed and scanned in studies on the reaction kinetics for the PU/PSt IPN.

As the reaction takes place, the volume of the system contracts. Although the initial thickness of a sample cell is constant, the volume contraction could change the sample thickness and induce an error between the actual and measured absorbances. The absorption peak at 700 cm^{-1}, which is basically constant, was chosen as the internal standard in order to eliminate the error.

The relationship between the conversion ratio (α) and the concentration of the monomers (C) can be expressed as:

$$\alpha = C_0 - C/C_0 \qquad (2)$$

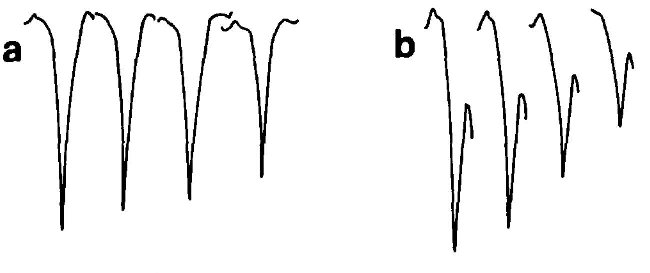

Figure 1 The absorption peak decreased as the reaction proceeded: (a) TDI at 2280 cm^{-1}; (b) St at 1650 cm^{-1}

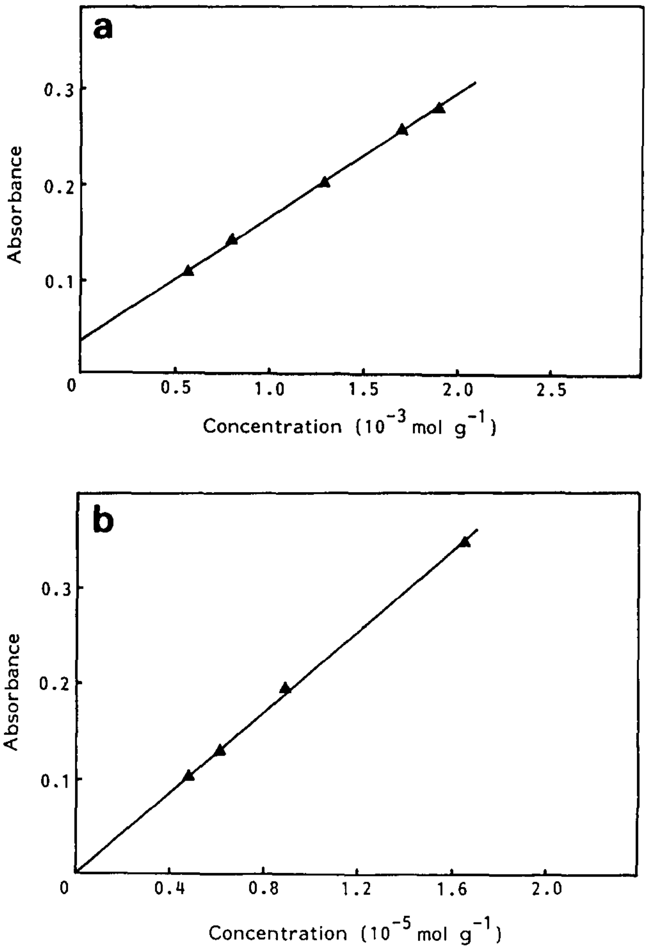

Figure 2 Absorbance *versus* concentration for (a) C=C and (b) NCO

where C_0 is the initial concentration of the absorbing monomers, and C is the concentration of monomers at time t.

The relationship between α and absorbance can be expressed as:

$$\alpha = \frac{C_1^0/C_2^0 - C_1/C_2^0}{C_1^0/C_2^0} = \frac{\dfrac{A_1^0/a_1b_0}{A_2^0/a_2b_0} - \dfrac{A_1/a_1b}{A_2/a_2b}}{\dfrac{A_1^0/a_1b_0}{A_2^0/a_2b_0}} = \frac{A_1^0/A_2^0 - A_1/A_2}{A_1^0/A_2^0} \qquad (3)$$

where C_1^0 and C_1 are taken as the initial concentration and the concentration at time t of St or TDI, respectively, A_1^0 and A_1 are the initial absorbance and the absorbance at time t of St or TDI at 1645 or 2280 cm^{-1}, C_2^0 is the initial concentration of St determined from the absorbance at 700 cm^{-1}, A_2^0 and A_2 are the initial absorbance and the absorbance determined by the change of sample thickness at time t of St at 700 cm^{-1}, b_0 and b are the initial thickness and the actual thickness at time t of the sample.

