were free of benzophenone and organotitanium species (TLC).

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Polymerization of Polyurethane–Polyester Interpenetrating Polymer Network (IPN)

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ABSTRACT: Reaction mechanisms involved in synthesizing a polyurethane–polyester interpenetrating polymer network were studied by Fourier transform infrared spectroscopy. Results show that the reaction kinetics of urethane polymerization is not the same in bulk as in the solution state. Polyurethane reaction in the IPN resembles a solution polymerization before gelation and a bulk polymerization after gelation. Copolymerization in typical unsaturated polyester resins tends to follow the azeotropic condition. On the other hand, the polyester reaction in IPN deviates substantially from that in a pure polyester resin in the presence of a polyurethane network.

Introduction

Multiphase polymers have been used extensively in the polymer industry to provide products with superior chemical and physical properties.[1,2] Mechanically blended polymers and graft and block copolymers are used most often. Blended polymers often experience phase stability problems due to the lack of permanent chemical bonding between the two polymer phases. Graft and block copolymers are generally applied to thermoplastic polymers. An interpenetrating polymer network (IPN) is different from those mentioned above. An IPN is a composite of two polymers cross-linked or reacted in the presence of each other.[1] It is generally thought that the interpenetrated and entangled chains of the two polymer networks can increase the phase stability and, therefore, enhance mechanical properties of the final product. Additionally, this seems to be the only way to blend two cross-linking polymers. There are two reactive phases in an IPN. If phase A reacts earlier than phase B, the product is called a sequential IPN. If both reactions take place at the same time, it is called a simultaneous IPN. If both phases are cross-linked, it is called a full IPN, while if one is cross-linked and the other is linear, it is called a semi-IPN.[3]

Recently, there has been increasing interest in using IPNs in reactive processes such as reaction injection molding (RIM).[4,5] It is believed that adding the second reactive phase may make up deficiencies of conventional RIM materials like polyurethanes (PU). Such a process is obviously more complicated than conventional polymerizations since one has to deal with two reactive phases at the same time and the two phases may interfere with each other during polymerization.

There are few studies concerning polyurethane-based IPNs. Most of them have focused on the morphology and physical properties of finished products.[3,6] For example, Kim et al.[7] studied a simultaneous IPN system composed of a PU and a polystyrene or poly(methyl methacrylate). Yoon et al.[8] studied a series of PU and polyacrylate IPNs. Djomo et al.[9] and Morin et al.[10] also studied PU–PMMA systems. Hutchinson et al.[11] developed a series of PU–polyester IPNs.

The processing aspects of IPNs have not been investigated until recently. Nguyen and Suh[12,13] studied the mixing and reaction of a PU–polyester IPN in the RIM process. They found that a much higher mixing energy, indicated by a high Reynolds number in their study, was required for an IPN to reach the same extent of reaction reached in polyurethanes. Hsu and Lee[14] studied the kinetics of a similar PU–polyester IPN by using thermal

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analysis. Their results showed that both polyurethane and polyester reactions may seriously interfere with each other in bulk polymerization. The degrees of cross-linking, reaction rate, reaction sequence, and resin composition all play important roles in determining the reaction rate and the final conversion. Lee et al.[15] further studied rheological changes in these IPN systems during polymerization. Again, strong interaction was found between the two reactive phases.

In order to apply IPNs to various reactive processing operations, a detailed understanding of reaction kinetics is essential. Because of the cross-linking nature of IPNs, many analytical instruments cannot be applied. The most often used instrument for kinetic measurement of thermoset polymers is a differential scanning calorimeter (DSC). DSC has the advantages of simplicity and fewer limitations and the capability of simultaneously yielding information regarding kinetics, energetics, and thermal properties. It has been applied extensively to kinetic studies in recent years.[16-23] However, it tends to be less accurate due to its empiricism and lack of detail in the kinetic sense. Other limitations of DSC for making kinetic measurements are low sensitivity at high conversions, especially if permanent residues are formed, and unsuitability for multicomponent reactions such as simultaneous IPNs.

Infrared analysis can directly measure the concentration of functional groups.[24-30] The recent development of computer-assisted Fourier transform infrared (FTIR) spectroscopy provides many advantages over a conventional dispersive infrared method including high scanning speed and signal-to-noise ratio, large energy throughput, and high resolution.[24] For kinetic studies, FTIR can provide detailed information regarding the reaction mechanism of complex polymerizations.

