

# Polymerization Kinetics of Polyurethane and Vinyl Ester Resin Interpenetrating Polymer Networks by Using Fourier Transform Infrared Spectroscopy

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## SYNOPSIS

Fourier transform infrared spectroscopy (FTIR) was applied to the study of polymerization kinetics of simultaneous interpenetrating polymer networks (SINs) composed of polyurethane (PU) and vinyl ester resin (VER), in which the pendent hydroxyl groups were capped with acetyl groups to minimize the possibility of chemical binding between the two networks. It was found that during the course of synthesis the two pairs of reactants interfere with each other in the SIN systems, giving rise to depressed reaction rates, although they follow different polymerization mechanisms. Increasing the reaction temperature could be more effective than increasing the free-radical initiator level with regard to the final conversions of both components. The reaction sequence could be varied through the amount of the step-growth polymerization catalyst and free-radical initiator as well as the reaction temperature adjustment. Using VER containing pendent hydroxyl groups could strongly affect the reaction kinetics of such SINs and lead to hybrid structures. The quick formation of one network would always depress the conversion of the other network in all SINs studied.

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## INTRODUCTION

A unique class of multiphase polymer materials is provided by interpenetrating polymer networks (IPNs) consisting of two (or more) chemically distinct components held together ideally and solely by their permanent mutual entanglements through individual curing of these components.<sup>1</sup> IPN materials have been studied extensively as polymer alloys with synergistic physical properties of technological interest. Frisch et al.<sup>2</sup> first reported simultaneous interpenetrating networks (SINs) composed of polyurethane in combination with epoxy resin, polyacrylate, or unsaturated polyester resin. Pernice and co-workers<sup>3</sup> pointed out that such SINs could be applied in the reaction injection-molding (RIM) process, and since then, there has been increasing interest in using IPNs as RIM materials. It is be-

lieved that adding the second reactive, usually rigid, phase may make up for deficiencies of conventional, usually elastic, polyurethane RIM products. We have demonstrated that the structure of IPNs is determined by the chemical nature of the components and by parameters affecting the kinetics of polymerization of each network.<sup>4,5</sup> Consequently, it directly responds to the different properties of the final materials. This necessitates detailed knowledge of all reactions and side reactions taking place during IPN synthesis. Some articles have come out dealing with the kinetics aspect of IPN formation.<sup>6-10</sup> However, most of the studies for the RIM process were related to SINs of PU and industrial unsaturated polyester resin.<sup>9,11-13</sup> In these systems, the interaction between the two constituent components may not be overlooked, as the hydroxyl and carboxyl end groups of polyester chains are easy to react with isocyanates.

SINs from PU and vinyl ester resin (VER) have been investigated in our laboratory for several years. VER can be cured by a free-radical copolymerization

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mechanism, and the main backbones of the epoxy resin will be maintained in the cured product. In this article, the kinetics study of PU and VER SINS using Fourier transform infrared spectroscopy at a temperature range from 60 to 110°C within 0.5 h are reported. The comparison of VER with or without its pendent hydroxyl groups has been also made to examine the intercomponent chemical binding effect.

## EXPERIMENTAL

### Synthesis of Vinyl Ester Resin

Vinyl ester resins (VERs) were first prepared by the adduction reaction of 1 mol bisphenol A-type epoxy resin E-51 (0.51 epoxide equivalent/100 g resin), i.e., diglycidyl ether of bisphenol A, supplied by Shanghai Synthetic Resin Plant and 2 mol  $\alpha$ -methylacrylic acid under argon gas protection with tertiary amine as a catalyst to obtain vinyl ester oligomer (VEO). When the acid number (AN) of the reaction mixture was below 6 mgKOH/g, the reaction continued under vacuum to reduce the AN further (AN < 0.6 mgKOH/g). Styrene (St) as comonomer was then introduced into this VEO (VEO/St = 64/36 wt ratio). The resulting VER was designated as VERH; as such, a VEO was possessed of pendent hydroxyl groups. To obtain the so-called VERA resin, in which the pendent hydroxyl groups were capped with acetyl groups, a suitable amount of acetyl chloride was added in drops to VEO. The system was exposed to vacuum again to eliminate hydrochloride and finally combined with St.

### Materials

Trifunctional polyoxypropylene polyol (5613, hydroxyl number [HN]: 54 mgKOH/g) was supplied by Arco Co. Toluene diisocyanate (TDI, 80/20) was provided by Olin Co. All other chemicals used in this study were standard laboratory reagents obtained from various manufacturers.

The polyols were dried at 100°C under vacuum for 12 h, then treated with 4 Å molecular sieves for over 1 week before use. 1,4-Butanediol (1,4-BDO) was distilled under vacuum in the presence of sodium wire. St was washed, dried, and distilled under vacuum and inhibited with 1,4-hydroquinone ( $10^{-4}$  g/g St). 2,2'-Azobis-isobutyronitrile (AIBN) was filtered and recrystallized from hot ethanol and dried under vacuum at room temperature.

Polyol 5613, 1,4-BDO, and TDI forms PU with a hard-segment content of 44%. The catalyst for

PU, dibutyltin dilaurate (DBTDL), was used as received at  $10^{-2}$  phr. The free-radical initiator AIBN was used at 1 phr of VERA or VERH.

### Instrumentation and Experimental Routine

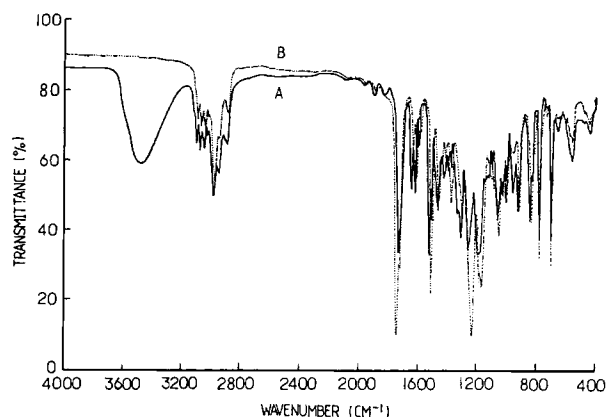
A Nicolet 5SX FTIR spectrometer at a resolution of  $4\text{ cm}^{-1}$  in the transmission mode was employed for both VER characterization and kinetics study of individual components and SINS.  $^1\text{H-NMR}$  spectroscopy was recorded with  $\text{CDCl}_3$  as the solvent and tetramethylsilane (TMS) as the reference on a Bruker WP-100SY.

