

# Polymer Networks Based on the Diepoxide–Diisocyanate Reaction Catalyzed by Tertiary Amines

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## SYNOPSIS

Reactions taking place in a system consisting of a diepoxide (DGEBA, diglycidylether of bisphenol A) and a diisocyanate (TDI 80 : 20, toluene diisocyanate), catalyzed by a tertiary amine (BDMA, benzyldimethylamine), were followed by differential scanning calorimetry (DSC), infrared spectroscopy (FTIR), and chemical titration of isocyanate groups in the pre-gel stage. It was found that the main reactions took place in series, in steps of increasing temperature: (i) isocyanurate formation, (ii) epoxy-isocyanate reaction leading to oxazolidone rings, and (iii) isocyanurate decomposition by epoxy groups producing oxazolidone rings. Isocyanurate rings were stable in the presence of epoxides and an isocyanate excess [reaction (ii) was faster than (iii)]. Epoxy homopolymerization (secondary reaction) occurred in parallel with steps (ii) and (iii). Step (i) took place by two different mechanisms and led to a maximum conversion, possibly limited by topological restrictions. A kinetic study of TDI trimerization in the presence of an equimolar amount of DGEBA and variable amounts of BDMA led to a third-order regression with an activation energy  $E = 43$  kJ/mol. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

The reaction between a diepoxide and a diisocyanate leads to polymer networks characterized by the presence of isocyanurate and oxazolidone rings in their chemical structure. These polymers exhibit excellent thermal, mechanical, and electrical properties and have been the subject of several studies.<sup>1–16</sup>

Main reactions taking place in an epoxy–isocyanate–tertiary amine system are shown in Figure 1 and may be described by the following equations:

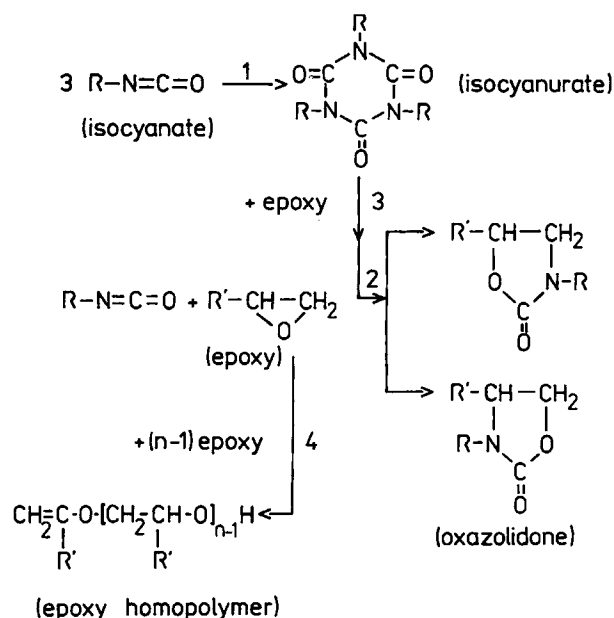


where I, E,  $I_3$ ,  $O_x$ , and  $E_n$  stand for isocyanate, epoxy, isocyanurate, oxazolidone, and polyepoxy, respectively.

The fraction of different structures present in the final network depends on the initial I/E ratio, the type of catalyst and the cure temperature (or cure cycle). For a diepoxide–diisocyanate system, the formation of both  $I_3$  (three functional crosslinking unit) and  $E_n$  (where epoxy acts as a tetrafunctional monomer) leads to the buildup of a polymer network. The production of  $O_x$  (bifunctional ring) leads to the presence of thermal-resistant structures in primary chains. An increase in the  $I_3/O_x$  ratio produces an increase in the glass transition temperature ( $T_g$ ) but a decrease in the fracture resistance. An adequate balance between both types of rings is normally sought after in the development of commercial products.<sup>12</sup>

Some aspects of the reactions taking place in a system consisting of a diepoxide (DGEBA, diglycidylether of bisphenol A) and a diisocyanate (MDI, 4,4'-diphenylmethane diisocyanate) catalyzed by a tertiary amine (BDMA, benzyldimethylamine), were recently reported.<sup>13</sup> Insight into reaction mecha-

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**Figure 1** Main reactions taking place in an epoxy-isocyanate system catalyzed by a tertiary amine.

nisms and kinetics was obtained by replacing MDI with a monoisocyanate (PTI, *p*-tolyleneisocyanate).<sup>16</sup> Using differential scanning calorimetry (DSC) and infrared spectroscopy (FTIR), it was established that the first reaction was the formation of isocyanurate rings [eq. (1)], characterized by two low-temperature peaks in DSC thermograms. At higher temperatures, the formation of oxazolidone rings [eqs. (2) and (3)] and epoxy homopolymerization [eq. (4)] took place. There are, however, some particular questions that need a further analysis: (a) explanation of the presence of two low-temperature peaks in DSC thermograms, and (b) competence between both reactions leading to oxazolidone rings [eqs. (2) and (3)]—does one prevail over the other?

The aim of this paper is to analyze the reaction scheme taking place in a DGEBA-TDI (toluene diisocyanate) system catalyzed by BDMA, with particular emphasis on the double peak at low temperatures ( $I_3$  formation) and the competence between eqs. (2) and (3) for the formation of oxazolidone rings. A kinetic study for the  $I_3$  formation is also reported.

## EXPERIMENTAL

### Materials

The diepoxide was based on diglycidylether of bisphenol A (DGEBA, Araldite GY 250, Ciba-Geigy) with a weight per equivalent, WPE = 187 g/eq. This

gives  $n = 0.12$  in the structural formula (Fig. 2). The resin was dehydrated at 90°C, under vacuum, before use. Toluene diisocyanate (TDI, 99.9% purity) was available as a mixture of 80% 2,4 and 20% 2,6 isomers. Benzyltrimethylamine (BDMA, Sigma), was used without further purification.

Reactions between TDI and DGEBA were conducted in bulk, using different stoichiometric ratios,  $r = \text{NCO}/\text{eq. epoxy}$  ( $r = I/E$ ). The BDMA concentration was varied in the 0.5–1% range, expressed in moles BDMA per NCO equivalent.