In this study, we discuss the reaction kinetics of a polyurethane–polyester IPN using Fourier transform infrared spectroscopic analysis.

Experimental Section

A. Materials. The polyurethane–polyester IPN, designated in this study as PU–PES IPN, contains two reactive parts: a polyurethane phase and an unsaturated polyester phase. The urethane phase is based on a poly(ϵ-caprolactonetriol) (TONE-0310, Union Carbide) in which 99% of the hydroxyl groups is primary and a liquid form of 4,4′-diphenylmethylene diisocyanate (MDI, 143-L, Dow). These materials are used as received at equal stoichiometry. Dibutyltin dilaurate (DBTDL, T12, M & T Chemicals) is used as the catalyst at a concentration of 7.6 ppm of polyol by weight. The PU product has a glass transition temperature near 80 °C.

The second phase contains an unsaturated polyester resin which is a 1:1 propylene–maleate polyester combined with 35% by weight styrene (P325, OCF). The number-average molecular weight of the unsaturated polyester resin is around 1600. Extra styrene is added to the resin so that the molar ratio of styrene to the unsaturation on polyester molecules is adjusted to 2:1. This ratio is typical for sheet molding compounds (SMC).[21] The polyester product has a glass transition temperature of about 130 °C. Different peroxide initiators are used to control the reaction rate of the second phase. They are *tert*-butyl peroxy-2-ethylhexanoate (PDO, Lucidol), a high-temperature initiator, and methyl ethyl ketone peroxide (MEKP, Lucidol) with 25% cobalt naphthanate, a room-temperature initiator. The former is used with a concentration of 3% by weight polyester phase, and the latter is with 1% by weight. The weight ratios of PU and PES are varied from 50/50 to 30/70 in this study.

The polyol was degassed at 30 °C under vacuum for 1 h before mixing to remove dissolved water and air. All ingredients were carefully weighed and then mixed vigorously by hand for less than 30 s before being loaded into the FTIR spectrometer for kinetic measurements. The reaction temperature was held at 60 °C throughout the entire course of polymerization. With PDO as the initiator for the second phase, the polyester reaction occurs much later than the polyurethane reaction, which resembles a sequential IPN (SEQ-IPN). With MEKP and a cobalt promoter as the initiator for the polyester phase, both PU and PES reactions occur almost at the same time, resembling a simultaneous IPN (SIM-IPN).

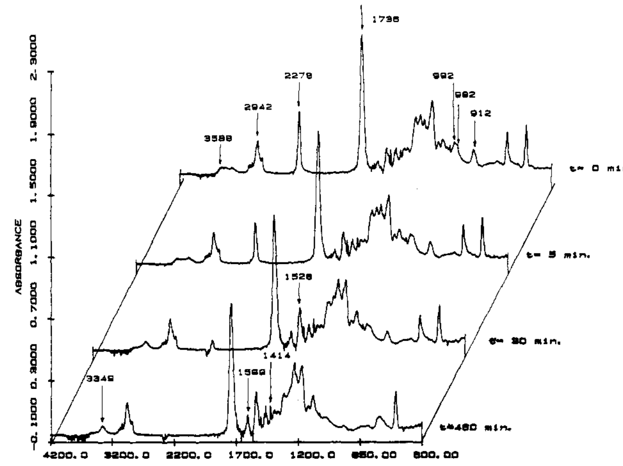

Figure 1. FTIR spectra for 50/50 PU–PES SIM-IPN reaction at 60 °C. MEKP–cobalt naphthanate is the initiator for PES reaction.

For comparison, a pure polyurethane reaction and a pure polyester reaction were also studied. The polyurethane reaction was conducted both in bulk and in the solution state using nitrobenzene (NBZ) as the solvent. The polyester reaction was conducted only in bulk with MEKP–cobalt naphthanate as the initiator.