To follow the reaction courses for all systems, the temperature chamber with two sodium chloride (NaCl) plates mounted was first heated to the desired temperature before any measurements. Ingredients of each component were weighed with a total weight from 10 to 20 g. All raw materials except TDI were then thoroughly mixed with a mechanical agitator at 1200 rpm for about 30 s and then TDI weighed in a syringe was quickly injected into the mixture, which was further stirred for 30 s. A homogeneous solution was obtained, from which a drop of the mixture was pasted between the two NaCl plates. Three consecutive scans were taken at each sampling time, and their average was stored for later data analysis. All IR spectra for the kinetics studies were shown in the absorbance mode.

Infrared analysis is based on the fact that each chemical group in a sample absorbs infrared radiation of some characteristic frequencies. The use of the Beer-Lambert law allows the determination of the concentration of an absorbing species in the reaction medium, if there exists an absorption peak that obeys the Beer-Lambert law,

$$A = \epsilon cl$$

where  $A$  is the absorbance;  $\epsilon$ , the molar extinction coefficient;  $c$ , the concentration of the absorbing molecule; and  $l$ , the thickness of the test sample. To compensate for thickness changes in the sample during polymerization, a ratio is taken between the absorbance of the group of interest and that of an internal standard, i.e., a group whose concentration does not change during the reaction course. In this study, the C—H peak at  $2924\text{ cm}^{-1}$  and the phenyl peak of St at  $700\text{ cm}^{-1}$  were chosen as the internal standard for PU and St as well as all SINS, respectively. The absorbance area determined by the tangent base-line method is used to calculate the reaction conversion from the change of the normalized absorbance,



**Figure 1** Infrared spectra for VER: (A) VERH; (B) VERA.

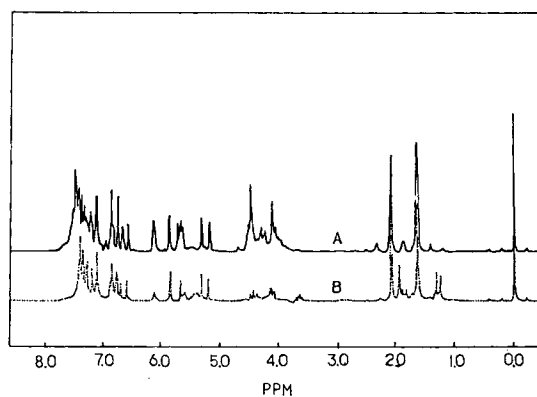
$$\alpha = 1 - A_t/A_0$$

where  $A_0$  and  $A_t$  are the normalized absorbance of the monomer functional group before the reaction and after a reaction time  $t$ .

## RESULTS AND DISCUSSION

### Characterization of Vinyl Ester Resin

Infrared spectra for VERs, VERA and VERH, are illustrated in Figure 1. It can be observed that the IR absorption peak of hydroxyl groups at about  $3480 \text{ cm}^{-1}$  is strong for VERH, while VERA shows almost no absorption at this area, indicating that the hydroxyl groups are capped with acetyl groups. Figure 2 shows the  $^1\text{H-NMR}$  spectra of VERA and VERH, where the peaks at the chemical shift around 4.0 ppm are assigned to the hydrogen atoms connected with oxygen atoms and the near disappearance of these peaks can be attributed to the elimination of hydrogen atoms from pendent hydroxyl groups. Both IR and NMR spectra exhibit that the characteristic peaks due to the ester group are enhanced for VERA after esterification, and the somewhat split peaks from different chemical environments are noted at about  $1730 \text{ cm}^{-1}$  and 2.0 ppm, respectively. All these observations are well consistent with the chemical analysis results for these two VERs (VERH: HN =  $143.5 \text{ mgKOH/g}$ , AN =  $0.4 \text{ mgKOH/g}$ ; VERA: HN =  $0 \text{ mgKOH/g}$ , AN =  $0.8 \text{ mgKOH/g}$ ). Therefore, SINs composed of PU and VERA can be considered as more ideal ones with only the minimum possibility of forming chemical bonds between the two networks.



**Figure 2**  $^1\text{H-NMR}$  spectra for VER: (A) VERH; (B) VERA.

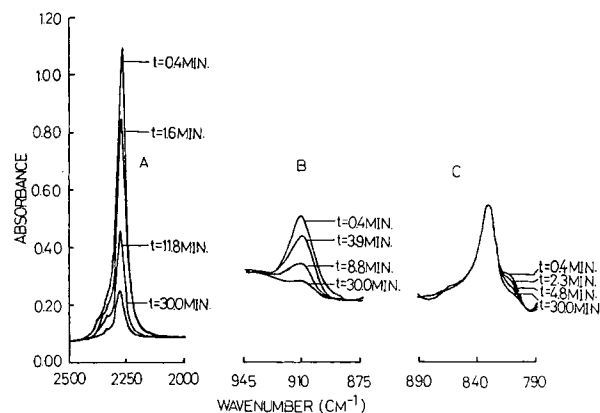
### Step Polymerization of PU

The Beer-Lambert law is valid for the absorption peak at  $2274 \text{ cm}^{-1}$  due to the isocyanate group [see Fig. 3(A)], as established in our laboratory and in the literatures.<sup>8-10</sup> The relationship between the isocyanate group conversion ( $\alpha$ ) and time for PU prepared at different temperatures are shown in Figure 4. The value of  $1/(1 - \alpha)$  obtained from Figure 4 against time is shown in Figure 5, where the straight lines with their intercepts of 1.0 reveal that the disappearing rate of isocyanate groups in polymerization of PU is simply expressed as