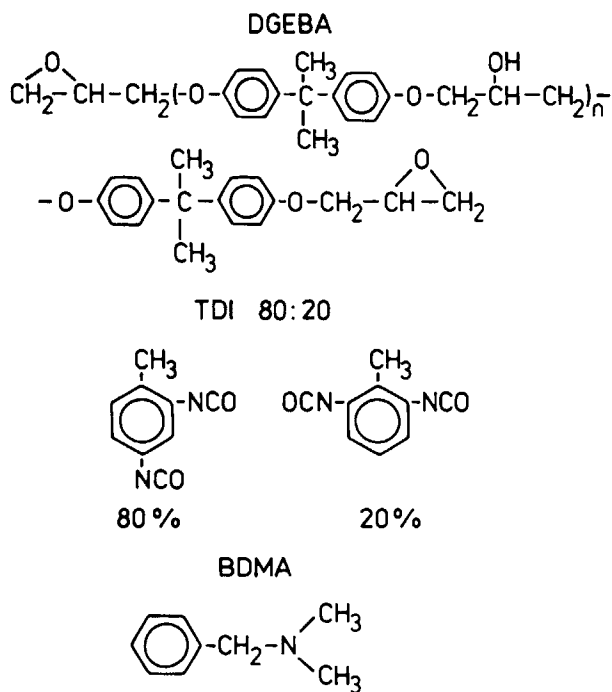
### Techniques

A DuPont 990 thermal analyzer, provided with a differential scanning calorimetry cell (DSC 910), was used in the scanning mode (10°C/min) under a nitrogen atmosphere. The operating range was between room temperature and 300°C. Glass transition temperatures ( $T_g$ ) were determined by thermal mechanical analysis (TMA, DuPont 943), using a 10°C/min heating rate.

Infrared spectra of samples dispersed in KBr were obtained using a Bruker IFS 25 FTIR in the transmission mode, with a standard resolution of 2  $\text{cm}^{-1}$ . FTIR peaks were assigned as follows<sup>13</sup>:

–3500  $\text{cm}^{-1}$  = hydroxyl

–2270  $\text{cm}^{-1}$  = isocyanate



**Figure 2** Chemical reagents.

- 1760  $\text{cm}^{-1}$  = oxazolidone
- 1710  $\text{cm}^{-1}$  = isocyanurate
- 910  $\text{cm}^{-1}$  = epoxy
- 830  $\text{cm}^{-1}$  = *p*-phenylene (reference peak)

By referring absorbances to the peak at 830  $\text{cm}^{-1}$ , a quantitative estimation of the concentration of different groups as a function of cure temperature could be performed.

In the kinetic study of isocyanurate formation, the evolution of —NCO concentration was determined by chemical titration, using an excess of *n*-butylamine and back-titrating with ClH.

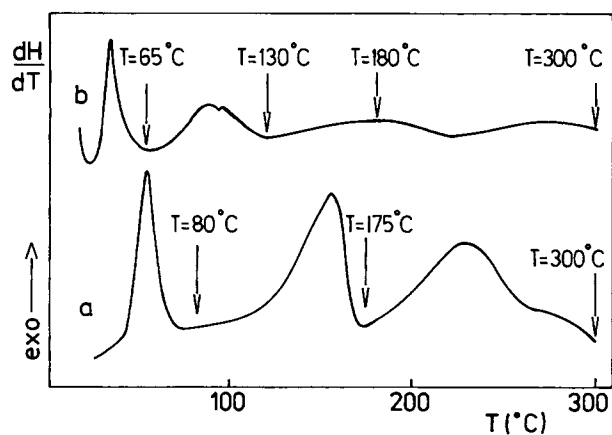
## RESULTS AND DISCUSSION

### Reaction Scheme

Samples with stoichiometric ratios  $r$  (I/E) comprised between 0.5 (epoxy excess) and 5 (isocyanate excess) were cured in the DSC, using 1% BDMA (mole per isocyanate equivalent). Typical thermograms are shown in Figure 3.

The case of an epoxy excess ( $r = 0.5$ ) will be first analyzed. Three exothermic peaks, at 52°C, 156°C, and 231°C, appear in the thermogram [Fig. 3(a)]. In order to establish the nature of the reactions involved, FTIR spectra of samples reacted in the DSC up to 80°, 175° and 300°C were recorded, i.e., after completing each one of the exothermic peaks. The resulting spectra are shown in Figure 4.

The evolution of the absorbances of different groups (with respect to the reference peak), is shown in Table I.



**Figure 3** DSC thermograms for the TDI-DGEBA reaction catalyzed by 1% BDMA (mole/NCO eq.): (a)  $r = 0.5$ , (b)  $r = 2$ .