B. Instrumentation and Experimental Procedure. A FTIR spectrometer (Nicolet, Model 20DX) with a resolution of 4 cm^{-1} in the transmission mode was used for kinetic measurements. After the reactants were mixed, 1 drop of mixture was pasted between two sodium chloride plates which were then mounted on a sample holder located in the FTIR instrument. Since the isocyanate functional group has a very strong IR absorbance, no spacer was used between the two NaCl plates. A temperature chamber was designed to maintain the reaction temperature at 60 °C. Three consecutive 1-s scans were taken at each sampling time, and their average was stored in a floppy disk for later data analysis. The sampling interval was 1 min during most of the reaction but was larger at higher conversion since the reaction was slow in that region. Measurement was ended at a preset time. All IR spectra in this study are shown in the absorbance mode.

The FTIR analysis is based on the peak change of functional groups or characteristic linkages during the reaction period. Therefore, there is more than one peak which may change when the reaction takes place. For example, Figure 1 shows FTIR spectra for a typical IPN system before and during reaction. In principle, intensities of the isocyanate peak (2278 cm^{-1}), hydroxyl peak (3588 cm^{-1}), amine peak (3349 cm^{-1}), and urethane peaks (trans at 1528 cm^{-1}, cis at 1414 cm^{-1}) can all be followed during the urethane polymerization.[31] However, the hydroxyl peak and the amine peak are found to be strongly affected by hydrogen bonding and tend to interfere with each other. The urethane peaks are located in a multipeak region where most peaks are overlapped with one another. Therefore, only the isocyanate peak can be easily followed during the polyurethane reaction.

Polyester reaction can also be determined from the spectra in spite of the existence of a polyurethane reaction. Polystyrene formation[32] is indicated by the peak at 1598 cm^{-1} which is also located in a region where too many peaks are overlapped with one another. Therefore, reaction conversion is better determined from the consumption of styrene C=C bonds at peaks 992 and 912 cm^{-1} (CH_2=CH deformation) and the consumption of polyester C=C bonds at peak 982 cm^{-1} (trans CH=CH deformation).

Infrared absorption is based on the fact that each chemical group in a sample absorbs infrared radiation of some characteristic

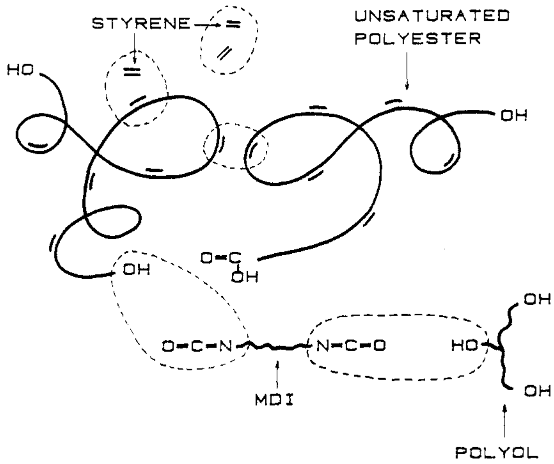

Figure 2. Schematical diagram of PU-PES IPN reactions.

frequencies. The amount of light intensity of transmission relative to the amount of light intensity incident on the sample can be related directly to the concentration of the absorbing species by Beer's law[33]

$$A_i = \beta_i l C_i \tag{1}$$

where A_i is the absorbance of species which can be determined from the peak height or peak area, β is the absorptivity which is characteristic of the absorbing species, l is the sample length, and C_i is the concentration of the absorbing species i. 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 reaction. In this study, the C–H peak at 2942 cm^{-1} is chosen as the internal standard and the peak area is used to calculate the absorbance. Reaction conversion can then be determined from the change of the normalized absorbance,

$$\alpha = 1 - \frac{\bar{A}_t}{\bar{A}_0} \tag{2}$$

where $\bar{A}_0$ and $\bar{A}_t$ are normalized absorbances of the monomer functional group before the reaction and after a reaction time t.

Results and Discussion

The reaction mechanism of PU-PES IPN is schematically described in Figure 2. The long chains represent unsaturated polyester molecules which are prepolymers with molecular weights ranging from 500 to 3000 and C=C bonds ranging from 6 to 10 per molecule. Styrene monomer serves as a cross-linking agent to link C=C bonds on the adjacent polyester molecules. Isocyanate reacts with polyol to form a urethane network. Grafting between the two networks may occur through the reaction of isocyanate groups and hydroxyl or carboxyl groups on the polyester molecules. Such a system may be considered as a grafted IPN.