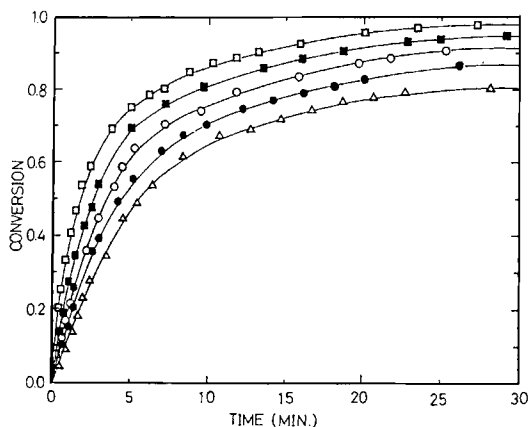
$$-d[\text{NCO}]/dt = k[\text{NCO}][\text{OH}]$$

or

$$-d[\text{NCO}]/dt = k[\text{NCO}]^2$$



**Figure 3** Decrease of characteristic absorption peaks as the reaction proceeds of PU/VERA (50/50) SIN at  $100^\circ\text{C}$ : (A) isocyanate group at  $2274 \text{ cm}^{-1}$ ; (B) styrene at  $910 \text{ cm}^{-1}$ ; (C) vinyl ester at  $812 \text{ cm}^{-1}$ .



**Figure 4** Conversion of NCO vs. time for PU at different temperatures: (□) 100°C; (■) 90°C; (○) 80°C; (●) 70°C; (△) 60°C.

because of initial reactants in stoichiometric ratio, i.e.,  $[\text{NCO}] = [\text{OH}]$ . For

$$\alpha = ([\text{NCO}]_0 - [\text{NCO}]) / [\text{NCO}]_0$$

the overall reaction kinetics can be written

$$d\alpha/dt = k[\text{NCO}]_0(1 - \alpha)^2$$

hence,

$$1/(1 - \alpha) = k[\text{NCO}]_0 t + 1$$

Table I gives the initial polymerization rates and second-order reaction rate constants for PU. According to Arrhenius equation,

$$k = A \exp(-E_a/RT)$$

the linear relationship between  $k$  and  $1/T$  is shown in Figure 6 and an activation energy of 29.9 kJ/mol is obtained.

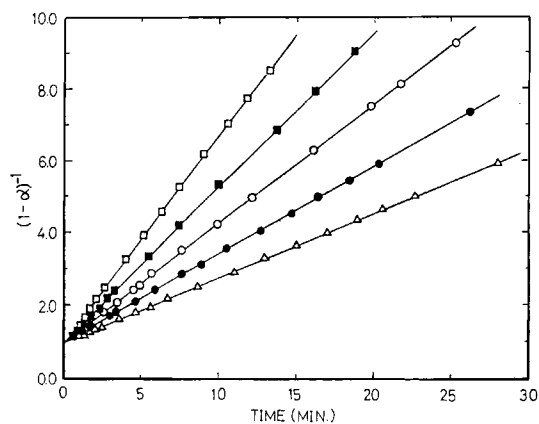
### Free-radical Copolymerization of VERA

Figure 3(B) and (C) show that the intensities of the bands, which are sensitive to the double bonds in styrene at  $910 \text{ cm}^{-1}$  and in VEO at  $812 \text{ cm}^{-1}$ , are considerably reduced during the polymerization course. The validity for applying the Beer-Lambert law to these two bands were checked in our laboratory and in the literature.<sup>9,10</sup> Figure 7 traces the typical kinetics for VERA at 80 and 100°C. It is of interest to note that a nearly linear correlation holds for conversion ( $\alpha$ ) from ca. 10% to ca. 60% (the lin-

ear coefficient is more than 0.98), i.e., the copolymerization rates exhibit almost no dependence on the concentration of reactants, and the conversion rate of overall  $\text{C}=\text{C}$  bonds ( $d\alpha/dt$ ) can be estimated during this conversion range, as listed in Table II. When the values of conversion were more than 60%, a decrease in the rate of copolymerization with increase of time was observed appreciably. For this copolymerization system, the St and acetyl group-capped VEO can be considered as difunctional and tetrafunctional monomers, respectively. If the crosslinking reaction for VERA is assumed to be only taking place by copolymerization, the critical extent of the reaction,  $P_c$  (conversion of overall  $\text{C}=\text{C}$  bonds), at gel point is given by<sup>14</sup>

$$P_c = 2/f_{\text{avg}}$$

where  $f_{\text{avg}}$  represents the average functionality of monomers; an  $f_{\text{avg}}$  of 2.50 estimated for such a copolymerization system gives a  $P_c$  value of 0.80. The crosslinkages in VERA, however, can be also formed by oligomer homopolymerization because the acetyl group-capped VEO itself could cure without a comonomer such as St. Consequently, the real  $P_c$  should be much lower than the value calculated from the Carothers equation, and the obvious decrease in copolymerization rate beyond 60% conversion could be therefore correlated with the network structure formation in the system. Thus, the unusual kinetics behavior mentioned before could be attributed to a strong diffusion restriction existing in this viscous medium, i.e., translational diffusion and segmental rearrangement diffusion.<sup>15</sup> It seems that at lower conversions (less than 60%) the rate of copolymerization may depend mainly on the translational dif-



**Figure 5**  $1/(1 - \alpha)$ -time plot for NCO of PU at different temperatures: (□) 100°C; (■) 90°C; (○) 80°C; (●) 70°C; (△) 60°C.

