Rheokinetic Changes during Polyurea Reactions in Solution

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Synopsis

The viscosity rise and conversion profile of polyurea reaction in solution were measured using a Haake viscometer and an FTIR, respectively. In a three-component polyurea system, it was found that the liquid–solid transition is dominated by the microphase separation from the formation of hard segments. The formation of soft segments mainly contributes to the initial viscosity buildup. A series of experiments were carried out to study the effects of resin composition, solvent concentration, and reaction temperature on the viscosity rise and gelation of polyureas.

INTRODUCTION

Since 1974, when the reaction injection molding (RIM) process was first used to produce automotive parts in the United States, changes in both RIM machinery and formulations have taken place. At first almost all RIM materials were segmented polyurethanes of which formulations were based primarily on butanediol or ethylene glycol as chain extenders. To increase the productivity of the RIM process and to improve the properties of RIM products, most RIM materials have shifted from polyurethanes to polyurethane–ureas. The main difference is that the latter system uses a low molecular weight diamine as a chain extender, instead of a diol, to form urea hard segments and polyether soft segments with urethane end groups. Currently there is a growing interest in total-urea systems in which hydroxyl-terminated polyethers used in the polyurethane–urea system are replaced by amine-terminated polyethers.[1-14] The reactivity of amines with aromatic isocyanates, even with no catalyst, is much higher than that of alcohols with aromatic isocyanates (i.e., activation energy 1–8 kcal/g mol vs. 10–15 kcal/g mol). Aliphatic diamines or triamines react almost instantaneously with aromatic isocyanates, whereas aromatic diamines react slightly slower. Due to the fast reaction rate, these systems often have difficulty filling large, complex molds.

Currently a major effort in the development of polyurea RIM is to slow down the reactivity of aliphatic amines and diamine chain extenders by modifying their chemical structure. For example, Schlotterbeck et al.[15] developed a new class of soft segment macromolecules for polyurea systems. This new macro-

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molecule family is called polyether–ketimines which have lower reactivities and viscosities. Casey et al.[3] applied the Hammett sigma correlation to study structure-reactivity relationships of several aromatic diamines. They reported that 2,4-diamino-anisole has about half the reactivity of 2,4-toluenediamine, whereas 3-methyl-6-*tert*-butyl-2,4-diamino-anisole has only one-sixth of the reactivity of 2,4-toluenediamine due to the steric hindrance of the *tert*-butyl group. Similar structure–reactivity relationships between diethyl-toluenediamine (DETDA) and dimethylthio-toluenediamine (DMTDA) were also reported.[16]

Typical commercial polyurea RIM formulations contain three components: an aromatic diisocyanate, a low molecular weight aromatic diamine, and a high molecular weight aliphatic triamine. Since polyurea reaction is a step-growth polymerization, the reaction kinetics are generally modeled as an nth-order reaction with an Arrhenius temperature dependence. Davis and Ebersole[17] conducted reactions where n-butylamine and aniline reacted competitively with phenyl isocyanate. Based on the composition of the product mixture, relative overall reaction rates were calculated. Pannone and Macosko[18,19] used adiabatic temperature rise measurements to monitor the extent of reaction of an aliphatic diamine and an aromatic diamine reacting competitively with an aromatic diisocyanate. The reaction of the aliphatic amine was considered instantaneous, whereas the reaction of aromatic amines and isocyanates was described by a third-order model (first order in isocyanate, second order in amine). Kinetic parameters determined from the RIM experiments predicted lower reaction rates in solution polymerization. This discrepancy, they claimed, is due to the polarity of the solvent (dimethylacetamide) which might have a strong effect on polyurea reaction.

In a recent study of polyurea RIM carried out by Hsu and Lee,[12] the solution polymerization data were successfully applied to the bulk polymerization. A kinetic model was proposed to treat the competitive reactions of aliphatic triamine and aromatic diamine. The parameters of the kinetic model were determined by an FTIR using data from solution polymerizations. Combined with a heat transfer model, the kinetic model predicted fairly well the adiabatic temperature rise of bulk polyurea reaction in RIM.

Viscosity rise has a great effect on mold filling. In polyurethane RIM, the resin viscosity rises slowly first and then sharply near the gel point. Mold filling must be completed before the sharp increase of viscosity such that short shots and knit lines can be avoided. The viscosity rise in two-component polyurethane systems has been studied by Lipshitz and Macosko[20] and by Richter and Macosko.[21] Few data, however, have been reported on viscosity rise for three-component polyurethane or polyurea RIM systems where phase separation plays a major role. Castro and Macosko[22] carried out viscosity rise measurements of several commercial RIM urethane systems on a Rheometrics mechanical spectrometer. The materials were used without catalyst to allow enough time for injecting the resin into the rheometer. They found that if the reduced viscosity was plotted against the reaction conversion, all data fell onto a single curve. A simple rheological model was proposed, which can reasonably predict the experimental data.

Due to the rapid reaction rate of urea formation, it is not practical to use commercial viscometers for rheological measurements. Vespoli and Alberino[7] designed an experimental mold to monitor the pressure rise as the material

filled a long runner and mold cavity. Viscosity parameters were then extracted from a mold filling model by fitting the measured molding pressure.

In order to conduct a quantitative analysis of polyurea RIM, a thorough understanding of the reaction kinetics and rheological changes during reaction is required. In this study, a series of polyurea reactions are conducted in solution to slow down the reaction rate such that rheological and kinetic information can be obtained from several conventional analytical instruments. This information is useful for understanding the roles which aliphatic and aromatic amines play in polyurea RIM.

EXPERIMENTAL

Materials

The basic ingredients of polyureas used in this study consist of an aromatic diisocyanate, an aliphatic triamine, and an aromatic diamine. These materials are summarized in Table I. The aromatic diisocyanate used is a liquid form of 4,4'-diphenylmethane–diisocyanate (MDI) (I1305, Dow Chemical). I1305 is a blend of a diisocyanate monomer (50% by weight) and a high molecular weight polymer (50% by weight). The equivalent weight of I1305 is 210. The aliphatic triamine is an amine-terminated polyether with a functionality of 3 and a molecular weight of about 5000 (Jeffamine T5000, Texaco Chemical). T5000 is 85% aminated with some secondary hydroxyl groups. The major aromatic diamine studied is an isomeric mixture of dimethylthio–toluenediamine (DMTDA, Ethyl). DMTDA has an equivalent weight of 107. For comparison, two other aromatic diamines were also studied: diethyl–toluenediamine (DETDA, Mobay) with an equivalent weight of 89, and *tert*-butyl–toluenediamine (TBTDA, Air Products) with an equivalent weight of 89. Figure 1 shows the chemical structures of DETDA, TBTDA, and DMTDA.