Figure 3 shows typical conversion vs. time plots for both the PU phase and the PES phase in a simultaneous IPN reaction. Conversion of the PES phase is based on consumption of the overall C=C bonds. Although both reactions start at about the same time, the PU reaction appears to be much faster. This is because, in an externally catalyzed step-growth polymerization involving polyurethanes, the reaction is mixing activated and the maximum rate usually occurs at the beginning of reaction. On the other hand, for a free-radical polymerization of unsaturated polyesters, the reaction is often thermally initiated. Even when a low-temperature initiator, MEKP, is used with the aid of a promoter, cobalt naphthanate, the initial reaction rate is still low and the maximum rate does not appear at the beginning of the reaction. When the initiator is changed to PDO, the reaction rate of the PES phase becomes much slower and the two reactions, PU and PES, occur in a sequential order.

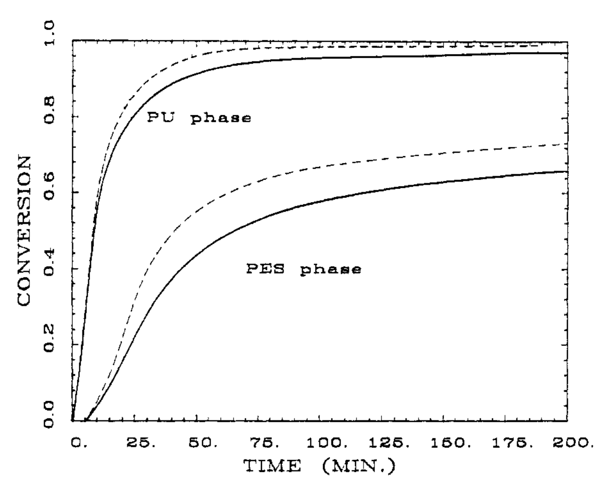

Figure 3. Conversion vs. time for PU-PES SIM-IPN reactions, measured by FTIR at 60 °C. Solid line: 50/50 PU/PES; dash line: 30/70 PU/PES.

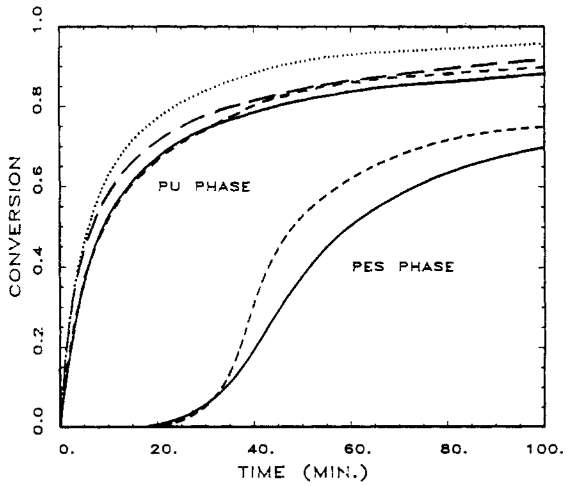

Figure 4. Conversion vs. time for PU-PES SEQ-IPN reactions, measured by FTIR at 60 °C: (– –) 50/50 PU/PES, (···) 30/70 PU/PES, (—) 50/50 PU/PES at equal stoichiometry, (- - -) 30/70 PU/PES at equal stoichiometry.

Varying the composition of IPN changes the reaction rates of PU and PES. Both reactions are speeded up when the weight fraction of PES is increased from 50% to 70%. For the PES reaction, this is apparently due to the increase in concentration of C=C bonds resulting from the addition of more PES. For the PU reaction, the isocyanate consumption rate increases because isocyanate groups in the PU phase may react with both the polyol groups and the hydroxyl and carboxyl groups at the ends of polyester molecules. When the polyester content is increased, the concentration of hydroxyl and carboxyl groups also increases and thus results in a faster consumption of isocyanate groups. The isocyanate peak in the PU reaction indicates that conversion of the PU phase increases in proportion to the PES concentration in the IPN system. For the 50/50 PU/PES IPN, the stoichiometric ratio between isocyanate and total hydroxyl groups is 0.828, while this ratio is 0.674 for the 30/70 PU/PES IPN.