**Table I** Polymerization Parameters of PU Formation

| Temperature<br>(°C) | Pure PU                                                               |                                                                        |                                   | PU in PU/VERA (50/50) SIN                                             |                                      |                                   |
|---------------------|-----------------------------------------------------------------------|------------------------------------------------------------------------|-----------------------------------|-----------------------------------------------------------------------|--------------------------------------|-----------------------------------|
|                     | Initial<br>Reaction<br>Rate<br>(mol L <sup>-1</sup> s <sup>-1</sup> ) | Reaction<br>Rate<br>Constant<br>(L mol <sup>-1</sup> s <sup>-1</sup> ) | —NCO<br>Conversion<br>(at 30 min) | Initial<br>Reaction<br>Rate<br>(mol L <sup>-1</sup> s <sup>-1</sup> ) | Reaction<br>Rate<br>Constant         | —NCO<br>Conversion<br>(at 30 min) |
| 60                  | 1.11 × 10 <sup>-2</sup>                                               | 7.89 × 10 <sup>-4</sup>                                                | 0.81                              | —                                                                     | —                                    | —                                 |
| 70                  | 1.51 × 10 <sup>-2</sup>                                               | 1.07 × 10 <sup>-3</sup>                                                | 0.87                              | 2.30 × 10 <sup>-3</sup>                                               | 6.51 × 10 <sup>-4</sup> <sup>a</sup> | 0.79                              |
| 80                  | 2.07 × 10 <sup>-2</sup>                                               | 1.47 × 10 <sup>-3</sup>                                                | 0.91                              | 2.80 × 10 <sup>-3</sup>                                               | 7.92 × 10 <sup>-4</sup> <sup>a</sup> | 0.83                              |
| 90                  | 2.71 × 10 <sup>-2</sup>                                               | 1.92 × 10 <sup>-3</sup>                                                | 0.94                              | 3.17 × 10 <sup>-3</sup>                                               | 1.23 × 10 <sup>-3</sup> <sup>b</sup> | 0.92                              |
| 100                 | 3.53 × 10 <sup>-2</sup>                                               | 2.50 × 10 <sup>-3</sup>                                                | 0.98                              | 4.20 × 10 <sup>-3</sup>                                               | 1.63 × 10 <sup>-3</sup> <sup>b</sup> | 0.98                              |
| 110                 | —                                                                     | —                                                                      | —                                 | 5.09 × 10 <sup>-3</sup>                                               | 1.98 × 10 <sup>-3</sup> <sup>b</sup> | 0.88                              |

<sup>a</sup> L mol<sup>-1</sup> s<sup>-1</sup>.<sup>b</sup> L<sup>1/2</sup> mol<sup>-1/2</sup> s<sup>-1</sup>.

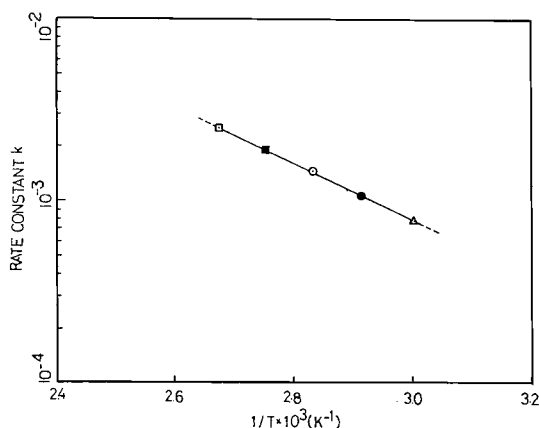
fusion of monomers, so as to give rise to almost the same rate of copolymerization. For the high-conversion stage (more than 60%), the copolymerization rate may result from segmental rearrangement diffusion, whose ability decreases with increasing crosslink density, so the copolymerization rate decreases appreciably. Hu and Ying observed a similar kinetics phenomenon in the copolymerization of some macromers with vinyl monomers,<sup>16</sup> which could be attributed to the diffusion-controlled reaction over almost the entire range of conversion.

### Reaction Kinetics of Components in SINs

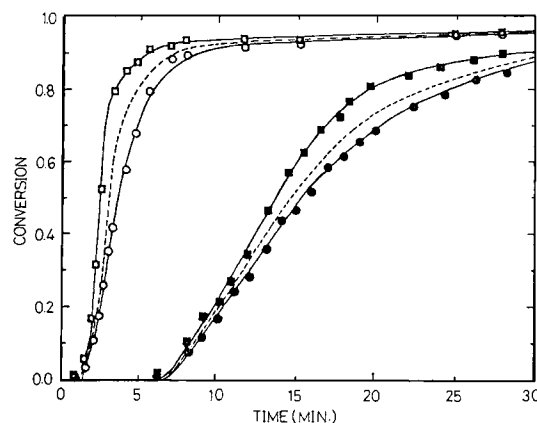
The reaction kinetics of PU and VERA in PU/VERA (50/50, weight ratio) SIN at different temperatures are presented in Figures 8 and 9, respec-

tively. If we apply simply the overall *n*th-order reaction to PU polymerization in this PU/VERA (50/50) SIN, the empirical reaction order with regard to the isocyanate group concentration would be still 2.0 at 70 and 80°C, but 1.5 from 90 to 110°C for better fitting of the experimental data, as described by the straight lines in Figure 10. Table I also gives the maximum reaction rates and reaction rate constants, and activation energies of 19.7 and 27.3 kJ/mol are estimated for lower temperatures (70 and 80°C, *n* = 2.0) and higher temperatures (90–110°C, *n* = 1.5), respectively.

Table I shows that although the early step-polymerization rate of PU increases with increasing temperature, it appears to be depressed in SIN formation compared with that in its pure system at the same temperature (see Figs. 4 and 8). Because of



**Figure 6** Arrhenius plot of rate constant–reciprocal of temperature for pure PU: (□) 100°C; (■) 90°C; (○) 80°C; (●) 70°C; (△) 60°C.



**Figure 7** Conversion of VERA vs. time at different temperatures. 100°C: (□) acetyl group-capped VEO; (○) St. 80°C: (■) acetyl group-capped VEO; (●) St. Dashed line: overall C=C conversion.