The reaction mechanism of the three-component polyurea is schematically described in Figure 2. The branched long chains represent polyether-based aliphatic triamines which react with isocyanates to form soft segments in polyurea. The linear short chains represent aromatic diamines which react with

TABLE I
Materials Used in This Study

Ingredient	Code	Compound
Diisocyanate	I1305 (Dow)	50% by weight of 4,4'-diphenylmethane diisocyanate (MDI) and 50% by weight of a high molecular weight polymer
Triamine	T5000 (Texaco)	Amine-termined polyether
Diamine	DETDA (Mobay)	Diethyl-toluenediamine
	TBTDA (Air Products)	*Tert*-butyl-toluenediamine
	DMTDA (Ethyl)	Dimethylthio-toluenediamine
Solvent	NB	Nitrobenzene
	—	2-Methoxyethyl ether
	—	N,N-dimethylacetamide

DETDA

H₂N ... (chemical structure)

3,5—diethyl—2,4—toluenediamine

3,5—diethyl—2,6—toluenediamine

TBTDA

tert—butyl—toluenediamine

DMTDA

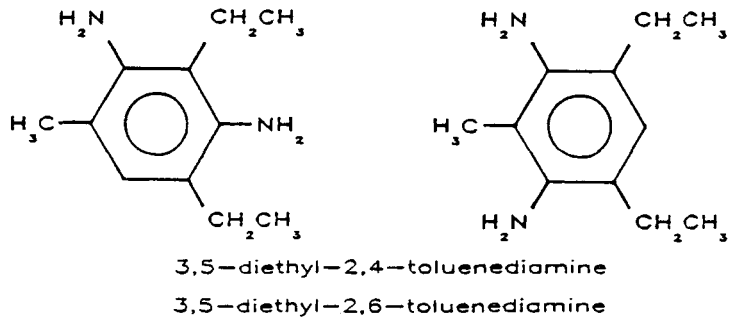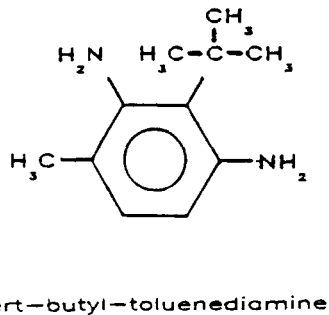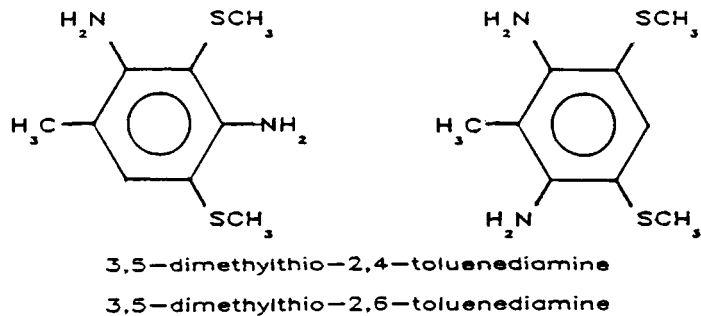3,5—dimethylthio—2,4—toluenediamine

3,5—dimethylthio—2,6—toluenediamine

Fig. 1. Chemical structures of DETDA, TBTDA, and DMTDA.

isocyanates to form hard segments in polyurea. Linkage between the two segments occurs through the formation of urea. To study the effect of resin composition on rheological changes, the ratio of aliphatic to aromatic amines was varied from 70/30 to 20/80 (by weight) with equivalent moles of isocyanate. In addition, pure soft-segmented polyureas and pure hard-segmented polyureas were prepared as references. Several selected polyurea reactions were also conducted at various dilution levels, i.e., 85, 75, and 65% solvent, to study the influence of solvent concentration. The temperature effect on gel time and
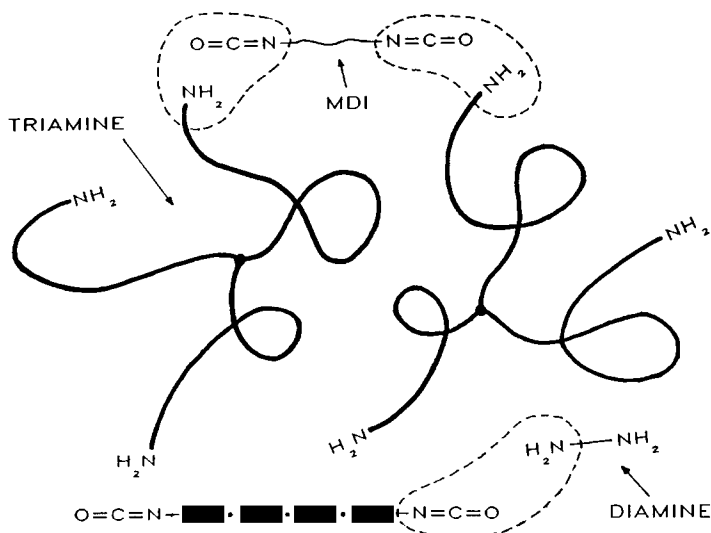
Fig. 2. Schematic diagram of three-component polyurea reaction.

conversion was investigated by varing the reaction temperature from 25 to 67°C for several polyurea systems.

One major concern in solution polymerization is the effect of solvent on the chemical reaction and phase behavior. Three solvents—nitrobenzene, 2-methoxyethyl ether, and N,N-dimethylacetamide—were used in this study and the one with the least interaction was selected for polyurea solution polymerization. Their effect on viscosity rise and conversion of the I1305/DMTDA reaction is shown in Figure 3. N,N-dimethylacetamide is a polar solvent which showed a very strong interaction with the urea reaction. It prevented the formation of hard segments as well as microphase separation and, consequently, there was almost no viscosity rise. The reaction rate was very high and the conversion in 75% solvent reached 100% at room temperature. On the other hand, when the solvent was changed to nitrobenzene, there was a very sharp viscosity rise in a short reaction time and the reaction conversion could only reach 60% at the same conditions. When 2-methoxyethyl ether was used, an intermediate viscosity response was found. For the latter two solvents, the conversion curve tended to level off when the system reached gelation. Based on these results, the nitrobenzene was found to have the least interaction with the urea system. Therefore, it was chosen as the solvent in this study.