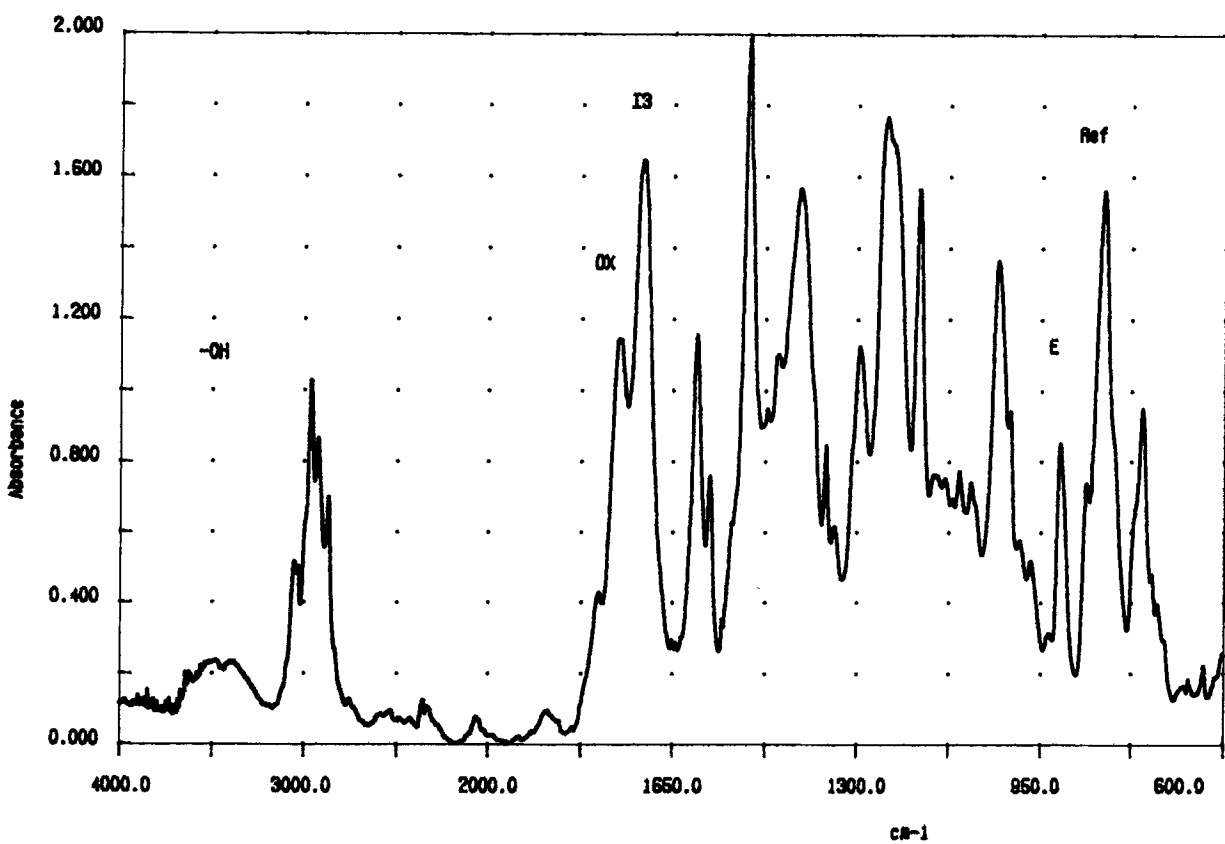
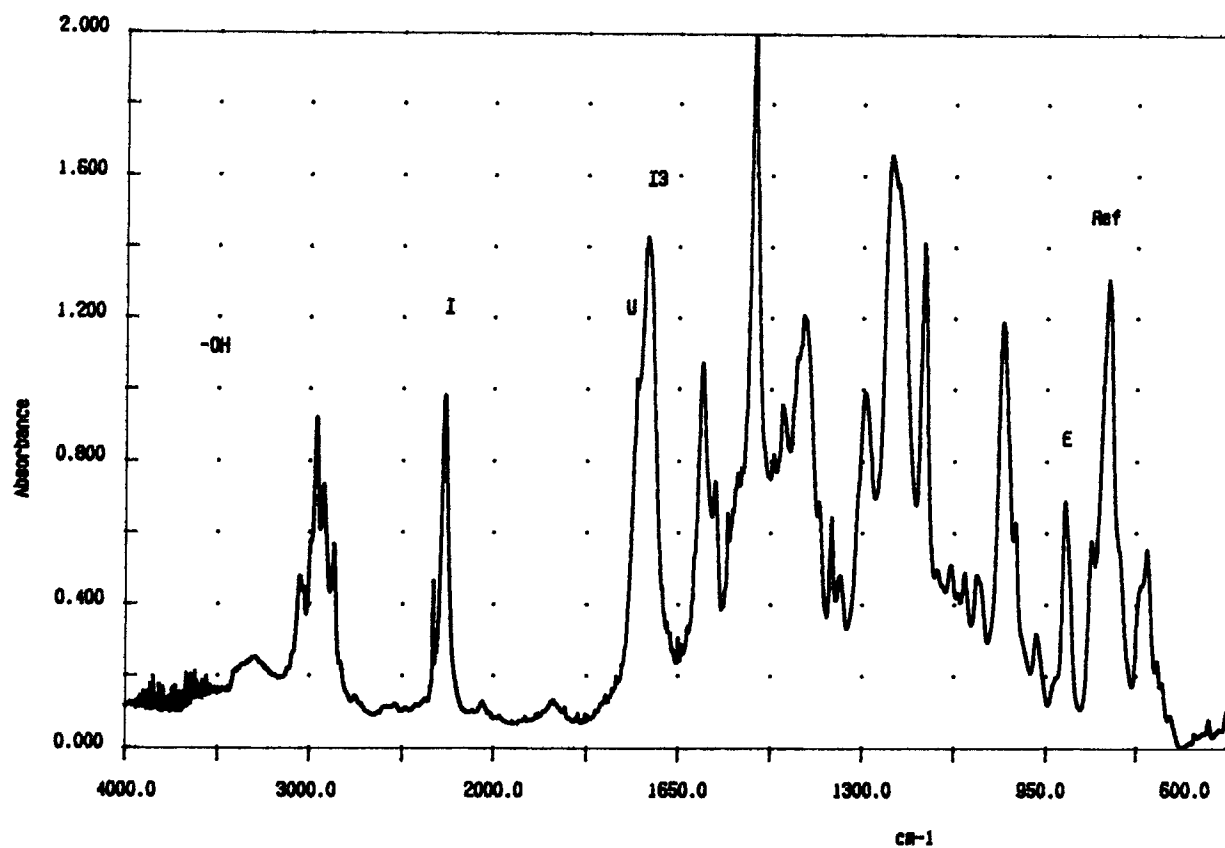
**Table I** Relative Absorbances of FTIR Peaks (with Respect to the Reference Peak at 830  $\text{cm}^{-1}$ ) for TDI-DGEBA Samples ( $r = 0.5$ , 1% BDMA) Cured to Different Temperatures

$T$ (°C)	80	175	300
E (910 $\text{cm}^{-1}$ )	0.50	0.44	0.16
I <sub>3</sub> (1710 $\text{cm}^{-1}$ )	1.08	1.09	0
O <sub>x</sub> (1760 $\text{cm}^{-1}$ )	0	0.75	1.51
I (2270 $\text{cm}^{-1}$ )	0.75	0	0
OH (3500 $\text{cm}^{-1}$ )	0	0.12	0.26

The main reaction taking place in the first exothermic peak is the formation of isocyanurate rings [eq. (1)]. This reaction does not proceed to completion (the isocyanate conversion is about 0.73), and there is no evidence of any effect arising from the different reactivity of NCO groups located in *o* and *p* positions in the toluene ring, i.e., only one single exothermic peak is present. There is, however, a secondary reaction included in the first exothermic peak which is the urethane formation between OH groups present in DGEBA (Fig. 2) and NCO groups. The formulation with  $r = 0.5$  contains 0.12 OH eq. per NCO eq. The presence of urethane groups is revealed by a shoulder at 1730  $\text{cm}^{-1}$  [Fig. 4(a)].<sup>8,15</sup>