**Table II** Copolymerization Parameters of VERA Formation

| Temperature<br>(°C) | Pure VERA                    |                                    |                           |      | VERA in PU/VERA (50/50) SIN |                                    |                           |                   |
|---------------------|------------------------------|------------------------------------|---------------------------|------|-----------------------------|------------------------------------|---------------------------|-------------------|
|                     | Induction<br>Period<br>(min) | $d\alpha/dt$<br>(s <sup>-1</sup> ) | Conversion<br>(at 30 min) |      | Induction<br>Period (min)   | $d\alpha/dt$<br>(s <sup>-1</sup> ) | Conversion<br>(at 30 min) |                   |
|                     |                              |                                    | VEO                       | ST   |                             |                                    | VEO                       | ST                |
| 60                  | 25.1                         | $3.55 \times 10^{-4}$              | 0.70                      | 0.71 | —                           | —                                  | —                         | —                 |
| 70                  | —                            | —                                  | —                         | —    | 23.0                        | —                                  | ~ 0 <sup>a</sup>          | ~ 0 <sup>a</sup>  |
| 80                  | 7.0                          | $9.80 \times 10^{-4}$              | 0.90                      | 0.88 | 10.8                        | $6.70 \times 10^{-4}$              | 0.62 <sup>b</sup>         | 0.56 <sup>b</sup> |
| 90                  | —                            | —                                  | —                         | —    | 3.7                         | $1.05 \times 10^{-3}$              | 0.87                      | 0.84              |
| 100                 | 1.2                          | $5.58 \times 10^{-3}$              | 0.95                      | 0.94 | 2.1                         | $1.99 \times 10^{-3}$              | 0.90                      | 0.91              |
| 110                 | —                            | —                                  | —                         | —    | 0.8                         | $9.93 \times 10^{-3}$              | 0.96                      | 0.95              |

<sup>a</sup> > 0.70 at 60 min.

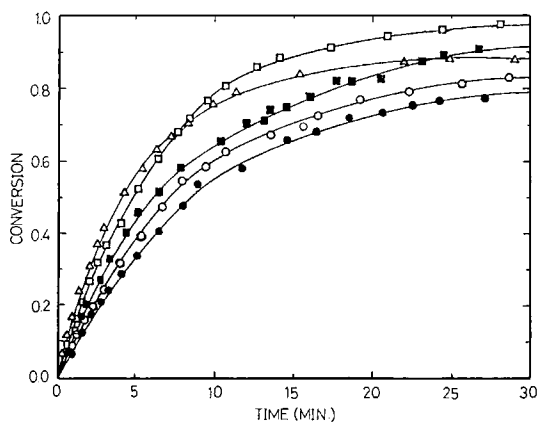
<sup>b</sup> > 0.80 at 45 min.

the existence of the induction period of free-radical copolymerization of VERA, the early stage of the PU network formation reaction could be considered as solution polymerization. Thus, the decreasing of the concentrations of polyol, extender, diisocyanate, and especially the step-polymerization catalyst (DBTDL) is the main reason for the depressed PU formation. However, the Sn<sup>2+</sup> in DBTDL may form some complex with the ester group in VEO,<sup>17</sup> giving rise to a reduced effective catalyst concentration and a decrease of polymerization rate for PU step-polymerization. If we increase the DBTDL concentration to 10<sup>-2</sup> (wt/wt of polyol), the formation rate of PU increases rapidly with the conversion of the —NCO group going prior to that of VERA, as shown in Figure 11.

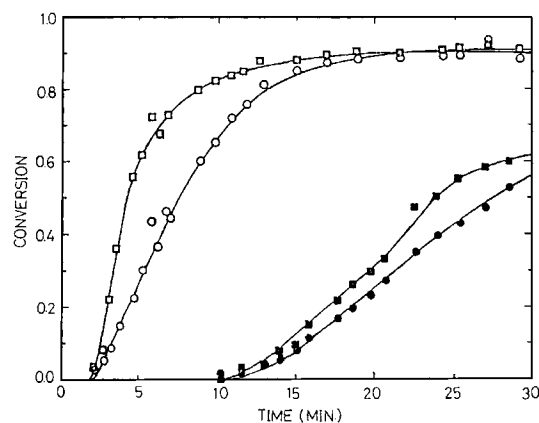
As the reaction temperature increases, especially at 90–110°C, the copolymerization of VERA exhibits

shorter induction periods and faster reaction rates as well as higher conversions (ca. 90%) at 30 min for both reactants, as listed in Table II. This contributes a sharp contrast to those at lower temperatures (70 and 80°C). The quick formation of the VERA network may interfere with the polymerization of PU, i.e., the reaction order  $n$  changes from 2.0 to 1.5, and the polymerization rate at 110°C is slower than that at 100°C after the early stage (see Fig. 8), as interpenetration of networks and entanglements of macromolecules occur during the synthesis of SIN. In this case, the morphologies of these SINs should be varying appreciably.

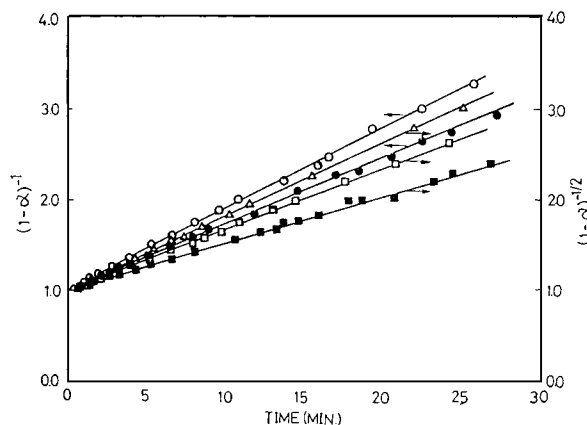
Figure 9 also displays an almost linear correlation between conversions of VERA reactants and time during the ca. 10–60% conversion range (the linear coefficient is more than 0.98). The copolymerization



**Figure 8** Conversion of NCO vs. time for PU/VERA (50/50) SIN at different temperatures: (Δ) 110°C; (□) 100°C; (■) 90°C; (○) 80°C; (●) 70°C.