All ingredients were degassed and demoisturized under vacuum at room temperature for at least 12 h to remove water and air. For kinetic and rheological measurements, a solution of isocyanate with nitrobenzene and a similar one of amines with nitrobenzene were first prepared in separate beakers of 150 cm^3. A desired amount of solution was loaded into a 50 mL disposable syringe for each solution and the two solutions were then impingement-mixed into a beaker, where a stirrer provides further mixing.

Instrumentation and Procedure

A Haake viscometer, Model MVII, was used to measure the system viscosity rise before gelation. The Model MVII has a cup with an inside diameter of 42
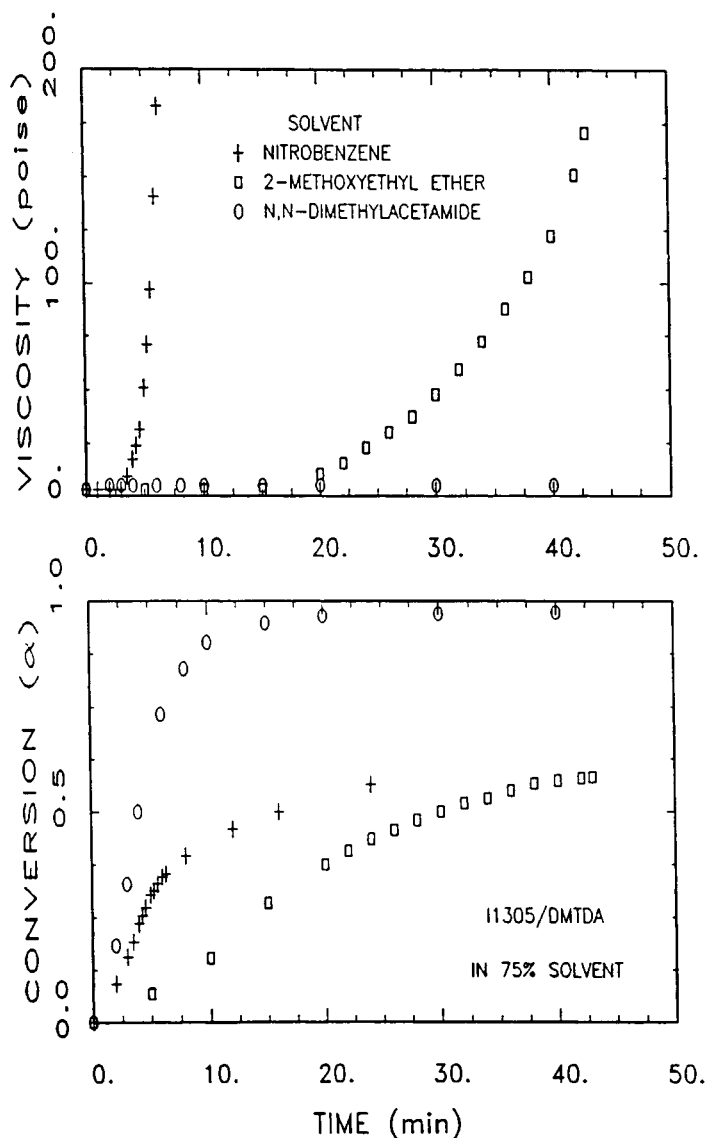
Fig. 3.   Effect of solvent on the viscosity rise and conversion of a polyurea reaction.

mm, and a rotor with an outside diameter of 36.8 mm and a length of 60 mm. Water of desired temperature was circulating in a heating jacket outside the measuring cup to control the system temperature. The temperature was monitored by reading a digital thermometer having a small thermocouple inserted into the gap between the cup and the rotor during reaction.

During polymerization, different shear rates ranging from 3.3 to 176.3 (1/s) were applied to the system by changing the gear ratio. The system viscosity was monitored continuously by using a chart recorder. Accuracy of the viscosity measurement depended on the sensitivity of the cable used in the Haake viscometer and also on the Weissenberg effect of the reacting polymer solutions

when they became viscoelastic. As the viscosity began rising sharply, material tended to climb the rotor, even at the lowest shear rate, due to the Weissenberg normal force effect. Consequently, the accuracy of any further viscosity measurement was severely reduced and the measurement was terminated. The gel point is defined by extrapolating the viscosity rise curve to infinity.

Isothermal dynamic mechanical measurements were performed using a Rheometrics dynamic analyzer (RDA-700) in a parallel plate mode. The plate was a serrated disk 1.25 cm in diameter. The frequency used was 1 Hz. The percent strain was adjusted between 1 and 25% to obtain a suitable torque signal. Measurements were taken for 30–60 min, depending on the reaction rate. The storage modulus G' and loss modulus G'' were recorded on a floppy disk for later data analysis.

An FTIR spectrometer (Nicolet 20DX) with a resolution of 4 cm^{-1} in the transmission mode was used for kinetic measurements. After the reactants were mixed, about 0.05 mL of mixture was pasted between two sodium chloride (NaCl) plates that were then mounted on a sample holder located in the FTIR sample chamber. Since the functional group of isocyanate has a very strong IR absorbance, no spacer was used between the two NaCl plates. A temperature chamber with a controller was designed to monitor the reaction temperature. Three consecutive, 1-s scans were taken, averaged, and stored on a floppy disk at each sampling time. The sampling interval was 1 min during most of the reaction, but was longer at high conversions because the reaction was very low in these regions. Measurement was ended at a preset time. All IR spectra in this study are expressed in absorbance.

Infrared absorption is based on the fact that each chemical group in a sample absorbs infrared radiation at several characteristic frequencies. The amount of light intensity transmitted 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[23]:

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

where A_i is the absorbance of species which can be determined from the peak height or peak area, β_i is the absorptivity that 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} was chosen as the internal standard. Reaction conversion can then be determined from the change of the normalized absorbance:

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

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

Before Beer's law is applied for any quantitative analysis, the absorptivities of reacting species need to be determined. Calibration curves of the isocyanate peak based on the changes of both the peak height and peak area have been

established previously[24] by preparing mixtures of isocyanate monomer and di-
chloromethane of known concentration. For the isocyanate peak, the calibration
curves based on both peak height and peak area formed straight lines. In this
study, the change of the peak area was followed to determine the reaction
kinetics of polyurea.