In order to compare the isocyanate conversion at equal stoichiometry, another set of IPNs was prepared by adding extra isocyanate to the mixture to offset the hydroxyl and carboxyl groups in the PES phase. Figure 4 shows the isocyanate conversion for sequential IPN reactions with various compositions. Apparently, at equal stoichiometry, the isocyanate consumption rate is lower than that oc-

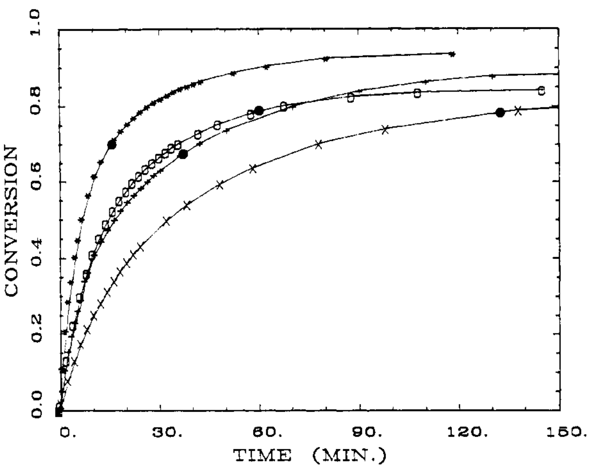

Figure 5. Isocyanate conversion vs. time for bulk and solution PU reactions at 60 °C: (+) bulk PU reaction without catalyst; (*) bulk PU reaction with 7.6 ppm of T-12; (O) solution PU reaction, PU/NBZ = 50/50, 7.6 ppm of T-12 in PU; (X) solution PU reaction, PU/NBZ = 30/70, 7.6 ppm of T-12 in PU.

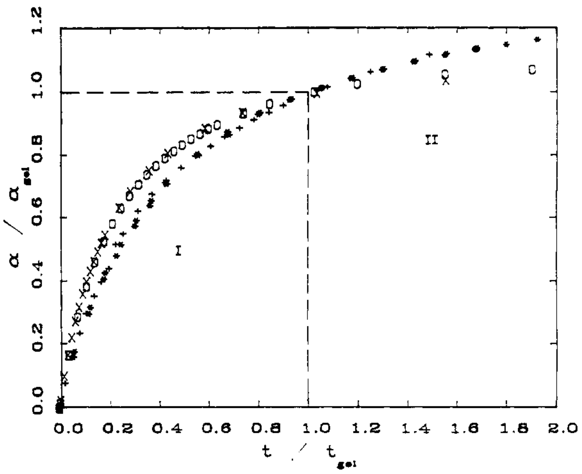

Figure 6. Reduced conversion vs. reduced time for bulk and solution PU reactions at 60 °C: (+) bulk PU, no catalyst; (*) bulk PU, 7.6 ppm of T-12; (O) solution PU, PU/NBZ = 50/50, 7.6 ppm of T-12 in PU; (X) solution PU, PU/NBZ = 30/70, 7.6 ppm of T-12 in PU.

curring at low NCO/OH ratio. The amount of PES has little effect on the PU reaction at low conversions. But when the PES starts to react, there seems to be a slight increase of isocyanate consumption, especially for the 30/70 IPN. The reason for such a change is still unknown.

Urethane polymerization resembles a solution process with PES serving as the solvent because during conversion the PES phase is always either unreacted or partially reacted. On the other hand, PES polymerization often occurs under a condition where the PU phase is either totally or partially reacted. Consequently the PES reaction can be considered as a solid-state polymerization. To further analyze the dual reactions in the IPN system, we compare them with the pure PU and PES polymerizations, respectively.

Figure 5 shows conversion vs. time for pure PU reactions both in bulk and in the solution state. As expected, increasing the catalyst increases the reaction rate, while increasing the solvent content decreases the reaction rate. The filled circles shown in Figure 5 indicate gel points for the reactions, which were reported in a separate work.[15] If we define a reduced conversion as $\alpha/\alpha_{\mathrm{gel}}$ and a reduced reaction time as t/t_{gel}, the experimental data in Figure 5 can be replotted as shown in Figure 6. The two curves for bulk PU reactions merge into a single curve, and the two curves for solution PU reactions also merge into a single curve with a slight deviation at high conversions. The two master curves, however, are not the same. Before gelation (i.e., region I), solution polymerization affords a higher reduced conversion than the bulk polymerization, while after gelation (i.e., region II) the trend is reversed. Although we still don't know the reason for such a difference, Figure 6 clearly demonstrates that the reaction kinetics of polyurethanes is not the same in bulk as in the solution state.

