Polymer Bulletin

Reaction of a diepoxide with a diisocyanate in bulk

I. Use of a tertiary amine catalyst

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SUMMARY

Reactions between a diepoxide and a diisocyanate can lead to copolymers having two kinds of heterocycles in their chemical structure : isocyanurate rings which are the result of the reaction of three isocyanate functions with themselves and oxazolidone rings which are the result of the reaction of an epoxy function with an isocyanate function.
Differential Scanning Calorimetry (DSC) and Fourier Transform Infrared Spectroscopy (FTIR) were used in order to understand the influence of a catalyst, like a tertiary amine, on the reaction mechanism of polymer formation. We also observed the influence of the stoechiometric ratio between the diisocyanate and the diepoxide on the glass-transition temperature of the obtained network.
We have identified the nature of the exotherms observed in DSC experiments and proposed an assignment of the different peaks observed in the FTIR spectra. We showed that the amount of catalyst and the stoechiometric ratio between the diisocyanate and the diepoxide strongly influence the structure of the final polymer and its thermal characteristics such as the glass-transition temperature.

INTRODUCTION

Improving thermal properties of polymer networks at a lower cost is of a great interest, especially if it can be ensured that other properties such as mechanical or electrical properties are not affected by the increase in the glass-transition temperature.
One way to obtain epoxy materials having good thermal properties, including high glass-transition temperature and good flame retardancy, is to insert heterocyclic rings in the polymer structure. The reaction between a diepoxyde and a diisocyanate can lead to copolymers having isocyanurate and oxazolidone rings in their chemical structure. These polymers exhibit better thermal (1,5), mechanical and electrical properties (1-4) in addition to better dimensionnal stability (2) than classical epoxy copolymers.
In the literature, the formation and the properties of pure polyisocyanurate (6-8) or pure polyoxazolidone (9-11) are mostly reported but only a few studies report the polymerization in bulk of a diepoxide with a diisocyanate to obtain a copolymer having the two kinds of heterocycles in their main structure (1,2,12,13). The resultant structure of these copolymers is believed to be as shown in Figure 1.
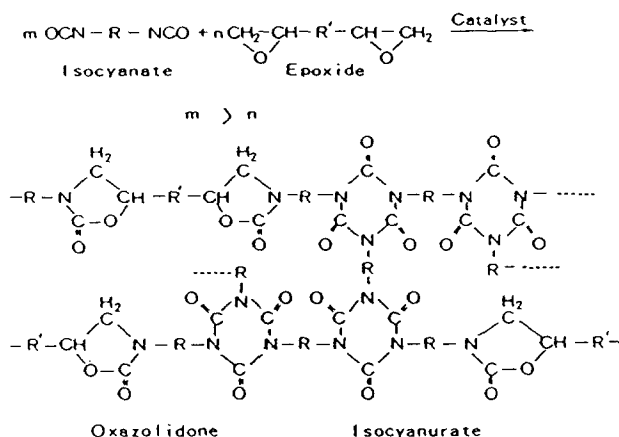
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Figure 1 : Expected chemical structure of a copolymer having isocyanurate and oxazolidone rings in its structure after the reaction between a diepoxide and a di-isocyanate (from (2)).

One can see that the trivalent isocyanurate leads to crosslinking when a diisocyanate is used. Increasing the isocyanurate content increases the cross-linking density and thus the glass-transition temperature (1,2,4), while increasing oxazolidone content lowers the cross-linking density and thus leads to a decrease in the T_g of the polymer.

Rencently J.S. SENGER et al. (14) followed this type of reaction by FTIR and Differential Scanning Calorimetry. Similar experiments have been performed in our laboratory.

The purpose of our work is to identify and understand the influence of the stoechiometric ratio between the diisocyanate and the diepoxide and the amount of a tertiary amine catalyst on the final structure of the polymer. In the next publication, the results obtained with other catalysts such as imidazole and blocked isocyanate will be presented.

EXPERIMENTAL
Materials

All the materials used in this study are commercially available and are low cost. The diepoxide used is a diglycidyl ether of bisphenol A (DGEBA), DER 332 (DOW CHEMICAL), with an equivalent weight of epoxy groups of 173.4 g/eq, as determined by acid titration. The main chemical species was pure DGEBA (M=340 g/mol) while the initial ratio of secondary hydroxyl to epoxy groups was equal to 0.015. The diisocyanate used was pure diisocya-nate-4,4'-diphenylmethane 44 M from BAYER. Its molecular weight is 250 g/mole and its functionality is equal to 2. The benzyl dimethylamine (BDMA) from ALDRICH was choosen as the catalyst. All materials were used without further purification.