**Figure 9** Conversion of VERA vs. time for PU/VERA (50/50) SIN at different temperatures. 100°C: (□) acetyl group-capped VEO; (○) St. 80°C: (■) acetyl group-capped VEO; (●) St.



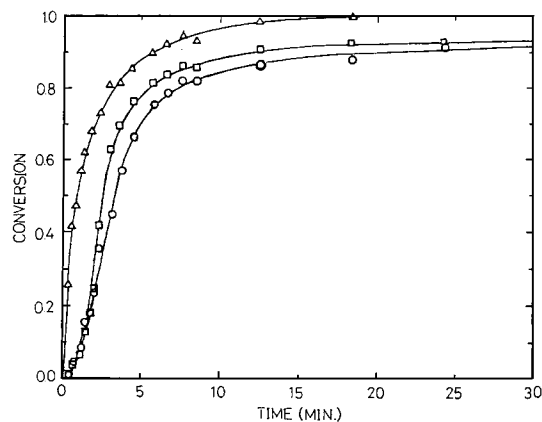
**Figure 10**  $(1 - \alpha)^{(1-n)}$ -time plot for NCO of PU in PU/VERA (50/50) SIN at different temperatures: (○) 80°C, (●) 70°C,  $n = 2.0$ ; (△) 110°C, (□) 100°C, (■) 90°C,  $n = 1.5$ .

rates are estimated and summarized in Table II. Although the free-radical copolymerization rate of VERA increases with increasing temperature, it also appears to be depressed in SIN formation compared with that in its pure system at the same temperature (see Figs. 7 and 9). It should be pointed out that when PU and VERA are combined to form the 50/50 SIN the concentrations of both reactants in VERA are halved because of the dilution effect of PU reactants, but the copolymerization rates of VERA at 80 and 100°C were only reduced by 32 and 64%, respectively. Thus, the reduction of copolymerization rates in SIN formation could not be correlated with the concentrations of the reactants. As the formation of PU follows the step-polymerization mechanism, with maximum reaction rates occurring at the beginning of the reaction, the copolymerization of VEO and St, which starts after the induction period, would experience a strong diffusion restriction exerted by the partially formed PU network.<sup>18</sup> At higher temperature (100°C), both networks are formed almost simultaneously. Some difference of morphology development between those at 80 and 100°C could be expected, giving rise to more reduction in the reaction rate at 100°C.

The above experimental results all support that the interaction between components of the two networks cannot be overlooked. The early stage of the PU reaction could be considered as solution polymerization; however, the morphology development upon the formation of the VERA network could affect its polymerization rate and reaction mechanism, especially at higher temperatures (90–110°C; at 110°C, the —NCO conversion was greatly depressed for the quick formation of VERA network;

see Fig. 8). The copolymerization reaction could occur only in the immediate presence of the partially formed PU network and render itself diffusion-controlled.

Table III lists reaction rates and conversions for PU and VERA in their SINs at various compositions. The formation rates of PU in SINs at 80 and 100°C are greatly decreased with increasing VERA content. The copolymerization of VERA is depressed in SINs compared with its pure system, but the reaction rates do not change appreciably at 80°C for composition above or below 50/50 and at 100°C for composition from 80/20 to 25/75. This unusual behavior may be related to morphology development during SIN formation. Chen et al.<sup>4</sup> and Huang et al.<sup>5</sup> studied the morphologies of these SINs at different compositions of PU and VERA and found that when the composition is more than 50/50 VERA constitutes the dispersing phase through the PU matrix and the diameter of the domains increases with increasing VERA content in SINs. Co-continuous morphology occurs at round 50/50 composition; phase inversion takes place with a further higher content of VERA existing in the system. Thus, when the composition is more than 50/50, the copolymerization rate of VERA is determined by the translational diffusion rate of St to the dispersing phase of VERA, so the copolymerization rate stays almost the same at 80°C; when the composition is less than 50/50, VERA forms the continuous phase and St is easy to diffuse, so the copolymerization rate is little affected by its concentration. By increasing temperature to 100°C, the diffusion ability of St should increase so that the difference of copolymerization rates is much less than that at 80°C over the wide range of compositions.



**Figure 11** Catalyst level effect in PU/VERA (50/50) SIN (100°C, AIBN 4 phr of VERA): (△) NCO; (□) acetyl group-capped VEO; (○) St.

Table III Effect of Processing Variables (Composition, Temperature, Initiator Amount) for PU/VERA SINS