Since amine tends to react with isocyanate right after mixing, the reference
spectrum (i.e., at $\alpha = 0$) cannot be easily obtained because 40 s are needed for
sample preparation and IR stabilization before the first scanning can be taken.
Therefore, an inert chemical with a similar structure as that of amine was used
for the determination of the reference spectrum. For TBTDA, 4-*tert*-butyl–
toluene (TBT), a chemical similar to TBTDA but without the amine group,
was selected to replace TBTDA. The chemical structures and IR spectra of
TBT and TBTDA are expressed in Figure 4. Except for the NH_2 group, TBT
and TBTDA have the same IR spectra. The $C-H$ peak area of TBT is very
close to that of TBTDA after normalization based on the peak of tert-butyl
group (1351 cm^{-1}). Hence, to determine the reference spectrum for any
TBTDA-containing polyurea system, equivalent moles of TBT were used to
substitute TBTDA.

For DMTDA-based systems, the reaction rate in solution was sufficiently
low and the reference spectrum could be easily determined.

RESULTS AND DISCUSSION

In order to understand the roles of soft and hard segments in the rheological
changes during polyurea reaction, viscosity measurements of pure soft and hard
segments diluted in nitrobenzene were first investigated. Figure 5 shows the
results of 85%-diluted T5000/I1305 polyureas with two different stoichiometric
ratios (amine to isocyanate) as well as 85%-diluted I1305/DETDA, I1305/
TBTDA, and I1305/DMTDA polyureas with equal stoichiometry. As shown
in Figure 5(a), the viscosity rise of the T5000/I1305 reaction with equal stoi-
chiometry was extremely fast and reached gelation within 18 s. When the ratio
r was changed to 1/4.5, the system showed only a small viscosity rise and never
gelled. These observations are consistent with the results predicted by Flory's
gelation theory.[25]

Although the I1305/DETDA, I1305/TBTDA, and I1305/DMTDA reactions
resulted in linear polymers, their viscosity rises shown in Figure 5(b) behave
like the chemical crosslinked systems because of the microphase separation
from the formation of hard segments. The microphase formation in urea re-
actions is due to factors such as hydrogen bonding, aromatic π-electron inter-
actions, chain flexibility, and chain packing. Among the three I1305/diamine
polyureas, the DETDA-based system showed the earliest onset of viscosity rise
as well as the shortest gel time. These differences are largely due to the hindrance
effect of side groups on diamines, which reduces the activity of the adjacent
amine group. As shown in Figure 1, the *tert*-butyl group in TBTDA has a
stronger steric hindrance than the ethyl group in DETDA so that the TBTDA
has a lower reactivity than DETDA. Compared with DETDA, the DMTDA
has a much lower reactivity because the methylthio group has a higher capability
of electron withdrawing than the ethyl group, which reduces the reactivity of
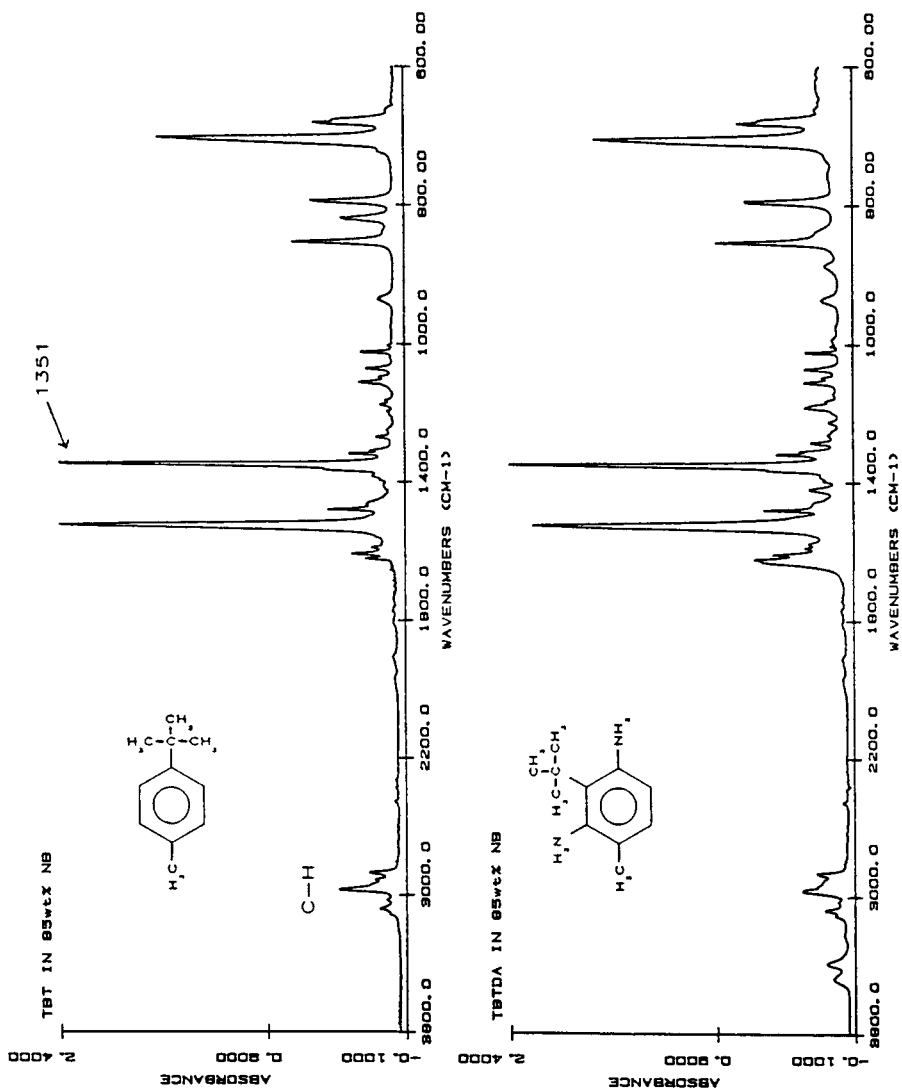the adjacent amine.