If the absorbances of reactive molecules at different times can be measured, the conversion ratio of monomers can also be calculated.

Comparison was made between the kinetics of PU formation determined by infra-red spectroscopy and by chemical titration. The results basically coincided (*Figure 3*). This showed that infra-red spectroscopy could be used to study reaction kinetics of the IPN.

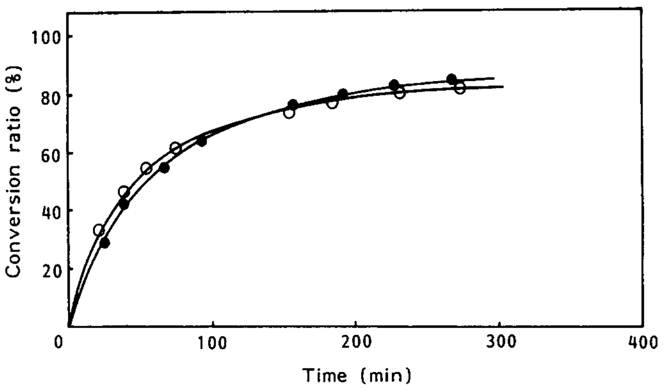

Figure 3 The conversion of NCO groups *versus* time: (○) titrimetry; (●) infra-red spectrometry. NCO/OH = 1:1; OcSn = 0% at 70°C

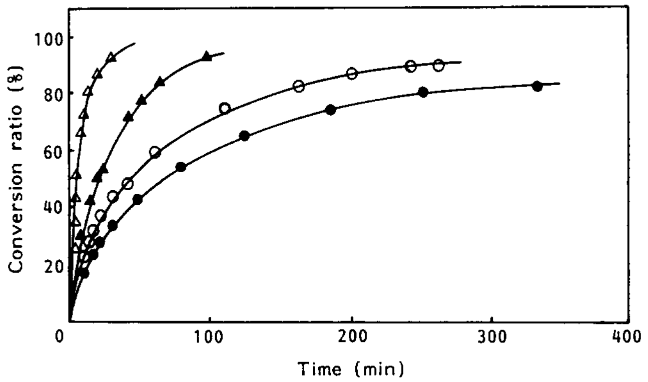

Figure 4 Conversion of NCO *versus* time. OcSn = 0.86%; reaction temperature (°C): △, 76; ▲, 60, ○, 50; ●, 40

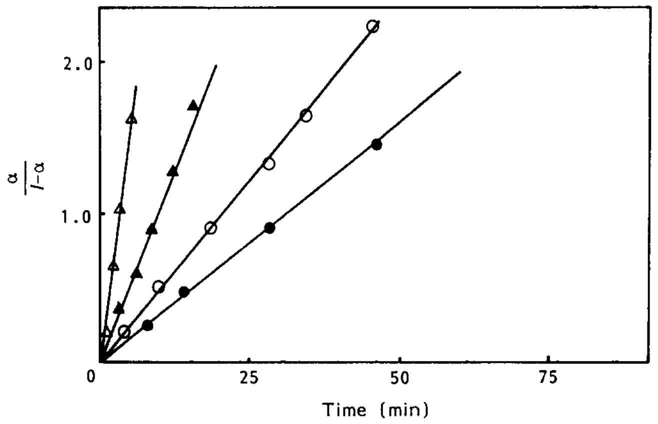

Figure 5 $\alpha/(1-\alpha)$ *versus* time OcSn = 0.86%; reaction temperature (°C): △, 76; ▲, 60; ○, 50; ●, 40

Kinetics of the individual components

The reaction kinetics of Polyol and TDI at different temperatures are shown in *Figure 4*. The value of $\alpha/(1-\alpha)$ is plotted against t in *Figure 5*. The straight lines obtained show that the reaction between Polyol and TDI follows the second-order mechanism. Energy of activation is 23.3 kJ mol^{-1}. *Figure 6* traces the kinetic curves for pure styrene. Obviously it is a radical polymerization and obeys a first-order mechanism.