The main process taking place in the second exothermic peak is the formation of oxazolidone rings by reaction between isocyanate and epoxy groups [eq. (2)]. In the presence of an epoxy excess isocyanate groups are completely reacted (a small peak at 2360  $\text{cm}^{-1}$  is caused by the presence of CO<sub>2</sub> in the atmosphere). The constancy of the concentration of isocyanurate rings (I<sub>3</sub>) reveals that they are stable in this temperature range, even in the presence of an epoxy excess. The appearance of free OH groups may be the result of some epoxy homopolymerization [eq. (4)] taking place in this temperature range; OH groups are generated in the course of a transfer step during the anionic homopolymerization.<sup>17,18</sup> Also, the decomposition of urethane groups may be invoked to explain the presence of hydroxyls after the heating to 175°C.

The decomposition of isocyanurate rings by reaction with the epoxy excess to give oxazolidone rings [eq. (3)] is the main reaction occurring in the third exothermic peak. This reaction proceeds to completion. There is also an increase in the OH concentration, possibly as a result of the epoxy homopolymerization. Therefore, the final network consists mainly of polyoxazolidone rings with some epoxy homopolymer fraction and free epoxy groups.



**Figure 4** FTIR spectra of TDI-DGEBA samples ( $r = 0.5$ , 1% BDMA), reacted to different temperatures: (a) 80°C, (b) 175°C, (c) 300°C.

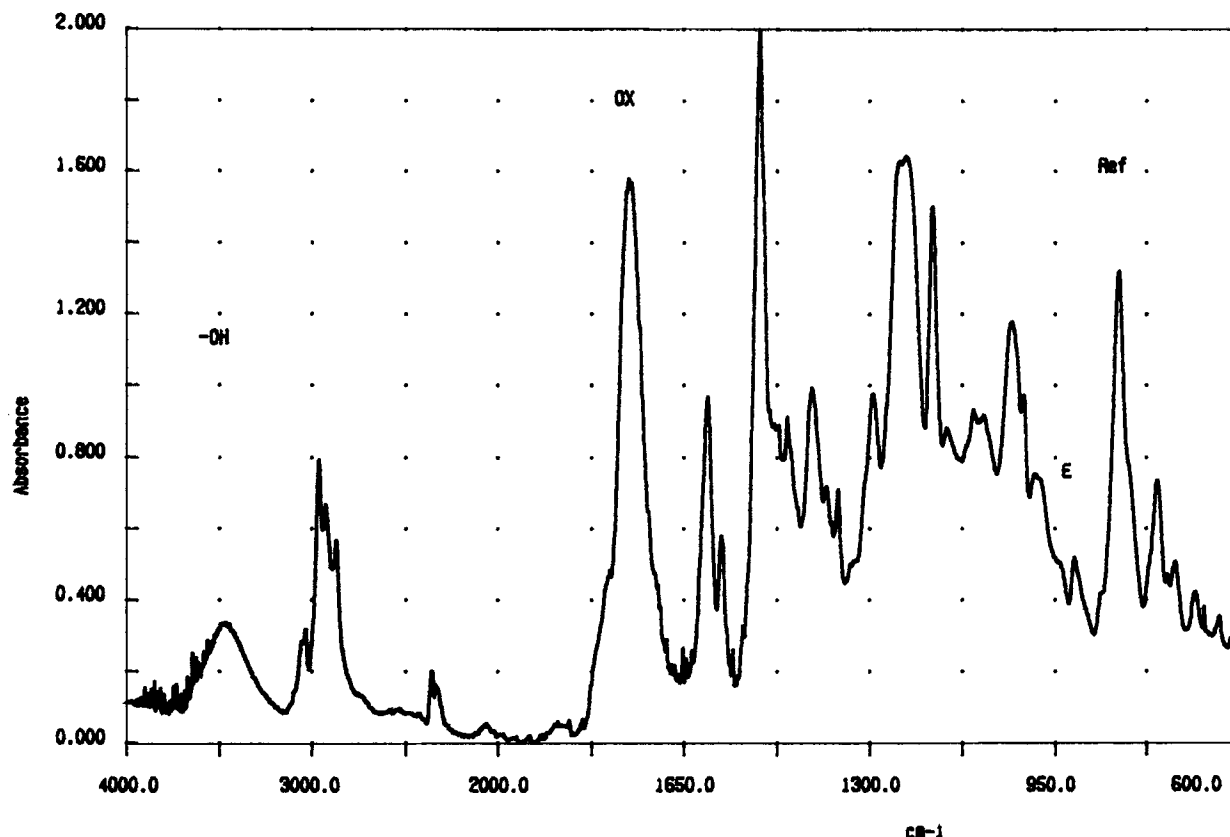


Figure 4 (Continued from previous page)

The evident result from this analysis is that reactions 1, 2, and 3 [eqs. (1)–(3)] take place in series, in steps of increasing temperature.

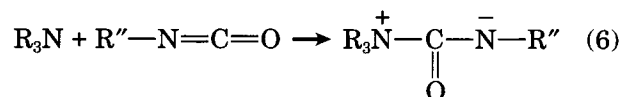
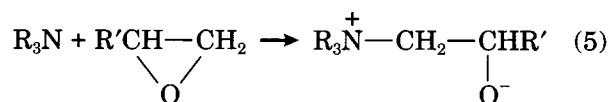
The case of an isocyanate excess ( $r = 2$ ) will be now analyzed. Four exothermic peaks, at 39°C, 95°C, 192°C, and 286°C, appear in the thermogram [Fig. 3(b)]. The last two peaks are rather flat and cover a broad temperature range. FTIR spectra of samples reacted in the DSC up to 65°C (after the first peak), 130°C (after the second peak), 180°C (about half of the third peak), and 300°C (about half of the fourth peak) were recorded. The resulting spectra are shown in Figure 5.

Absorbances of different groups with respect to the reference peak are shown in Table II as a function of cure temperature.