By use of the reduced conversion and time, results of the sequential IPN reactions can be replotted as shown in Figure 7. The reduced isocyanate conversion of the PU phase seems to be independent of IPN composition except at high conversions. Before gelation, the reduced isocyanate conversion corresponds to that of the PU solution polymerization, but after gelation, the reduced isocyanate conversion of IPN tends to resemble that of PU bulk polymerization. This result suggests that in a sequential PU–PES IPN, PES serves as a solvent during PU reaction before the system reaches gelation. After the gelation point, the PU reaction more closely resembles a bulk polymerization. The deviation is probably due to the existence of the PES phase (e.g., PES reaction or PU–PES grafting). At equal stoichiometry (i.e., NCO/OH = 1), the result is similar to that shown in Figure 7 except that the reduced isocyanate conversion after gelation corresponds more closely to PU bulk polymerization. The same analysis, however, cannot be applied to simultaneous IPN since both reactions occur at the same time and the PES reaction may contribute toward the occurrence of gelation. Therefore, the reduced conversion and the reduced time may not be related solely to the PU reaction.

As shown in Figure 2, the PES reaction is a copolymerization of unsaturated polyester and styrene. There are three possible reactions: styrene–polyester, styrene–styrene, and polyester–polyester. The reaction rates of styrene monomer, C=C bonds in unsaturated polyesters, and overall C=C bonds can be expressed as

$$\frac{-\mathrm{d}C_{\mathrm{s}}}{\mathrm{d}t} = k_{\mathrm{SS}}C_{\mathrm{S}^{\bullet}}C_{\mathrm{S}} + k_{\mathrm{ES}}C_{\mathrm{E}^{\bullet}}C_{\mathrm{S}} \tag{3}$$

$$\frac{-\mathrm{d}C_{\mathrm{E}}}{\mathrm{d}t} = k_{\mathrm{SE}}C_{\mathrm{S}^{\bullet}}C_{\mathrm{E}} + k_{\mathrm{EE}}C_{\mathrm{E}^{\bullet}}C_{\mathrm{E}} \tag{4}$$

$$\frac{-\mathrm{d}C}{\mathrm{d}t} = -\left(\frac{\mathrm{d}C_{\mathrm{S}}}{\mathrm{d}t} + \frac{\mathrm{d}C_{\mathrm{E}}}{\mathrm{d}t}\right) = k_{\mathrm{SS}}C_{\mathrm{S}^{\bullet}}C_{\mathrm{S}} + k_{\mathrm{ES}}C_{\mathrm{E}^{\bullet}}C_{\mathrm{S}} + K_{\mathrm{SE}}C_{\mathrm{S}^{\bullet}}C_{\mathrm{E}} + K_{\mathrm{EE}}C_{\mathrm{E}^{\bullet}}C_{\mathrm{E}} \tag{5}$$

where S stands for styrene, E for C=C bonds in unsaturated polyesters, $\mathrm{S}^{\bullet}$ and $\mathrm{E}^{\bullet}$ for radicals with styrene or polyester at the end, and C for concentration, and k_{SS}, k_{ES}, k_{SE}, and k_{EE} are rate constants.

These reaction rates can be determined experimentally from infrared spectra.[34] The consumption of styrene monomer can be followed by measuring the change in peaks at 912 and 992 cm^{-1}, while the consumption of C=C bonds in unsaturated polyesters may be followed by the change in the peak at 982 cm^{-1}. As shown in Figure 1, the styrene consumption can be easily determined from the peak change at 912 cm^{-1}, but the consumption of C=C bonds in polyesters cannot be followed directly from the peak at 982 cm^{-1} because it overlaps the other styrene peak at 992 cm^{-1}.