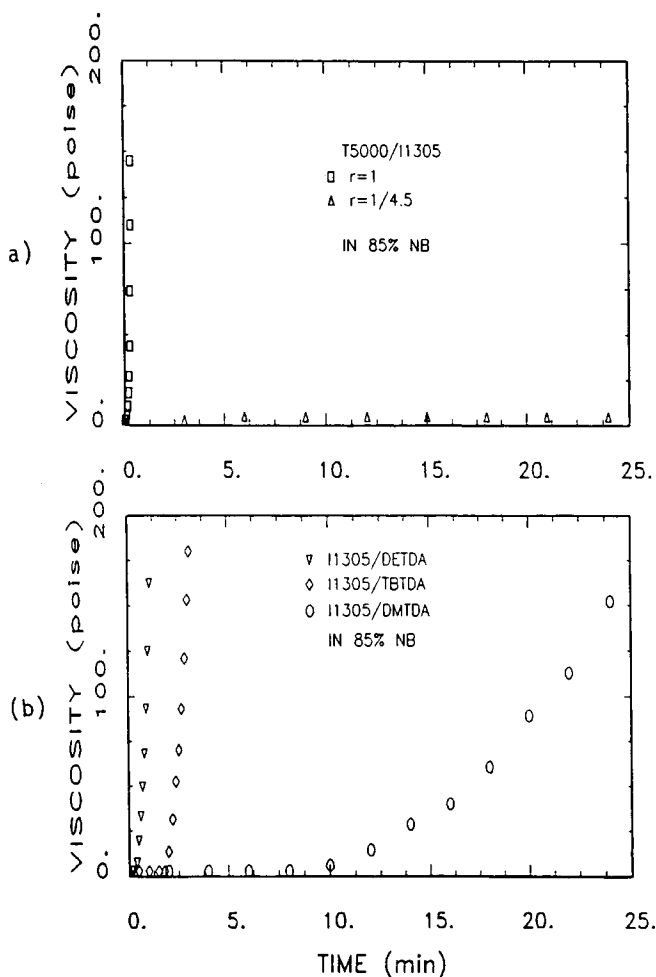Fig. 4.   Comparison of IR spectra between TBT and TBTDA.

Fig. 5.　Viscosity vs. time for (a) T5000/I1305 reactions and (b) I1305/diamine reactions at 25°C.

Figure 6 shows the effect of amine ratio (by weight) on the viscosity rises during the reaction of three-component polyureas in 85% nitrobenzene. The stoichiometric ratio of total amine to isocyanate is equivalent to one in each system. As shown in the figure, the three-component polyurea system with an amine ratio of 70/30 (i.e., 70% triamine and 30% diamine by weight with equivalent moles of isocyanate) has a longer gel time and a slower viscosity rise than the systems with amine ratios of 50/50 and 20/80. In other words, with more aromatic diamine in a three-component polyurea, the gelation tends to take place earlier. These results can be explained by the unequal reactivities of the aliphatic amine and the aromatic amine with isocyanates. In a three-component polyurea system, the reactions of aliphatic and aromatic amines with isocyanates are competitive. Since aliphatic amines react much faster than aromatic amines (i.e., activation energy 1.5 kcal/g mol vs. 4–8 kcal/g mol [12,18]), one would expect that chemical crosslinking by the aliphatic triamine
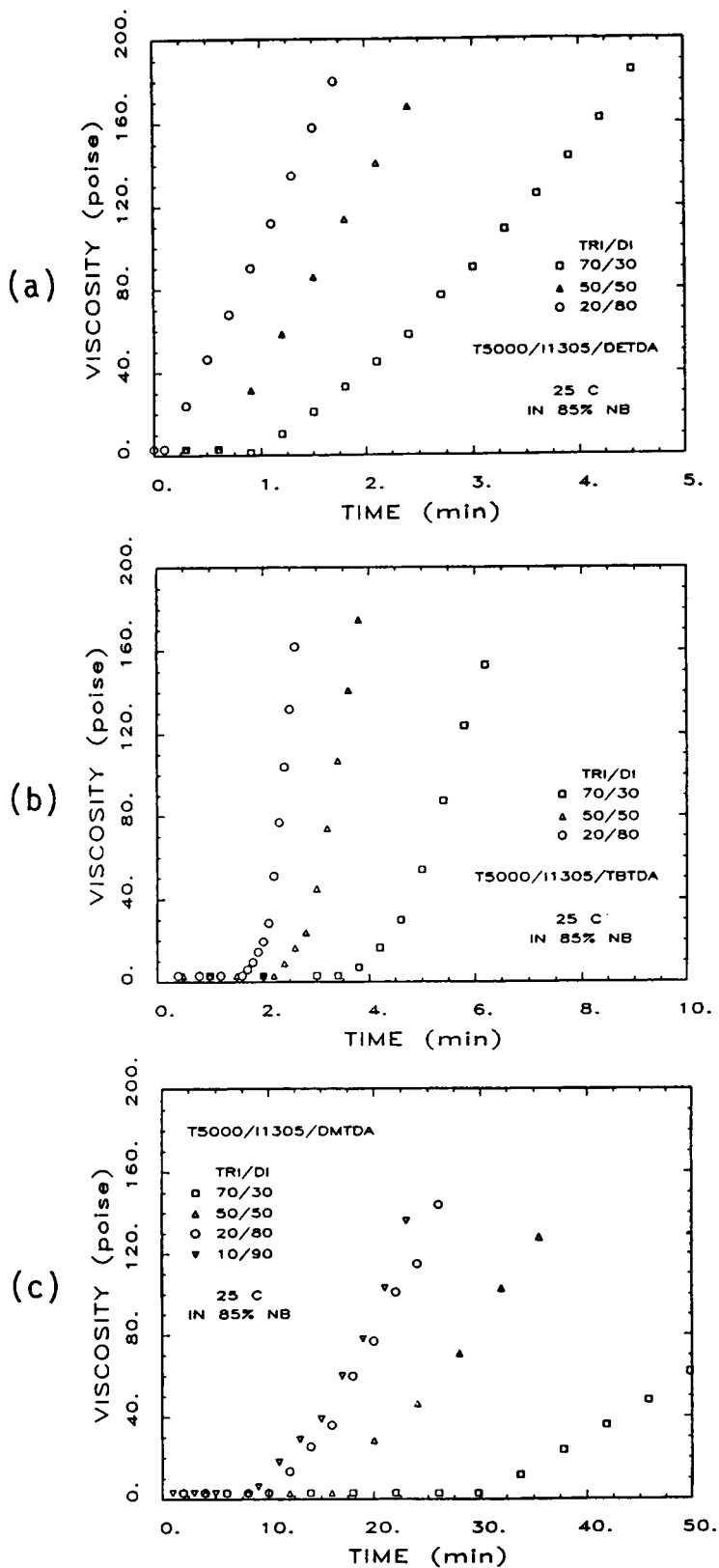
Fig. 6. Viscosity vs. time for (a) DETDA-based reactions, (b) TBTDA-based reactions, and (c) DMTDA-based reactions.