Reactions between MDI and DGEBA with different ratios, r, were conducted in bulk. This ratio, r, is defined as the number of diisocyanate moles over the number of diepoxide moles. The mixture of these two components was prepared as follows : solid MDI was preheated at 50 °C in order to obtain a liquid and mixed at this temperature with DGEBA. The prepared mixtures were almost clear and homogeneous at room temperature. The catalyst is then introduced just before conducting the experiments.

Measurements

Differential Scanning Calorimetry (DSC) experiments were performed with a METTLER TA 3000 apparatus, equipped with an IBM PC computer. The calibration was made with an indium standard. The scanning rate was 10 °C/min for exothermic reactions and 7.5 °C/min for the analyses of glass-transition temperatures. The DSC runs were performed under argon, and the weight of the samples was always between 5 and 10 mg.

Infrared spectra were obtained using a 1% dispersion of samples in KBr and testing the resulting disc with a NICOLET MX-1 spectrometer.

According to the literature (2,3,10,12-14) the FTIR peaks can be assigned as follows :
* at 2270 cm^{-1} : isocyanate peak
* at 1760 cm^{-1} : oxazolidone peak
* at 1710 cm^{-1} : isocyanurate peak
* at 1610 and 1510 cm^{-1} : aromatic ring (references)
* at 910 cm^{-1} : epoxide peak

RESULTS AND DISCUSSION

The literature reports that the formation of isocyanurate rings is favoured when a tertiary amine is used as the catalyst, and that the presence of epoxy groups can act as a cocatalyst (1,6,13) thus greatly increasing the trimerization rate. In agreement with this hypothesis, our experiments showed that the presence of BDMA involves very high exotherms and short gel times. For example, the gel time of a mixture having a large excess of isocyanate (r=3) can be as short as a few seconds at room temperature in the presence of 1% BDMA by weight. Such phenomena could be of interest for some applications like the RIM process which requires a very short gel time. On the contrary, such catalyst systems are not of interest for applications requiring a long pot-life.

Exotherm identification

Typical DSC thermograms of the MDI/DGEBA reaction in the presence of 0.2% by mole of BDMA (with respect to isocyanate) are shown in Figure 2 for an epoxy excess (r=0.5) and an isocyanate excess (r=2). In the latter case, recrystallization and fusion of MDI occurs at 0°C and 30°C, respectively (Fig.2b). This phenomenon cannot be seen when r is 0.5 because of the dilution of the diisocyanate in the DGEBA.

Both thermograms exhibit two exothermic peaks : the first one at low temperatures, between 50 and 150°C depending on r, and the second one at higher temperatures, between 250 and 380 °C depending on r.

The heat of the polymerization for the two exothermic peaks for different values of r are shown in Table 1.

r	ΔH (J/g) First exotherm	ΔH (J/g) Second exotherm
0.5	92	145.3
1	154.6	142.7
2	185.6	35.9
3	192.2	9.5

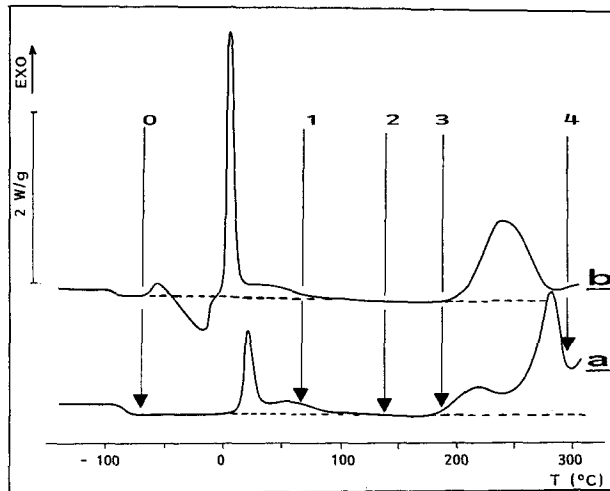Table 1 : Heat of polymerization for the first and the second exotherms (Fig. 2) for different values of r.

Figure 2 : DSC thermograms of MDI/DGEBA reaction catalyzed by 0.2%
by mole of BDMA in isocyanate for a) r = 0,5 and b) r = 2

When r is increased, the first peak becomes larger while the second
one becomes smaller. This means that an isocyanate excess favours the
reaction which occurs at the lower temperature and an epoxy excess favours
the reaction which takes place at the higher temperature.

In spite of the low reliability of the heat values for the first
exotherm (this reaction begins quickly at room temperature and the enthalpy
obtained by DSC scan is lower than the real one) the observed tendancies are
quite interesting.