Reaction kinetics of different components in the IPN

The curves of the reaction kinetics of Polyol and TDI in the IPN at different temperatures are shown in *Figure 7*. Their reaction rate increases with increasing reaction temperature. The second-order kinetic equation could be used to treat the data in *Figure 7*. The relationship between $\alpha/(1-\alpha)$ and t is plotted in *Figure 8*, from which the linear relationship is apparent. It is shown that the formation of PU in the IPN still follows a second-order mechanism. Compared with the formation activation energy of PU, it can be seen that in the IPN the activation energy of formation of PU significantly inreased to 47.0 kJ mol^{-1}.

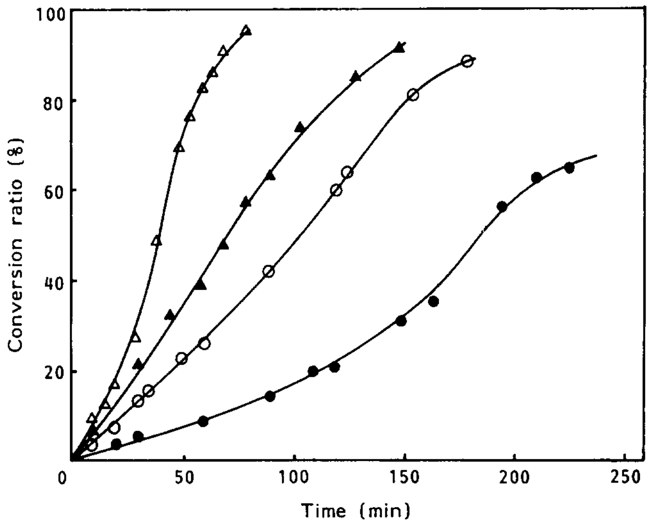

Figure 6 Conversion of St *versus* time. AIBN = 0.41%; reaction temperature (°C): △, 90; ▲, 80; ○, 70; ●, 60

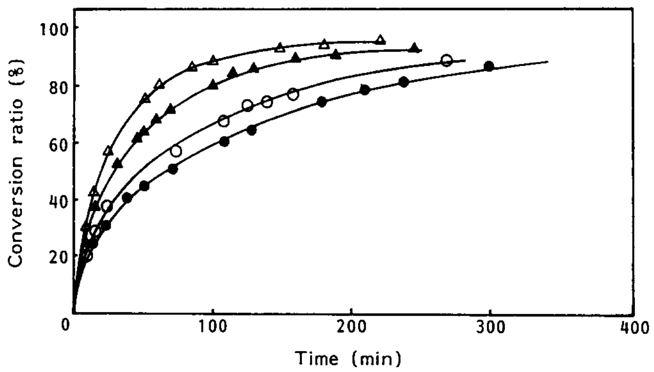

Figure 7 Conversion of NCO group in IPN *versus* time. PU/PSt = 25/75; OcSn = 0.238%; AIBN = 0.41%; reaction temperature (°C): △, 90; ▲, 80; ○, 70; ●, 60

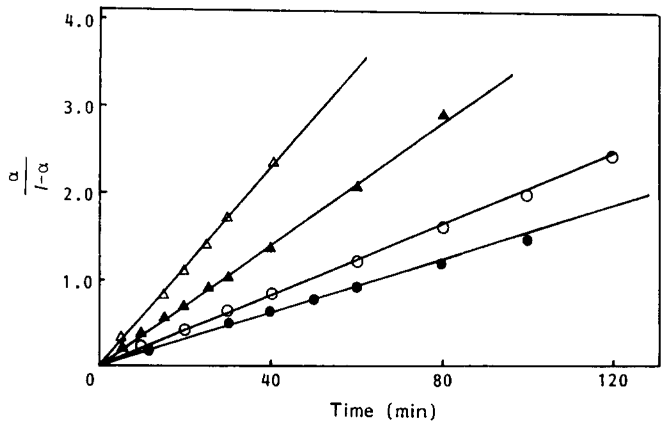

Figure 8 $\alpha/(1-\alpha)$ of NCO in IPN *versus* time. PU/PSt = 25/75; OcSn = 0.238%; AIBN = 0.41%; reaction temperature (°C): △, 90; ▲, 80, ○, 70; ●, 60

Figure 9 shows the reaction kinetics of styrene in the IPN. A first-order kinetic mechanism is valid. The curves of *Figures 6* and *9* are similar, but the reaction rate of St in the environment of IPN is much smaller than that of pure St.