| PU/VERA<br>(Wt/Wt) | Temperature (°C)                                                      |                                   |                              |                           |      |                                                                       |                                   |                              |                           |      |                                                                       |                                   |                              |                           |      |
|--------------------|-----------------------------------------------------------------------|-----------------------------------|------------------------------|---------------------------|------|-----------------------------------------------------------------------|-----------------------------------|------------------------------|---------------------------|------|-----------------------------------------------------------------------|-----------------------------------|------------------------------|---------------------------|------|
|                    | 80                                                                    |                                   |                              |                           |      |                                                                       | 100                               |                              |                           |      |                                                                       |                                   |                              |                           |      |
|                    | PU                                                                    |                                   |                              | VERA                      |      |                                                                       | PU                                |                              |                           | VERA |                                                                       |                                   |                              |                           |      |
|                    | Initial<br>Reaction<br>Rate<br>(mol L <sup>-1</sup> s <sup>-1</sup> ) | —NCO<br>Conversion<br>(at 30 Min) | Induction<br>Period<br>(Min) | Conversion<br>(at 30 Min) | St   | Initial<br>Reaction<br>Rate<br>(mol L <sup>-1</sup> s <sup>-1</sup> ) | —NCO<br>Conversion<br>(at 30 Min) | Induction<br>Period<br>(Min) | Conversion<br>(at 30 Min) | St   | Initial<br>Reaction<br>Rate<br>(mol L <sup>-1</sup> s <sup>-1</sup> ) | —NCO<br>Conversion<br>(at 30 Min) | Induction<br>Period<br>(Min) | Conversion<br>(at 30 Min) | St   |
| 100/0              | 2.07 × 10 <sup>-2</sup>                                               | 0.92                              | —                            | —                         | —    | 3.53 × 10 <sup>-2</sup>                                               | 0.97                              | —                            | —                         | —    | 1.60 × 10 <sup>-3</sup>                                               | —                                 | —                            | —                         | —    |
| 80/20              | 4.76 × 10 <sup>-3</sup>                                               | 0.93                              | 23.3                         | 0.37                      | 0.41 | 1.60 × 10 <sup>-2</sup>                                               | 0.95                              | 3.8                          | 0.70                      | 0.65 | 1.60 × 10 <sup>-3</sup>                                               | 0.95                              | 3.8                          | 0.70                      | 0.65 |
| 65/35              | 3.51 × 10 <sup>-3</sup>                                               | 0.86                              | 15.0                         | 0.50                      | 0.47 | 7.07 × 10 <sup>-3</sup>                                               | 0.97                              | 3.4                          | 0.83                      | 0.85 | 1.86 × 10 <sup>-3</sup>                                               | 0.97                              | 3.4                          | 0.83                      | 0.85 |
| 50/50              | 2.80 × 10 <sup>-3</sup>                                               | 0.84                              | 10.8                         | 0.62                      | 0.56 | 4.20 × 10 <sup>-3</sup>                                               | 0.98                              | 2.1                          | 0.90                      | 0.91 | 1.99 × 10 <sup>-3</sup>                                               | 0.98                              | 2.1                          | 0.90                      | 0.91 |
| 25/75              | 1.50 × 10 <sup>-3</sup>                                               | 0.83                              | 8.6                          | 0.81                      | 0.75 | 2.57 × 10 <sup>-3</sup>                                               | 0.85                              | 1.7                          | 0.91                      | 0.90 | 2.23 × 10 <sup>-3</sup>                                               | 0.85                              | 1.7                          | 0.91                      | 0.90 |
| 0/100              | —                                                                     | —                                 | 7.0                          | 0.90                      | 0.88 | —                                                                     | —                                 | 1.2                          | 0.95                      | 0.94 | 5.58 × 10 <sup>-3</sup>                                               | —                                 | 1.2                          | 0.95                      | 0.94 |
| 50/50 <sup>a</sup> | 2.83 × 10 <sup>-3</sup>                                               | 0.82                              | 6.2                          | 0.78                      | 0.74 | —                                                                     | —                                 | —                            | —                         | —    | —                                                                     | —                                 | —                            | —                         | —    |
| 25/75 <sup>a</sup> | 1.41 × 10 <sup>-3</sup>                                               | 0.80                              | 3.7                          | 0.83                      | 0.83 | —                                                                     | —                                 | —                            | —                         | —    | —                                                                     | —                                 | —                            | —                         | —    |

<sup>a</sup> AIBN 2 phr of VERA.

The experimental data in Table III also shows that at the initiator amount of 1 phr (AIBN in the VERA phase) the network formation rates and final conversions (at 30 min) of both PU and VERA reach higher values when the reaction temperature increases from 80 to 100°C at the same composition, which indicates a more perfect network formation of both components. When the initiator level is doubled for the PU/VERA SIN prepared at 80°C, both the conversion rate and conversion of VERA are less than those of 1 phr AIBN at 100°C, even in the case of PU/VERA (25/75) SIN, in which the VERA phase dominates. If we apply 4 phr AIBN to the synthesis of PU/VERA (50/50) SIN at 100°C, VERA reveals a very short induction period and the conversion of VERA reactants is soon higher than that of PU, as shown in Figure 12. The quick formation of the VERA network finally results in a relatively lower conversion of PU network (0.82), compared with that of SIN adding 1 phr AIBN (0.98). Thus, the reaction sequence of the networks can be varied through the reaction temperature and initiator amount adjustment.

#### PU/VERH SIN

All SIN reactions presented so far have been considered to be ideal with only negligible chemical bonds between the two components. Then, it is of interest to examine the SINS prepared with VERH, which is closer to the industrial product.

For examining the reactivity between the —OH groups in VERH and TDI, as well as the effect of TDI on the copolymerization of VERH, we first conducted conversion measurements at 80 and 100°C for a VERH and TDI mixture designated as

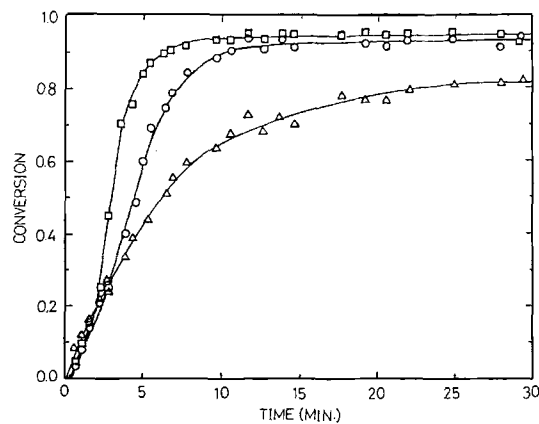
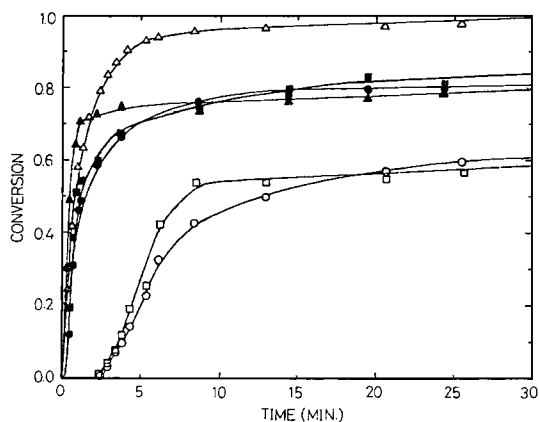


Figure 12 Initiator level effect in PU/VERA (50/50) SIN (100°C, AIBN 4 phr of VERA): (Δ) NCO; (□) acetyl group-capped VEO; (○) St.