In order to explain the chemical reaction which induces these
exotherms, samples of the MDI/DGEBA mixture were removed from DSC cells at
points 1 through 4 (Fig. 2) and analyzed by FTIR.

The different exotherms observed in DSC experiments can be assigned
(Fig. 3). After the points 1 and 2 (Fig. 2), the peak of the isocyanate
functions at 2270 cm^{-1} becomes smaller and the peak of the isocyanurate
rings appears and grows. Therefore the exotherms observed at low tempera-
tures are attributable to the trimerisation of isocyanate giving isocya-
nurate heterocycles. In this temperature region the presence of two
different exotherms can be explained by the difference in reactivity of the
two isocyanate groups. When the first group has already reacted, the second
which is less reactive will then react at a slightly higher temperature.

At the position of the arrows 3 and 4 (Fig.2) the samples were analyzed
and the appearance of a peak at 1760 cm^{-1} is noted (Fig.3). We can conclude
that the second group of exotherms (250-380°C) is related to the formation
of oxazolidone rings. Moreover it is very interesting to observe that
oxazolidone rings are formed by two different mechanisms which could explain
that we observe two different peaks at high temperatures :

i) reaction between free isocyanate functions which have not reacted
with epoxy functions ; their peak at 910 cm^{-1} becomes weaker (Fig.3 spectra
3 and 4)

ii) reaction of epoxy functions with isocyanurate rings which were
formed in the first step of the reaction : the peak at 1710 cm^{-1}, charac-
teristic of these heterocycles, becomes weaker compared to the reference
peak at 1510 or 1610 cm^{-1}. This phenomenon has been observed by other
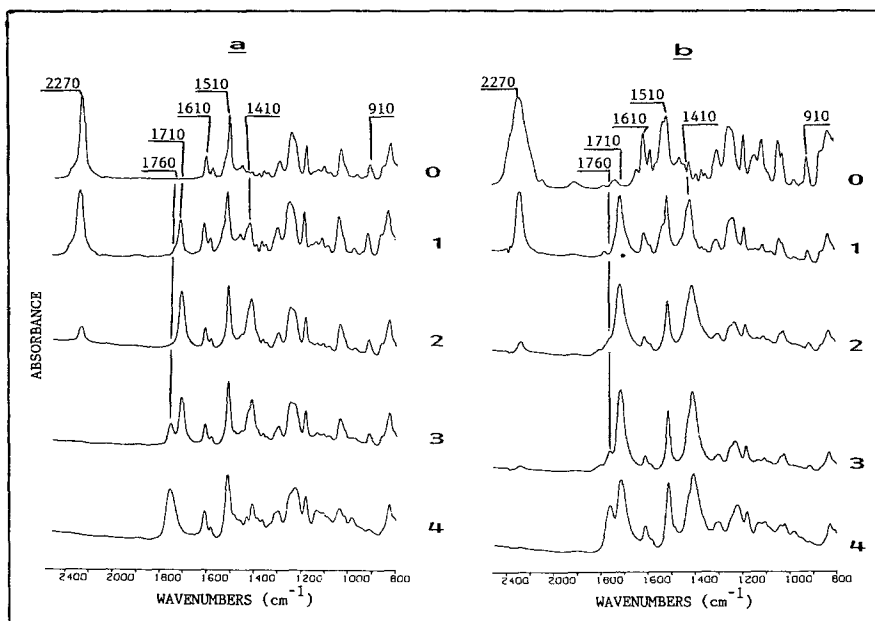authors with the same kind of catalyst (1) or with imidazole (2,13,14).

Figure 3 : Evolution of the FTIR spectra of the MDI/DGEBA
mixture in the presence of BDMA during the DSC
experiments.
a) r = 0.5 and b) r = 2

Thermal stability of isocyanurate rings have already been investigated (6,8) and related to the way that the heterocycles were formed. The presence of catalyst could disrupt the isocyanurate rings to again produce the isocyanate groups which then can react with epoxy groups (Figure 4).
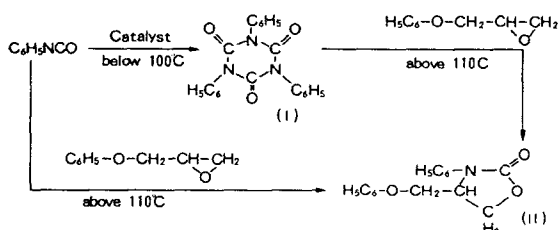

Figure 4 : possible chemical reactions between a diepoxide and a
diisocyanate (from (2)).