The least-squares fitting or cross-correlation method[35] has been used to separate overlapping peaks. In our study, the simple subtraction method was used. We first established calibration curves for styrene C=C bonds and polyester C=C bonds by preparing a series of styrene and

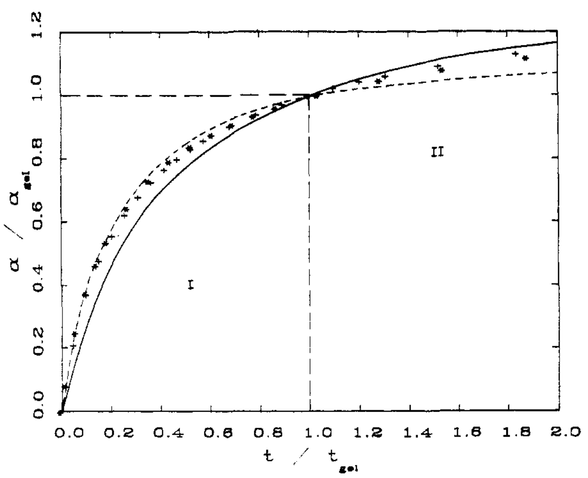

Figure 7. Reduced PU conversion vs. reduced time for PU–PES sequential IPN reactions at 60 °C: (+) 50/50 PU/PES SEQ-IPN, (*) 30/70 PU/PES SEQ-IPN; (—) bulk PU reactions, (---) solution PU reactions.

polyester solutions in nitrobenzene with known concentrations. The peak area vs. concentration gives a linear relationship for all three peaks. The absorptivity for each peak can be determined from the slope of the calibration line. The styrene conversion can be determined from the peak area change at 912 cm^{-1}, i.e.,

$$\alpha_S = 1 - \left(\frac{\bar{A}_t}{\bar{A}_0}\right)_{912} \qquad (6)$$

Another conversion, α_p, can be defined as the peak area change at 982 and 992 cm^{-1}, i.e.,

$$\alpha_p = 1 - \left(\frac{\bar{A}_t}{\bar{A}_0}\right)_{982+992} \qquad (7)$$

and the conversion of C=C bonds in polyesters can be calculated as

$$\alpha_E = 1 - \frac{1}{BI}[(1 - \alpha_p)(1 + BI) - (1 - \alpha_S)] \qquad (8)$$

where $B = \beta_{982}/\beta_{992}$ and $I = (C_E/C_S)_0$. Therefore, the overall conversion of C=C bonds can be expressed as

$$\alpha_T = \frac{\alpha_S + I\alpha_E}{1 + I} \qquad (9)$$

Based on eq 6–9, the conversion for each individual reaction in the PES phase can be determined. A typical result is shown in Figure 8. Since the network structure in the PES phase depends strongly on the copolymerization mechanism, information regarding the relative conversion of styrene vs. polyester in the PES phase is of great importance. Figure 9 reveals such plots, where the dotted curve represents a pure PES reaction with MEKP and cobalt naphthanate as initiator, and the symbols are data from all IPN reactions. If polyester–polyester reaction is negligible, under the steady-state assumption, the relative reaction rate of styrene monomer vs. polyester C=C bonds in the copolymerization can be expressed as

$$\frac{dC_S}{dC_E} = 1 + r_S\frac{C_S}{C_E} \qquad (10)$$

where $r_S = k_{SS}/k_{SE}$. If the copolymerization occurs under azeotropic conditions (i.e., $C_E/C_S = 1 - r_S$), then

$$\frac{dC_S}{dC_E} = \frac{C_S}{C_E} \qquad (11)$$

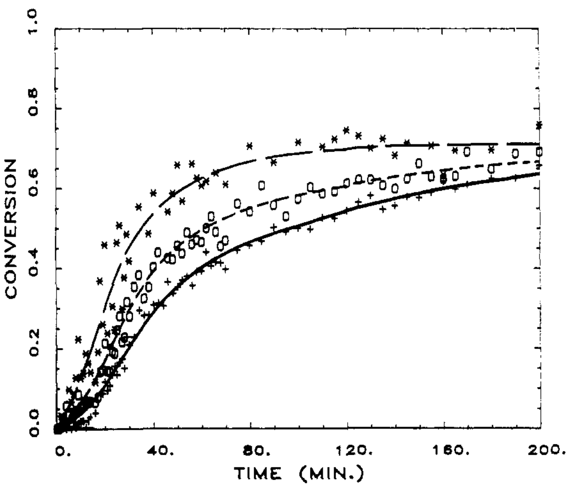

Figure 8. Conversion vs. time of PES reactions for 30/70 PU-PES SIM-IPN at 60 °C: (+) total styrene; (*) C=C bonds of polyester; (O) overall C=C bonds.