The main reaction taking place in the first two exothermic peaks is the formation of isocyanurate rings (eq. 1). As for  $r = 2$ , the ratio OH/NCO is equal to 0.03 and the amount of urethane linkages is almost negligible [there is no shoulder in the FTIR spectra shown in Figs. 5(a) and 5(b)]. As arises from Table II, most of the  $I_3$  formation takes place after the cure up to 65°C. However, the areas under the first two DSC peaks are of the same magnitude [Fig.

3(b)]. This may be explained by the advance of the lowest-temperature reaction during sample preparation and manipulation.

The presence of two DSC peaks for the formation of isocyanurate rings is possibly the result of the presence of two different initiation mechanisms for the isocyanate trimerization.<sup>16</sup> According to Dabi and Zilkha,<sup>19–21</sup> two initiators can be active in the anionic mechanism:



The initiator produced by eq. (5) is more active at low temperatures than the one formed in eq. (6). The reduction in the activity of the former at high temperatures has a correlation with the behavior of the anionic homopolymerization of epoxides initiated by tertiary amines (a decrease in reaction rate is observed at high temperatures).<sup>22</sup>

Another possibility explaining the presence of two

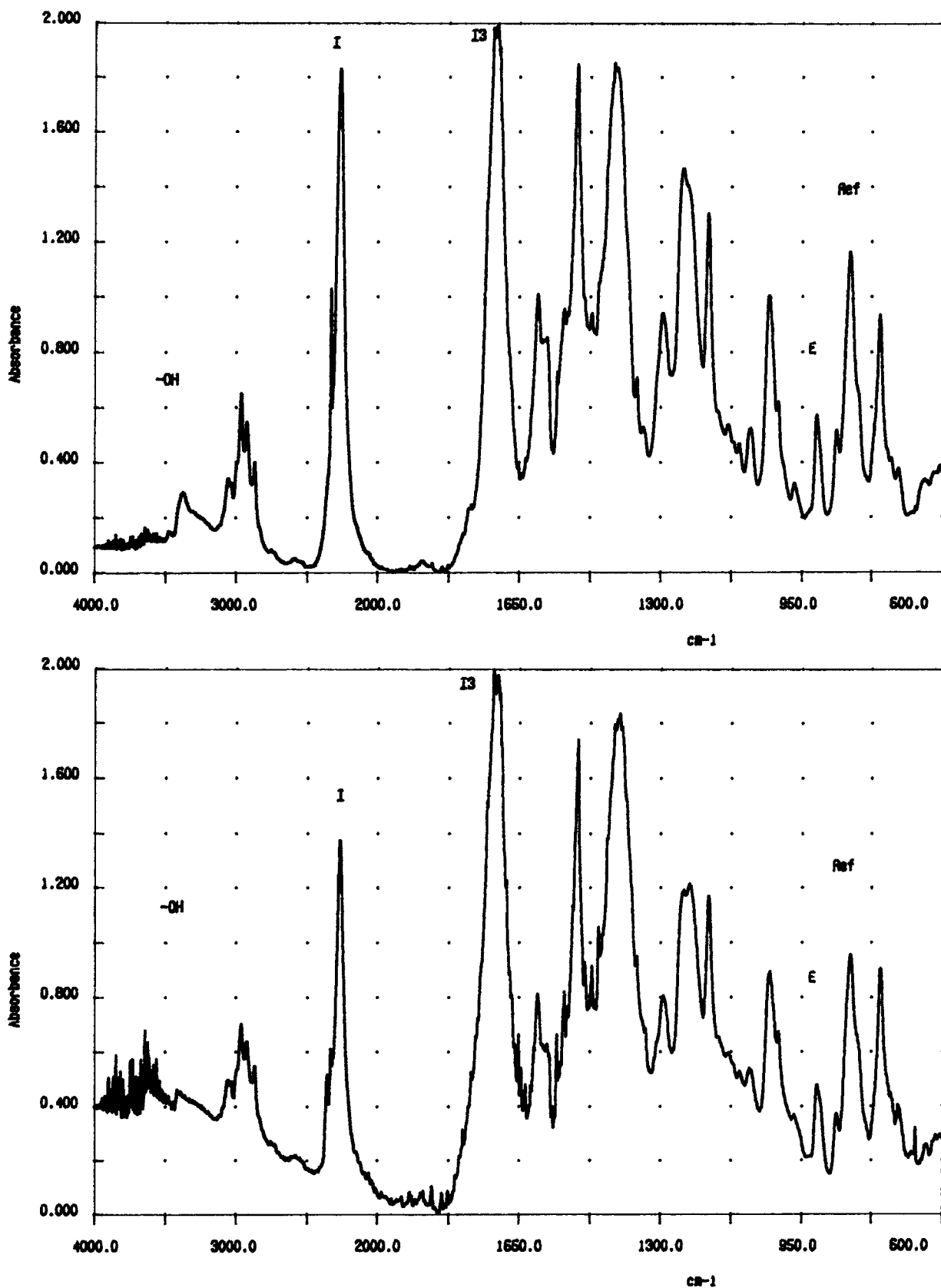


Figure 5 FTIR spectra of TDI-DGEBA samples ( $r = 2$ , 1% BDMA), reacted to different temperatures: (a) 65°C, (b) 130°C, (c) 180°C, (d) 300°C.