The proportions of OcSn to TDI and AIBN to St as individual components were equal to that in the IPN. Since, in the course of polymerization, two pairs of reactants must interfere with each other in the IPN system, the reaction rate of each component in the IPN is depressed. It was found that the PU formation rate was faster than that of PSt (see *Figures 7* and *9*). As the conversion ratio of NCO groups reaches about 75%, the conversion of the St monomer only reaches about 20% by 80 min (80°C). Thus, it was considered that the effect of the presence of the St polymerization on the formation of PU is different from the effect of the presence of the polymerization of Polyol and TDI on the formation of PSt.

Because both the conversion ratio of St monomer and the molecular weight of PSt were low in comparison with those of PU, in the earlier stage of the reaction, St acted as a solvent for the reaction of Polyol and TDI. Thus, decreasing the concentration of Polyol and TDI was the main reason that the rate of PU formation observed in the IPN was lower than that of pure PU system.

The effects of the presence and reaction of Polyol and TDI on the polymerization of St were far more complicated. After the reaction between Polyol and TDI started, the conversion ratio of the NCO group and the viscosity of the system increased rapidly. In particular, after the PU network had formed, part of the St monomer must have been restrained by the PU network, and the mechanisms of polymerization of St changed gradually from kinetic to diffusive control. It was noticed that the polymerization of St in the IPN also had a gel effect, as can be seen in *Figure 9*.

The effect of PU/PSt ratio

The kinetic curves of Polyol and TDI and that of St for different PU/PSt composition ratios are shown in *Figures 10* and *11*, respectively.

The reaction rate of Polyol and TDI increased and that of St decreased by increasing the proportion of PU to PSt. Thus the effect of the PU network formed on the diffusion of St was more pronounced, and the polymerization rate of St decreased rapidly.

Since all of the components before reaction were miscible in the homogeneous phase, it can be considered that the mixing was on the molecular level. After the reaction started, the viscosity of the system increased rapidly due to the fast formation of PU. The whole system soon attained the gelation point at a low conversion ratio of St. The unreacted St was difficult to diffuse and the polymerization of the St monomer was confined in the cage composed of the PU network. The theory of the cage effect can be used to interpret the formation of the particular cellular structure morphology in IPNs[10].

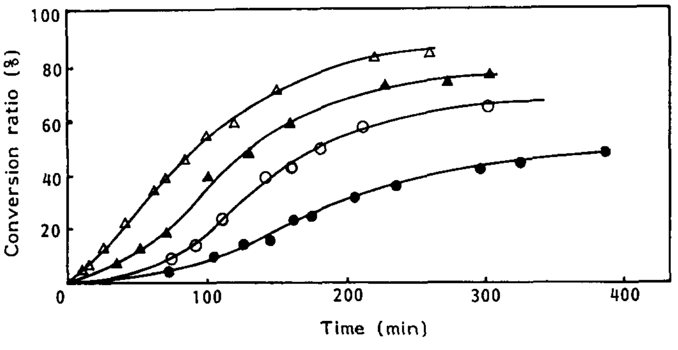

Figure 9 Conversion of St in IPN *versus* time. PU/PSt = 25/75; OcSn = 0.238%; AIBN = 0.41%; reaction temperature (°C): △, 90; ▲, 80, ○, 70; ●, 60

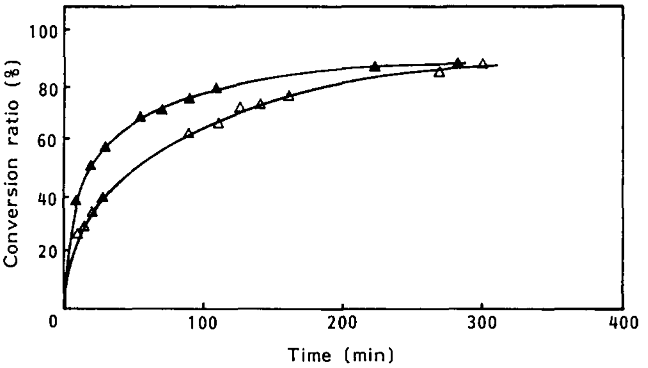

Figure 10 Conversion of NCO group in IPN *versus* time for different PU/PSt ratios. AIBN = 0.41%; OcSn = 0.238%; ▲, PU/PSt = 50/50; △, PU/PSt = 25/75