with diisocyanate would dominate both the viscosity rise and the gel formation
in the reaction system. However, gelation in most three-component polyurea
reactions is often not determined by the reaction of aliphatic triamine. The
reason is that, although the stoichiometric ratio of total amine functional groups
to isocyanate functional groups is kept near 1, the "effective" stoichiometric
ratio during the reaction of aliphatic triamine and diisocyanate can be much
less than 1 because aromatic amines have much lower reactivity than aliphatic
amines. For the three-component systems shown in Figure 6, the molar ratio
of T5000/I1305/DMTDA = 70/68/30 by weight is nearly 1/7.7/6.7, which
means that the "effective" stoichiometric ratio during the reaction of aliphatic
triamine and diisocyanate is about 1/7.7. Under this condition, no chemical
crosslinking will occur. Therefore, the formation of soft segments in this poly-
urea system contributes to only an increase in molecular weight, which results
in a viscosity rise instead of gelation. The gelation of this system is dominated
by the microphase separation from the formation of hard segments.

   In a highly dilute solution, the amount of soft segments formed may not be
enough to cause any viscosity rise. Consequently, the measured rheological
changes often reflect the formation of hard segment domains. Figure 7 shows
the effect of solvent concentration on the viscosity rise and gelation of the
DMTDA-based three-component polyurea systems. For the 85 and 75%-solvent
diluted systems, viscosity gradually increased from a low initial value to gelation.
When the amount of solvent was reduced to 70% or lower, there was an initial
viscosity jump at the very beginning of the reaction, followed by a viscosity
rise to gelation. If DMTDA is replaced by an equal amount of solvent, i.e.,
formation of soft segments only, the system shows only an initial viscosity
jump which has the same value as that in the three-component system. This
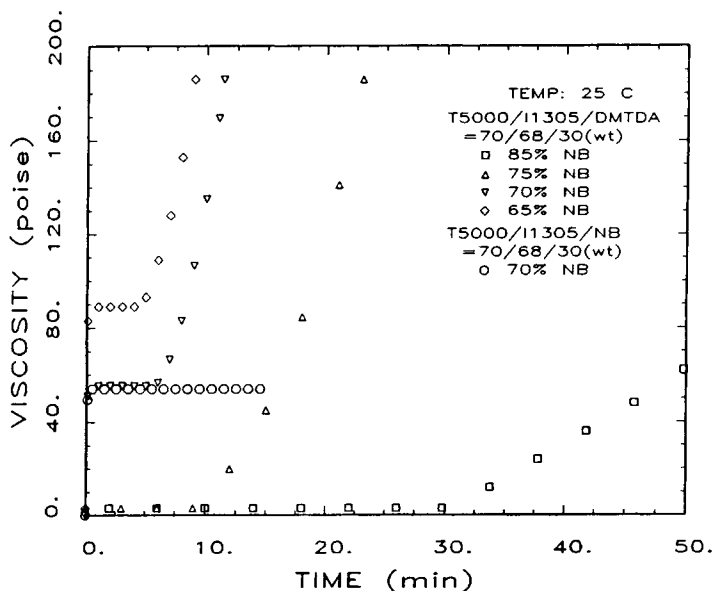

Fig. 7.   Effect of solvent concentration on the viscosity rise of a three-component polyurea
reaction.

is demonstrated in Figure 7 for a 70%-solvent diluted system. This result suggests that the initial viscosity jump is due to the reaction of aliphatic amines and isocyanates, whereas the gelation is governed by the microphase separation from the formation of hard segments. In a three-component RIM polyurea system, increasing the amount of hard segments will decrease the initial viscosity jump and speed up the gelation.

Figure 8 shows conversion vs. time plots of DMTDA- and TBTDA-based polyurea reactions in 85% nitrobenzene at 25°C. Shown in Figure 8(a) is the effect of amine ratio (by weight) on the conversion profiles of the three-component polyureas. The conversion profiles of the corresponding I1305/DMTDA and I1305/TBTDA reactions are shown in Figure 8(b). The reaction of I1305/ TBTDA polyurea has a limiting conversion of 0.65. The conversion profiles of both 70/30- and 20/80-segmented polyureas (i.e., T5000/I1305/TBTDA polyurea systems with amine ratios 70/30 and 20/80) resemble that of I1305/ TBTDA polyurea. In the early stage of the reaction, the 70/30-segmented polyurea has a higher conversion, but a lower reaction rate than the 20/80-
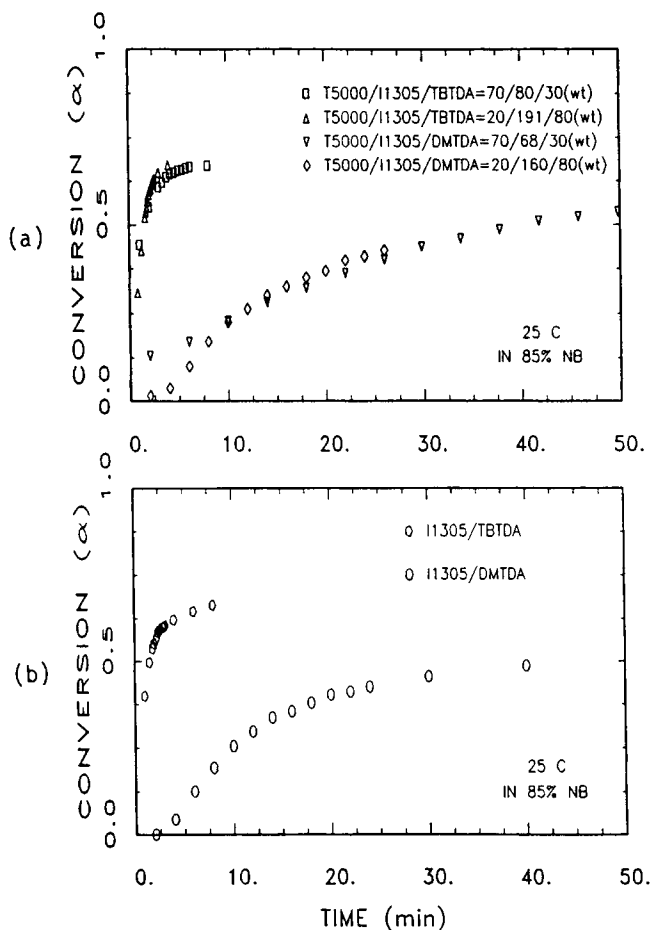

Fig. 8. Conversion vs. time for TBTDA and DMTDA-based reactions: (a) three-component systems; (b) two-component systems.

segmented polyurea. The reason is the former contains more aliphatic amine than the latter.