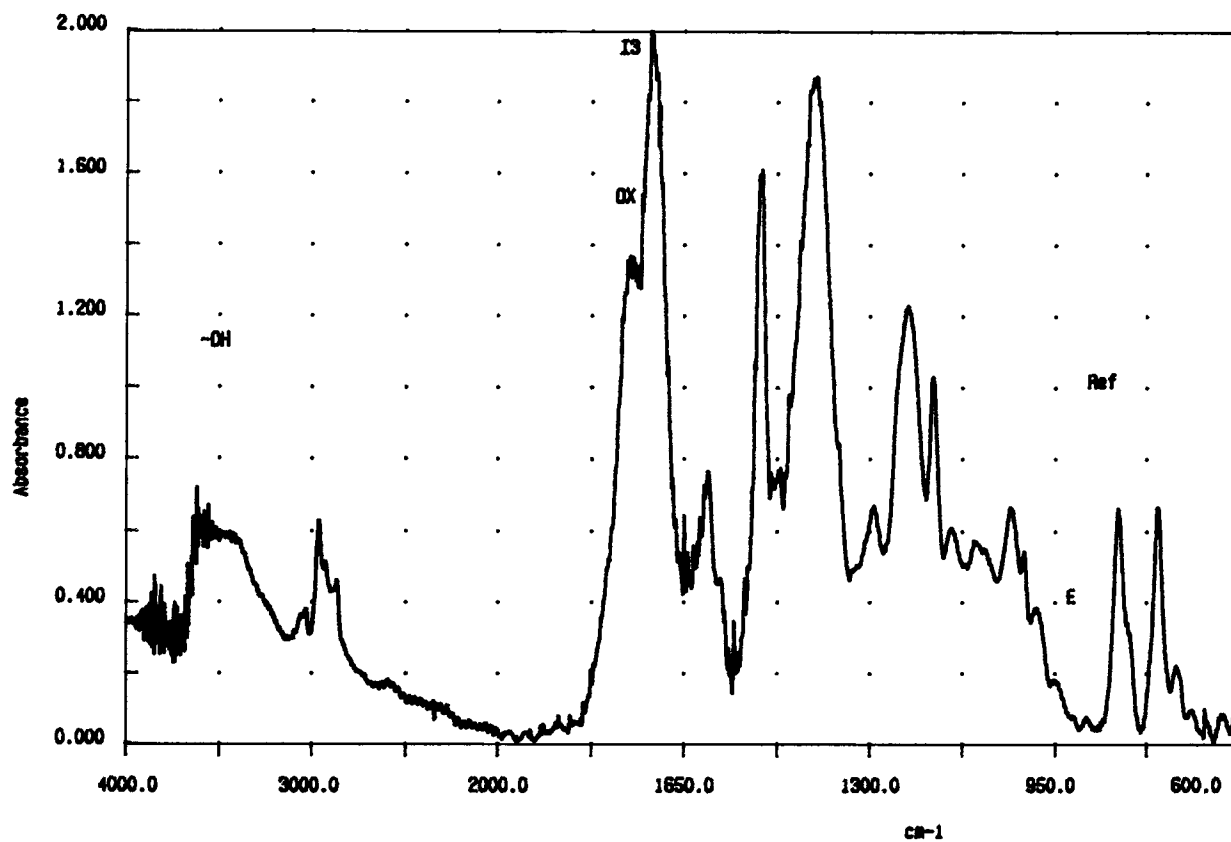
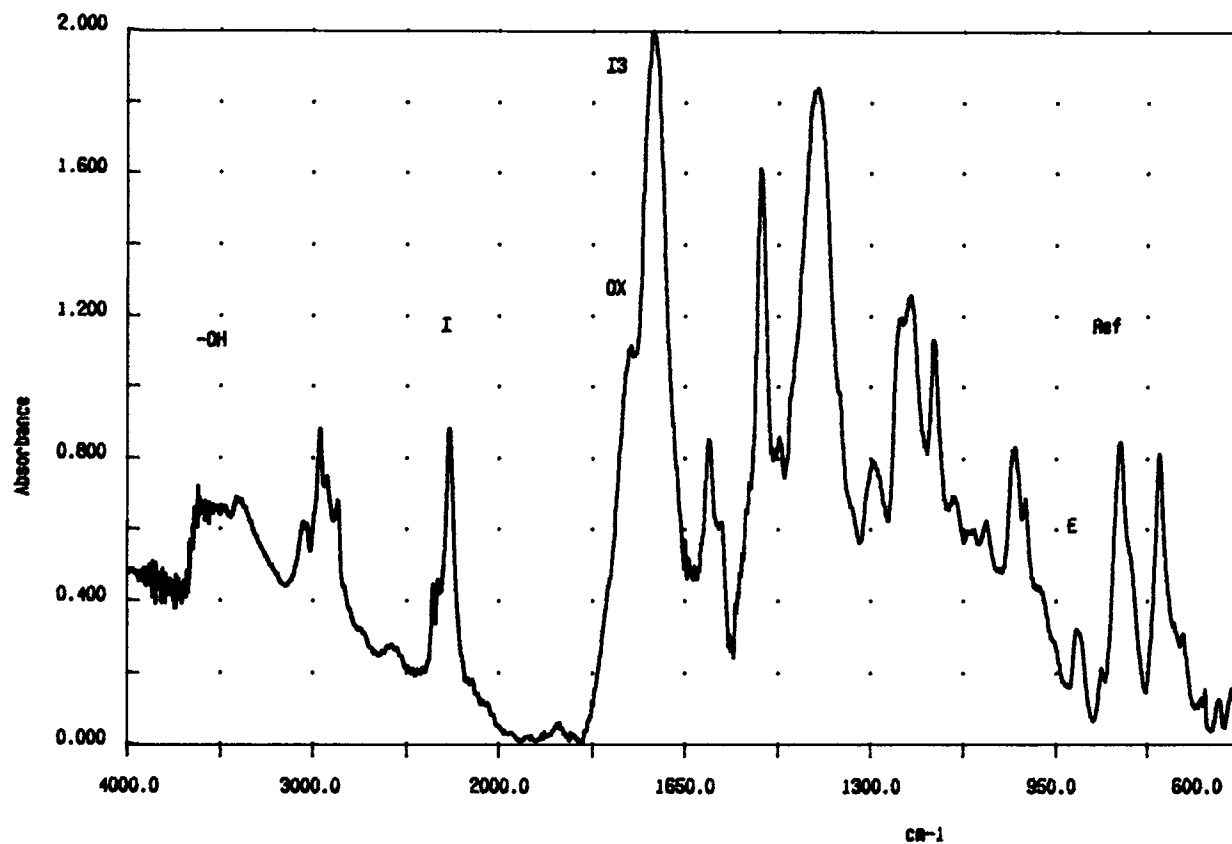


Figure 5 (Continued from previous page)

**Table II** Relative Absorbances of FTIR Peaks (with Respect to the Reference Peak at  $830\text{ cm}^{-1}$ ) for TDI-DGEBA Samples ( $r = 2$ , 1% BDMA) Cured to Different Temperatures

$T$ ( $^{\circ}\text{C}$ )	65	130	180	300
E ( $910\text{ cm}^{-1}$ )	0.41	0.40	0.29	$\rightarrow 0$
$I_3$ ( $1710\text{ cm}^{-1}$ )	1.99	2.31	2.29	2.69
$O_x$ ( $1760\text{ cm}^{-1}$ )	0	0	1.24	1.84
I ( $2270\text{ cm}^{-1}$ )	2.03	1.69	1.02	0
OH ( $3500\text{ cm}^{-1}$ )	0	$\rightarrow 0$	0.29	0.45

DSC peaks and accounting for the formation of isocyanurate rings is the different reactivity of NCO groups of TDI. This hypothesis may be discarded, however, as only one DSC peak was found for formulations containing an epoxy excess.