VERH/TDI for simplicity hereafter, in which the amount of TDI corresponded to that of hydroxyl groups in VERH ( $10^{-2}$  phr DBTDL added as a catalyst). Figure 13 shows the conversion curves of the urethane reaction and free-radical copolymerization. A fairly large conversion of the isocyanate group (ca. 0.80) in the VERH/TDI mixture at  $80^{\circ}\text{C}$  is observed before the induction period of free-radical copolymerization, implying that TDI should react easily with  $-\text{OH}$  groups existing in VEO to form the so-called unsaturated linear PU first, followed by the copolymerization between the double bonds existing in these linear PUs and St. In such a case, the viscosity of the reaction medium is expected to be much higher than that of pure VERH, giving rise to a lower conversion of free-radical copolymerization because of the diffusion restriction of St, as listed in Table IV. When the temperature increases to  $100^{\circ}\text{C}$ , the decomposition of AIBN is fast enough to initiate the copolymerization reaction, and its reaction rate and conversion as well as the rate of urethane formation at early stage increase. However, the reaction of the  $-\text{OH}$  groups and TDI is impeded after the early stage as the networks soon formed, giving rise to a lower conversion of  $-\text{NCO}$  groups.

Also summarized in Table IV are results from PU/VERH SIN and PU/VERH/TDI SIN at a composition of 50/50. In the PU/VERH SIN, the  $-\text{OH}$  groups in VERH were neglected for the metering of TDI, i.e., only the  $-\text{OH}$  groups in poly(ether polyol) and the extender were counted for the amount of TDI, while in the PU/VERH/TDI SIN, all the concentrations of  $-\text{OH}$  groups were considered and a stoichiometric relation between the  $-\text{OH}$  and  $-\text{NCO}$  groups was maintained. Compared with



**Figure 13** Conversions vs. time for VERH/TDI mixture at different temperatures.  $80^{\circ}\text{C}$ : ( $\Delta$ ) NCO; ( $\square$ ) VEO; ( $\circ$ ) St.  $100^{\circ}\text{C}$ : ( $\blacktriangle$ ) NCO; ( $\blacksquare$ ) VEO; ( $\bullet$ ) St.

**Table IV** Intercomponent Chemical Binding Effect for 50/50 PU/VERH SINS

| Chemical System | Temperature ( $^{\circ}\text{C}$ )                          |                                      |                               |                                  |      |                                                             |                                      |                               |                                  |      |
|-----------------|-------------------------------------------------------------|--------------------------------------|-------------------------------|----------------------------------|------|-------------------------------------------------------------|--------------------------------------|-------------------------------|----------------------------------|------|
|                 | 80                                                          |                                      |                               |                                  |      | 100                                                         |                                      |                               |                                  |      |
|                 | Urethane Reaction                                           |                                      | Free-radical Copolymerization |                                  |      | Urethane Reaction                                           |                                      | Free-radical Copolymerization |                                  |      |
| VERH            | Initial Reaction Rate ( $\text{mol L}^{-1} \text{s}^{-1}$ ) | $-\text{NCO}$ Conversion (at 30 Min) | Induction Period (Min)        | $d\alpha/dt$ ( $\text{s}^{-1}$ ) | St   | Initial Reaction Rate ( $\text{mol L}^{-1} \text{s}^{-1}$ ) | $-\text{NCO}$ Conversion (at 30 Min) | Induction Period (Min)        | $d\alpha/dt$ ( $\text{s}^{-1}$ ) | St   |
| VERH/TDI        | $2.58 \times 10^{-2}$                                       | 0.99                                 | 4.5                           | $1.76 \times 10^{-3}$            | 0.89 | $4.12 \times 10^{-2}$                                       | —                                    | 0.6                           | $8.83 \times 10^{-3}$            | 0.94 |
| PU/VERH         | $3.13 \times 10^{-2}$                                       | 1.00                                 | 2.5                           | $1.61 \times 10^{-3}$            | 0.58 | —                                                           | 0.80                                 | 0.4                           | $7.05 \times 10^{-3}$            | 0.83 |
| PU/VERH/TDI     | $5.21 \times 10^{-2}$                                       | 0.95                                 | 5.0                           | $1.37 \times 10^{-3}$            | 0.54 | $1.76 \times 10^{-1}$                                       | —                                    | —                             | —                                | —    |
|                 |                                                             |                                      | 7.0                           | $1.16 \times 10^{-3}$            | 0.50 |                                                             | 0.89                                 | 0.3                           | $5.48 \times 10^{-3}$            | 0.85 |

PU/VERA (50/50) SIN at 80 and 100°C, the reaction rates of both the urethane reaction and copolymerization exhibit higher values. This may be attributed to a relatively higher concentration of PU precursors (—NCO, —OH), and the heat released upon the fairly fast urethane reaction during sample preparation may increase the mixture temperature, which, in turn, promotes the decomposition of the initiator (AIBN). However, the copolymerization conversions are lower at a given reaction time. The same consideration for prohibiting the free-radical copolymerization in the VERH/TDI system could be applied to explain the lower conversion of copolymerization in these two systems as TDI should react with the —OH groups in VERH. Although the conversions of urethane formation reach high levels in these two SINS, the perfect structure of PU could not be formed, since some VEO molecules have been incorporated into PU chains. Thus, the structure of these SINS is rather hybrid because of the existence of an intercomponent chemical binding.

In conclusion, we have demonstrated that FTIR could be applied to the kinetics study of PU/VER SINS, so as to optimize the operation parameters involved in the production of SINS by RIM technology. It should be pointed out that, however, the reaction period of 0.5 h in this study is still too long for real RIM production, as mechanical mixing was utilized throughout our work here and a rather low DBTDL concentration was employed (compared with that of 0.1–1% in common industrial RIM practice). Further studies using a mini-RIM machine connected with FTIR to make on-line analysis are to be undertaken for a better understanding of the kinetics behavior of real RIM SIN synthesis.

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