The results of DMTDA-based systems are very similar to those of TBTDA-based systems. All three DMTDA-containing polyureas have limiting conversions between 0.50 and 0.55. Apparently the type of chain extender has a strong effect on both the reaction rate and the limiting conversion in polyurea reaction.

In the analysis of rheology and kinetics of reactive systems, it is useful to express the viscosity as a function of conversion. Figure 9 shows viscosity vs. conversion plots of DMTDA- and TBTDA-based polyurea reactions in 85% nitrobenzene. The gelation of these systems took place around a conversion of 0.6 and 0.7 for TBTDA-based systems and 0.45 and 0.55 for DMTDA-based systems. The viscosity curves of the corresponding I1305/TBTDA and I1305/DMTDA reactions are similar to their three-component systems.

In order to apply the solution polymerization data to the bulk polymerization of polyurea, the influence of solvent concentration and reaction temperature
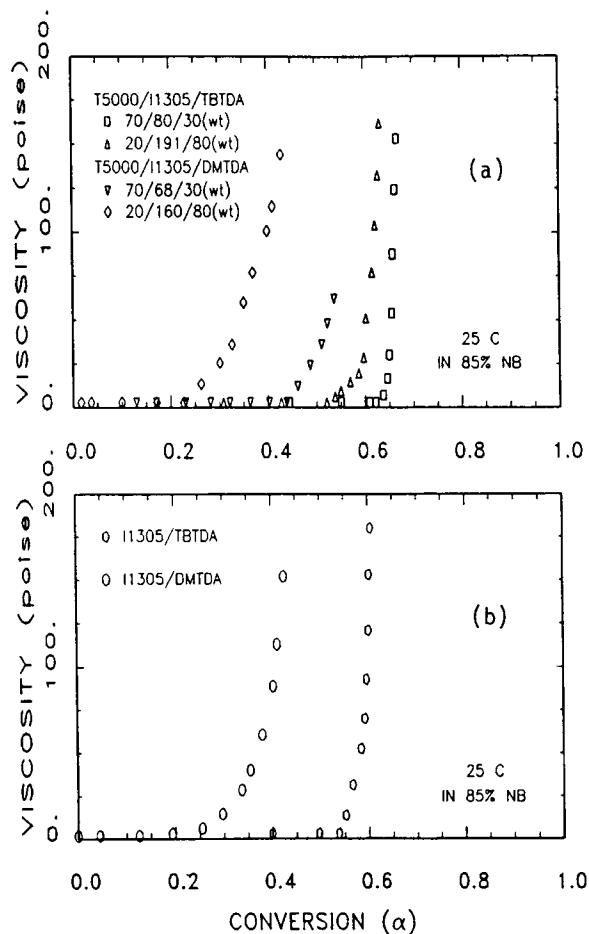

Fig. 9.   Viscosity vs. conversion for TBTDA and DMTDA-based reactions: (a) three-component systems; (b) two-component systems.

needs to be understood. Figure 10 shows the effect of solvent concentration on the viscosity rise and gel conversion for DMTDA-based polyureas diluted with 85, 75, and 65% nitrobenzene. The system with a lower solvent concentration has a lower gel conversion.

Figure 11 shows the effect of reaction temperature on the conversion, viscosity rise, and gel conversion of I1305/DMTDA system in 85% nitrobenzene at 25, 47, and 67°C. As expected, at a higher reaction temperature, the system has an earlier onset of viscosity rise and a higher limiting conversion. Because of tight 3-D hydrogen bonding in polyureas, when the hard segments form, they tend to slow down, and sometimes stop further reaction. Therefore, a higher mold temperature is recommended for reaching the complete reaction in the polyurea RIM process. The gel conversion of the I1305/DMTDA system is also influenced by the reaction temperature as displayed in Figure 11(c). The system at a higher reaction temperature tends to gel at a higher conversion but the difference becomes less at higher temperatures. Similar results were also found in the DMTDA-based three-component polyurea systems. These findings
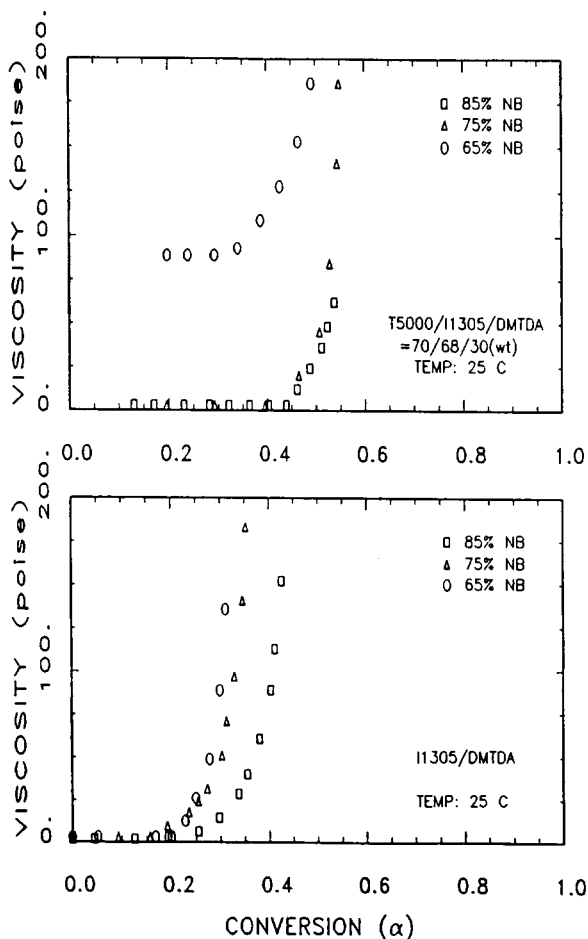