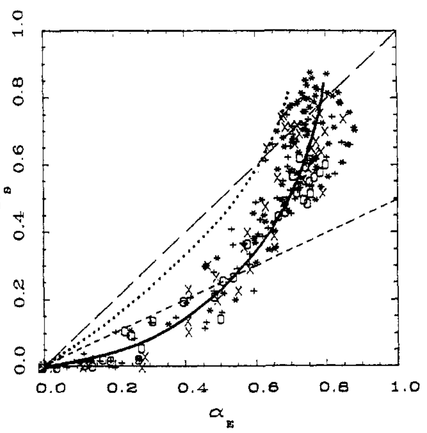

Figure 9. Total styrene conversion vs. polyester C=C conversion for pure PES reaction (···) and PU–PES IPN reactions at 60 °C: (+) 50/50 SIM-IPN, (*) 30/70 SIM-IPN, (O) 50/50 SEQ-IPN, (X) 30/70 SEQ-IPN.

If styrene monomer only reacts with polyester C=C bonds (i.e., an alternating copolymerization), then

$$\frac{dC_S}{dC_E} = 1 \qquad (12)$$

For typical unsaturated polyester resins (e.g., sheet molding compounds), styrene monomer is often present at a level of 100% stoichiometric excess relative to C=C bonds in the polyester,[21] which implies that $d\alpha_S/d\alpha_E = 1$ for a copolymerization under the azeotropic condition, while $d\alpha_S/d\alpha_E = 0.5$ for an alternating copolymerization. Such extreme cases are shown as the diagonal broken line and the lower dashed line, respectively, in Figure 9.

For pure PES reaction, results shown in Figure 9 reveal that the copolymerization route is located between the azeotropic and the alternating copolymerization lines in the early stage of reaction and then shifts gradually to the azeotropic line. At high conversions, the styrene reaction is more favorable than the polyester reaction as indicated by the up-bending curve. This may be because polyester molecules are much more immobile than styrene monomers. At high conversions (i.e., low concentration of C=C bonds), the reaction is entirely diffusion controlled. Polyester molecules are trapped in the PES network, which makes further reaction very difficult (i.e., r_S becomes larger).

The scattering of data points in Figure 9 is due to noise in IR spectra and to errors introduced into the calculation method, which are usually inevitable in the quantitative analysis of IR spectroscopy, especially for kinetic studies. Nevertheless, a few trends can still be noted from the figure. First, the copolymerization mechanism seems to be independent of IPN composition and type of initiator used in this study. All data, although scattered, tend to form a single curve. Second, if a single curve can be drawn from these data, it falls under the lower dashed line at low conversions. This indicates that in a polyurethane network, the polyester–polyester reaction is more favorable at low conversions than styrene–polyester and styrene–styrene reactions, which is quite different from the observation in pure PES reaction. One possible reason is that the PU phase may have enhanced intramolecular reaction of polyester molecules.

At high conversions, the curve bends upward, which indicates more reaction of styrene than of polyester. Figure 9 also shows that at the same polyester conversion, more styrene has been consumed in the pure PES reaction than in the IPN reaction due to interaction of the PU phase.

Conclusions

We have demonstrated that Fourier transform infrared spectroscopy is a very useful tool for analyzing the kinetics of complicated polymerizations. Using a reduced conversion and reaction time, we are able to show that reaction kinetics of urethane polymerization is not the same in bulk as in the solution state. In PU–PES IPN, PES has a "solvent effect" on the PU reaction, while PU has a "solid effect" on the PES reaction. Such interactions may change the reaction mechanisms of both PU and PES polymerizations. Adding the PU phase changes the PES reaction mechanism, but varying the IPN composition and the type of initiator does not seem to have a strong effect.

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