It is interesting to compare the ratio of absorbances,  $I/I_3$ , for systems with both epoxy and isocyanate excesses. This ratio is equal to 0.69 for the system with  $r = 0.5$  cured up to  $80^{\circ}\text{C}$  and 0.73 for the system with  $r = 2$  cured up to  $130^{\circ}\text{C}$ . Thus, a similar NCO conversion in the trimerization is obtained for both cases, possibly due to topological constraints. For the system containing an epoxy excess ( $r = 0.5$ ), however, the maximum conversion can be attained with the initiator formed by eq. (5) whereas for the system with an isocyanate excess ( $r = 2$ ), both initiation mechanisms are active in different temperature ranges (i.e., first two peaks in the DSC thermogram).

During the third exothermic peak [Fig. 3(b), sample cured up to  $180^{\circ}\text{C}$ ] the main reaction is the isocyanate-epoxy reaction leading to oxazolidone rings [eq. (2)]. As revealed from Table II,  $I_3$  concentration remains constant; showing again that if free isocyanates are available, isocyanurate rings remain stable in the presence of epoxy groups [i.e., eq. (2) prevails over eq. (3)]. Epoxy homopolymerization does also take place in this temperature range, as arising from the appearance of a peak at  $3500\text{ cm}^{-1}$  in the FTIR spectrum [Fig. 5(c)].

Main reactions occurring at the highest temperatures [fourth exothermic peak of Fig. 3(b)] are the same as those observed in the third exothermic peak, i.e., isocyanate-epoxy reaction leading to oxazolidone rings [eq. (2)] and epoxy homopolymerization [eq. (4)]. The  $I_3$  concentration remains practically constant (the slight increase observed in Table II may be the result of the error introduced in the estimation of individual absorbances when  $O_x$  and  $I_3$  peaks are overlapped). The residual epoxy content is almost negligible.

Therefore, the formation of oxazolidone rings always takes place by the epoxy-isocyanate reaction [eq. (2)], but possibly by different mechanisms depending on the temperature range. The isocyanurate rings remain stable in the presence of an isocyanate excess.

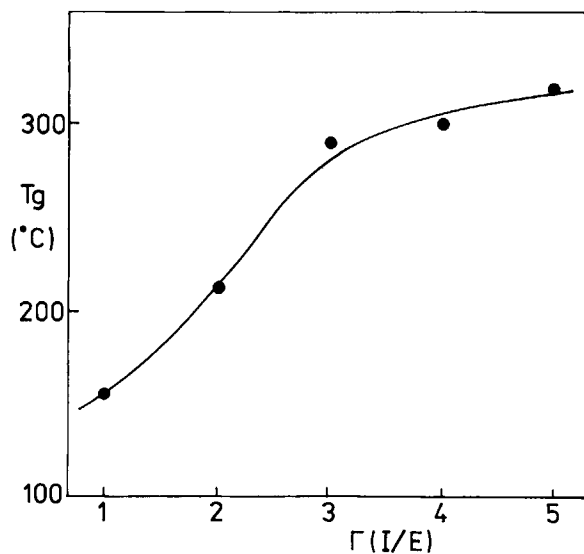
Increasing the I/E ratio in the initial formulation leads to an increase in the fraction of isocyanurate over oxazolidone rings and in the corresponding glass transition temperature of the resulting networks.<sup>13</sup> Figure 6 shows the  $T_g$  vs.  $r$  curve obtained for the TDI-DGEBA system cured with 1% BDMA up to  $300^{\circ}\text{C}$ .

### Kinetics of the Isocyanate Trimerization

The kinetics of the low-temperature trimerization reaction was studied for a TDI-DGEBA system with  $r = 1$ , following the residual isocyanate concentration by chemical titration. The BDMA concentration was varied in the range 0.5–1%. Formulations with  $r = 1$  contain an OH concentration of 0.06 eq./NCO eq. Therefore, although the observed decrease in the NCO concentration will be partially due to urethane formation, in the foregoing analysis only NCO trimerization will be considered.

A set of small preweighed samples was cured at a constant temperature in the range  $10^{\circ}$ – $30^{\circ}\text{C}$ . Samples were removed from a thermostatic bath at prespecified times and the NCO contents determined by titration. Conversion was defined as

$$X = [\%NCO(t_0) - \%NCO(t)]/\%NCO(t_0) \quad (7)$$



**Figure 6** Glass transition temperature as a function of the initial stoichiometric ratio for TDI-DGEBA samples cured with 1% BDMA up to  $300^{\circ}\text{C}$ .



The gel conversion was determined from the first appearance of an insoluble fraction in the dissolution process previous to chemical titration.

Figures 7 and 8 show the evolution of NCO conversion for different BDMA amounts and cure temperatures. As expected, the polymerization rate increased with both an increase in BDMA concentration and cure temperature.

The experimental value of the gel conversion was  $X_{\text{gel}} = 0.6$  (independent of the BDMA concentration). Alberino<sup>23</sup> reported a value of  $X_{\text{gel}} = 0.60$  for the trimerization of 4,4'-diisocyanato diphenyl methane (MDI) and  $X_{\text{gel}} = 0.72$  for the case of 2,4 toluene diisocyanate (2,4 TDI). Both reactions were carried out in a 40 wt % solution in *N,N*-dimethylformamide, using 2,4,5-tris (dimethylamino-methyl) phenol (0.25 wt % based on the isocyanate).