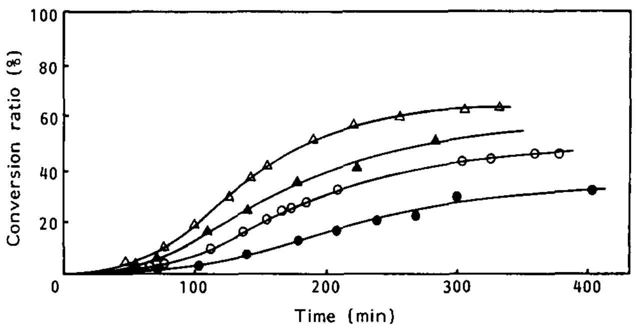

Figure 11 Conversion of St in IPN *versus* time for different PU/PSt ratios. AIBN = 0.41%; OcSn = 0.238%; △, PU/PSt = 25/75, 70°C; ▲, PU/PSt = 50/50, 70°C; ○, PU/PSt = 25/75, 60°C; ●, PU/PSt = 50/50, 60°C

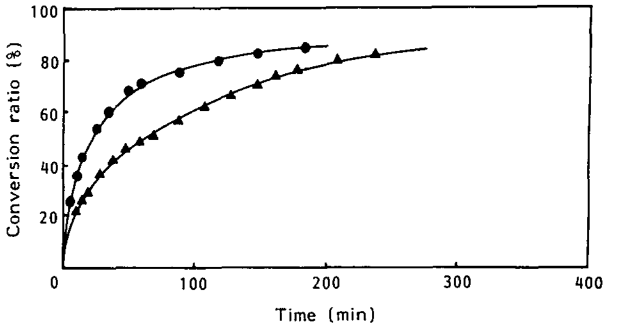

Figure 12 Effect of different concentrations of OcSn on the conversion of NCO groups in IPN at 60°C. PU/PSt = 25/75; AIBN = 0.41%; ▲, OcSn = 0.238%; ●, OcSn = 0.475%

The effect of OcSn concentration

Increasing the concentration of OcSn enhanced the reaction rate of Polyol and TDI (*Figure 12*), but the change of OcSn concentration had no effect on the reaction rate of St in the IPN (*Figure 13*).

Meyer *et al.* reported that OcSn could induce the polymerization of acrylic monomers and affect the

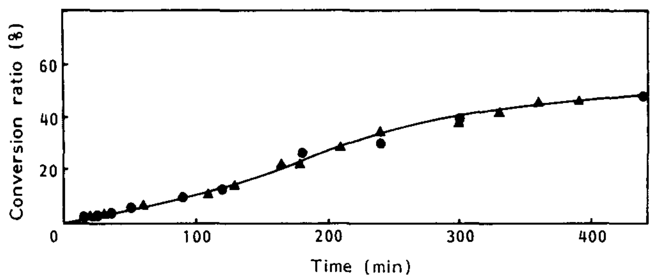

Figure 13 Effect of different concentrations of OcSn on the conversion of St in IPN at 60°C. PU/PSt = 25/75; AIBN = 0.41%; ▲, OcSn = 0.238%; ●, OcSn = 0.475%

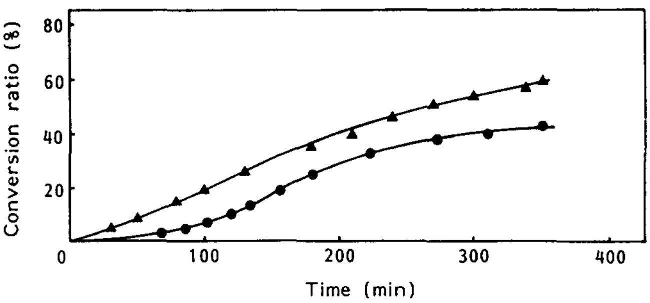

Figure 15 Effect of different concentrations of AIBN on the conversion of St in IPN at 60°C. PU/PSt = 25/75; OcSn = 0.238%; ▲, AIBN = 2%; ●, AIBN = 0.41%

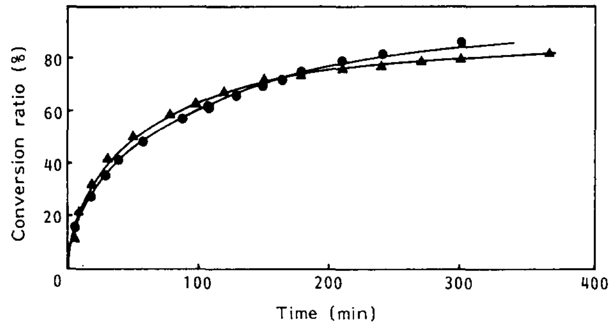

Figure 14 Effect of different concentrations of AIBN on the conversion of NCO in IPN at 60°C. PU/PSt = 25/75; OcSn = 0.238%; ▲, AIBN = 2%; ●, AIBN = 0.41%