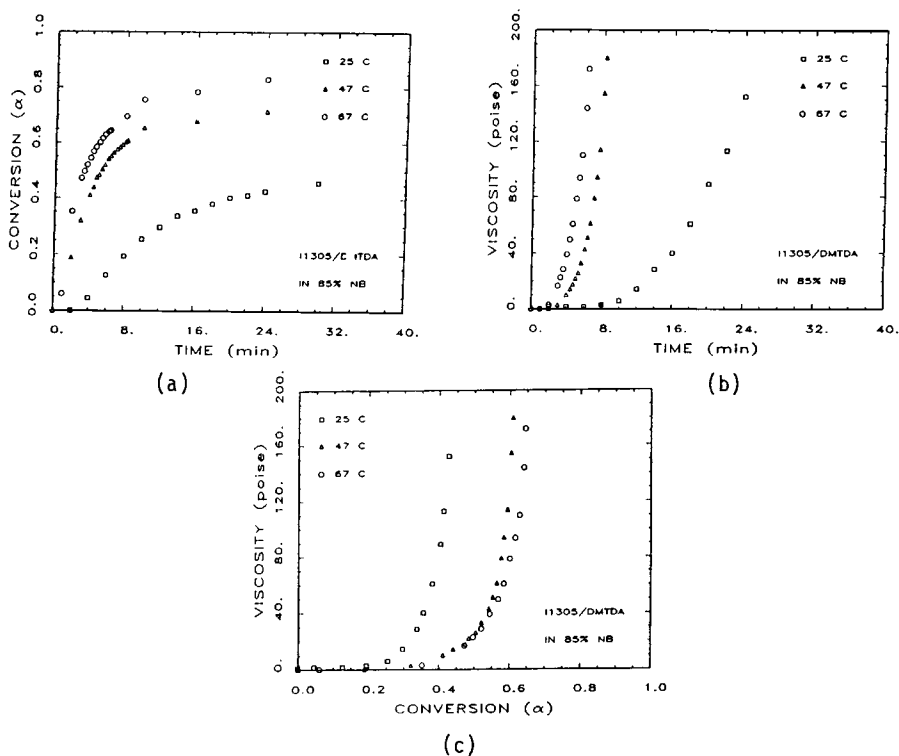Fig. 10.   Effect of solvent concentration on the gel conversion of DMTDA-based reactions.

Fig. 11.   Effect of temperature on (a) conversion, (b) viscosity rise, (c) gel conversion of a two-component polyurea reaction.

suggest that microphase separation from hard segment formation is temperature sensitive, especially at lower temperatures.

Figure 12 shows the viscosity rise, G', and G'' vs. time and conversion for the T5000/I143L/DMTDA polyurea reaction in 80% NB at 23°C. I143L is a MDI-based diisocyanate (Dow Chemical). It shows that the crossover of G' and G'' curves occurred during the soft-segment formation. Physical gelation due to the formation of hard segment results in a rapid increase of both G' and G''.

CONCLUSIONS

The solution polymerization technique was used to slow down the reaction rate of polyureas such that rheological and kinetic information could be obtained. The reaction of aliphatic triamine and aromatic diisocyanate is almost instantaneous, which results in an extremely fast viscosity rise and a very short gel time when the stoichiometric ratio is equal to 1. Such gelation is caused by chemical crosslinking through the reaction of triamines and diisocyanates. However, in a three-component polyurea system (including aliphatic triamine, aromatic diamine, and an equal molar amount of diisocyanate), the effective stoichiometric ratio is far from 1 during the reaction of aliphatic triine and diisocyanate because of the relatively lower reactivity of the aromatic diamine.
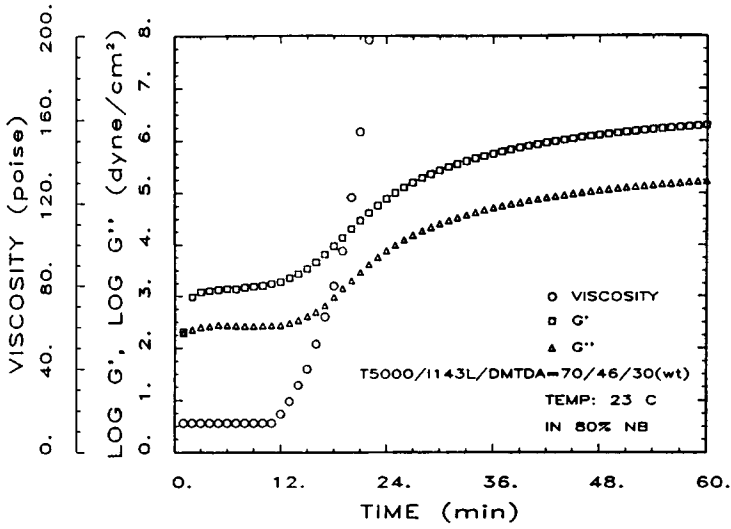
(a)
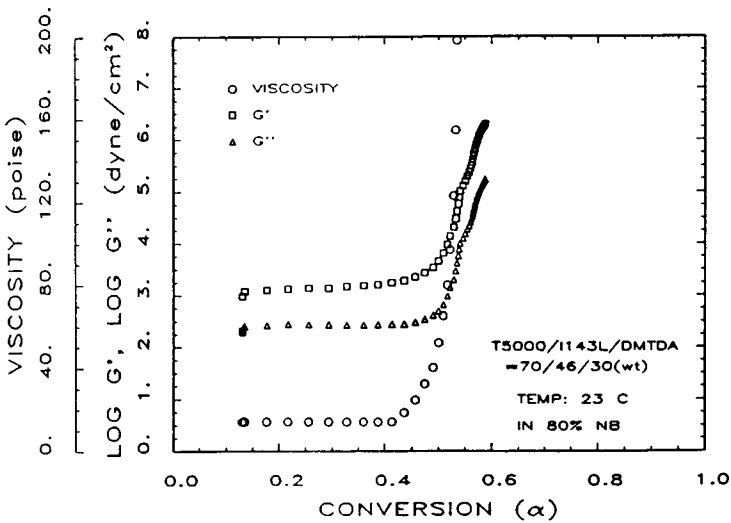
(b)

Fig. 12.   Viscosity, G' and G'' vs. (a) time and (b) conversion for a three-component polyurea reaction.

Consequently, the formation of soft segments in a three-component polyurea system only contributes to a sudden viscosity buildup at the beginning of the reaction.

The reaction of aromatic diamine and diisocyanate forms a linear polymer. However, due to the microphase separation from the formation of hard segments, this system may result in a gelation. It was observed that, in the three-

component polyureas, the system with a higher hard segment content has a shorter gel time.

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