Assuming a third order in the schematic reaction given by eq. (1), the following kinetic law may be written:<sup>24</sup>

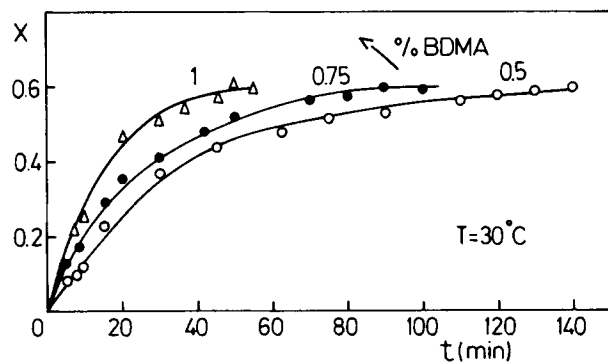
$$-\frac{dI}{dt} = (3/3!) k I^3 = (1/2) k I^3 \quad (8)$$

where the factor 3 stands for the disappearance of three isocyanate functionalities in the elementary step, and the factor 3! stands for the presence of three undistinguishable combinations leading to the same product.

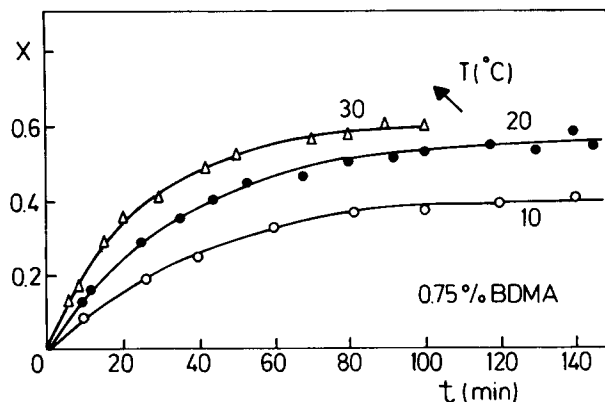
Writing eq. (8) in terms of conversion [eq. (7)] and integrating, we get

$$[1/(1-X)^2] - 1 = k I_0^2 t = k' t \quad (9)$$

Figure 9 shows a reasonable fitting of kinetic curves with the third-order model. Values of the specific rate constant are shown in Table III;  $k'$  shows a



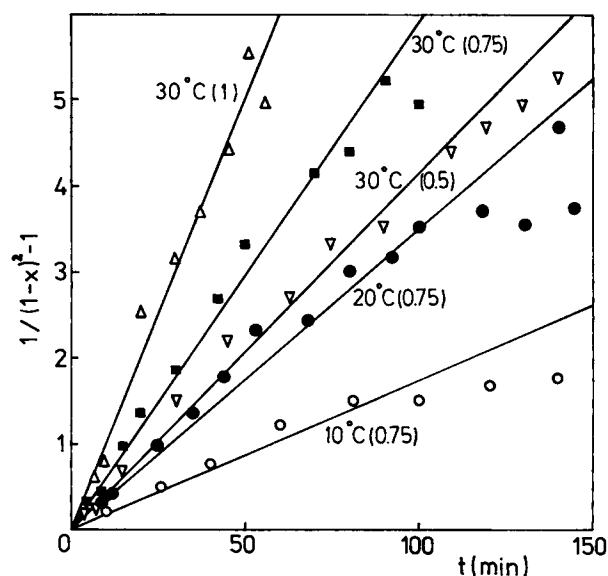
**Figure 7** Conversion of isocyanate groups as a function of time for a TDI-DGEBA system ( $r = 1$ ), cured at 30°C in the presence of different BDMA concentrations.



**Figure 8** Conversion of isocyanate groups as a function of time for a TDI-DGEBA system ( $r = 1$ ), cured with 0.75% BDMA, at different temperatures.

roughly first-order dependence on the BDMA concentration. From an Arrhenius plot, an activation energy equal to  $E = 43$  kJ/mol was obtained.

Kresta et al.<sup>25</sup> studied the kinetics of isocyanate trimerization for phenyl isocyanate dissolved in acetonitrile in the presence of triethylamine (TEA). They found a first-order kinetic law; however, when an equimolar mixture of TEA and 1,2-epoxy-3-phenoxypropane (PGE) was used, a second-order kinetics was observed. Caille et al.<sup>16</sup> analyzed the trimerization of *p*-tolylene isocyanate (PTI) dissolved in DGEBA ( $r = 0.5$ ) in the presence of either BDMA or 2-ethyl-4-methylimidazole (EMI). They



**Figure 9** Third-order regression of kinetic curves for different temperatures and BDMA concentrations (values between brackets).

**Table III** Values of the Third-Order Specific Rate Constant for Different Temperatures and BDMA Concentrations

$k'$ (min <sup>-1</sup> )	$T$ (°C)	% BDMA
0.0417	30	0.5
0.0594	30	0.75
0.1027	30	1
0.0352	20	0.75
0.0175	10	0.75

found a first-order kinetics with activation energies equal to 47 kJ/mol for EMI and 56 kJ/mol for BDMA. This range of activation energies is close to the value obtained in the present study.

## CONCLUSIONS

Main reactions taking place in an epoxy-isocyanate system catalyzed by a tertiary amine are: (i) isocyanurate formation, (ii) epoxy-isocyanate reaction producing oxazolidone rings, and (iii) isocyanurate-epoxy reaction leading to oxazolidone rings. These reactions take place in series, in steps of increasing temperature. This means that isocyanurate groups are stable in the presence of epoxy groups if an isocyanate excess is available, i.e., reaction (ii) proceeds at a faster rate than (iii). The epoxy homopolymerization (secondary reaction) takes place in parallel with steps (ii) and (iii). Step (i) takes place by two different mechanisms characterized by two DSC peaks in formulations containing an isocyanate excess. Most of the conversion in the isocyanate trimerization is the result of a mechanism where the anionic initiator is produced by ring-opening of the epoxide by the tertiary amine. But the reaction continues by a different mechanism (possibly the action of the tertiary amine alone) in a higher temperature range. Complete conversion was never attained, however, possibly due to topological restrictions.

A kinetic study of the isocyanate trimerization in the presence of epoxides and a tertiary amine led to a third-order regression with an activation energy  $E = 43$  kJ/mol. The gel conversion was  $X_{\text{gel}} = 0.60$ , independent of the tertiary amine concentration.

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