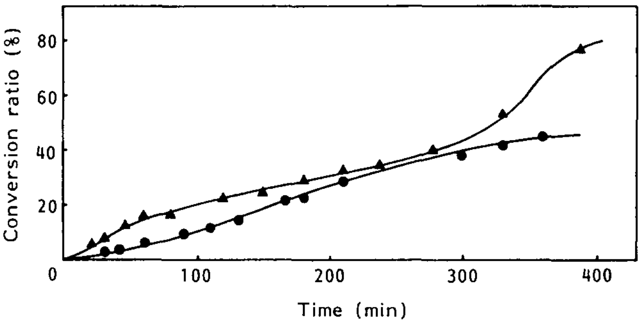

Figure 16 Effect of different concentrations of DVB on the conversion of C=C in IPN at 60°C. PU/PSt = 25/75; AIBN = 0.41; OcSn = 0.238%; ▲, DVB/St = 5/100; ●, DVB/St = 0/100

polymerization rate[11]. Recently, Jin and Meyer attempted to verify the effect of OcSn on the polymerization of methyl methacrylate, but the result found by Meyer could not be repeated[9]. Jin's result was the same as ours.

The effect of AIBN

Figures 14 and *15* show the reaction kinetics of Polyol and TDI and those of St, respectively, with different concentrations of AIBN. The two plots in *Figure 14* basically coincided. This may signify the amount of AIBN added had no effect on the rate of formation of the PU network. Increasing the dose of the radical initiator, AIBN, enhanced the rate of formation of PSt (*Figure 15*).

As discussed above, we know that the reaction rates of different components in the IPN system can be controlled by changing the amount of AIBN or OcSn used. This is very important for the IPN system since the component polymerized first tends to form the more continuous phase[12], while the mechanical properties of the IPN largely depend on its morphology. If the PU network formed first, the IPN would probably exhibit rubbery properties.

The effect of crosslinking agent, DVB

Figure 16 shows the rate of disappearance of the double bond in the presence of DVB. It was noticed that the kinetic plot was different from that for pure St. The kinetic curve in the presence of DVB characterized two stages of acceleration. It is well known that the two double bonds in DVB have different reactivities. The vinyl double bond in the DVB molecule is more reactive than that in the St molecule. The first accelerating stage must be concerned with the reaction of DVB, while the later stage of acceleration must be related to the gel effect of PSt. Thus, it was considered that the role played by DVB was probably heterogeneous in the IPN, because DVB radicals could not only initiate polymerization of St but also terminate each other. This made the crosslinking density of PSt higher or lower in different regions.

Investigation of the reaction mechanism of PU/PSt IPN

As discussed above, both the formation of pure PU and the formation of PU in the IPN follow a second-order mechanism, whereas the formation of pure PSt and the formation of PSt in the IPN obey a first-order mechanism. The synthesis of PU/PSt IPN took place by a different reaction mechanism. Although the two different components in the PU/PSt IPN system interfere with each other, it is evident that they did not affect the inherent reaction mechanism of each component.

CONCLUSIONS

Infra-red spectroscopy has been shown to be a powerful method for IPN kinetic studies. All of the components in the PU/PSt IPN follow the Beer–Lambert law. NCO absorption at 2280 cm^{-1} and the C=C peak at 1645 cm^{-1} show a gradual decrease as the respective polymerizations proceed. The reaction kinetics curve of Polyol and TDI obtained by the infra-red method fits well with that obtained by chemical titration. The interaction between different components only affects their reaction rate. The rates of polymerization of St and Polyol with TDI are decreased in the IPN, compared with the pure system, but there is no interference between their individual reaction mechanisms. The formation of pure PU and of PU in the IPN follow second-order kinetics, and the formation of pure St and of St in the IPN follow a first-order mechanism. Increasing the amount of PU (or PSt) in the IPN gives a faster formation rate of PU (or

PSt) and a slower formation rate of PSt (or PU). Increasing the amount of AIBN (or OcSn) gives a higher polymerization rate of St (or Polyol and TDI), but the change of AIBN (or OcSn) concentration has no, or only a small, effect on the formation rate of PU (or PSt). The reaction rate of double bonds in the IPN is increased by introducing the crosslinking agent, DVB. The formation rate of PU is obviously higher than that of PSt. A cage effect of the PU network has been proposed.

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