In our case, and according to the literature, FTIR spectra of the mixture do not change after a second DSC run. The copolymers seem to reach a chemical stability when all the possible reactions have taken place.
In Figures 5a and 5b we can compare the structures obtained after complete polymerization with the two different selected stoechiometric ratios.
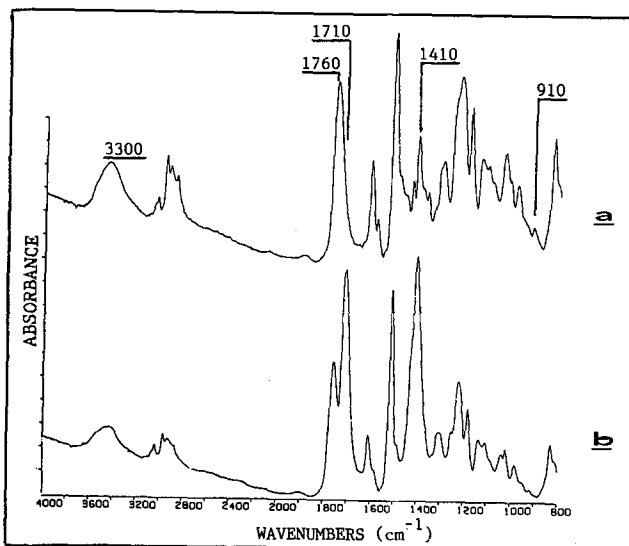
Figure 5 : FTIR spectra of completely polymerized materials.
a) r = 0.5 and b) r = 2

With an excess of epoxy (r=0.5) the final polymer is almost pure polyoxazolidone with residual epoxy functions and no isocyanurate. With an excess of isocyanate (r=2) the final polymer is a mixture of the two heterocycles with all of the epoxy and isocyanate reactive functions haven disappeared.

There are still two problems that we have not solved. Firstly, the attribution of the peak at 1410 cm $^{-1}$ is not sure. Some authors think that this peak is due to the absorption of the isocyanurate functions (15,16) but it seems that the oxazolidone rings could have a contribution too (16). In our experiments, this peak changes exactly the same way as the peak at 1710 cm $^{-1}$. If we consider that this peak is only due to the isocyanate trimer, we can conclude that the polymer obtained with an excess of epoxy (r=0.5) is not a pure polyoxazolidone because the peak at 1410 cm $^{-1}$ is still present (Fig. 5a). Secondly, we can observe a peak at 3300 cm $^{-1}$ in the FTIR spectra which could be attributed to hydroxyl groups appearing when oxazolidone rings begin to be formed. Other authors have observed this phenomenon but no explanation has been established yet (2,3,14). Since FTIR spectroscopy is insufficient to understand this phenomenon, we are currently using NMR anlyses in order to answer this question.

Influence of the amount of catalyst

When the amount of catalyst is increased (Fig. 6), the exotherms increase and shift to lower temperatures. At high temperatures the height of the exotherm peak decreases and the peak broadens. With the help of our previous peak assignment we can conclude that increasing the percentage of catalyst favours the isocyanurate ring formation but not the oxazolidone ring formation. This could lead to a higher cross-linking density and a weaker mobility of the network. In fact, the glass-transition temperatures observed during a second scan are 160 and 165 °C for the matrices prepared with 0.1 and 0.5 % of BDMA, respectively. Epoxy homopolymerization cannot be excluded, but this kind of reaction is difficult to follow with FTIR.
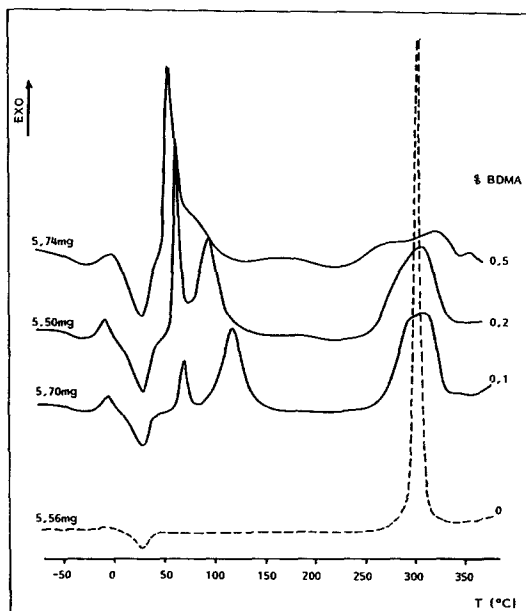
Figure 6 : DSC thermograms for increasing amounts of catalyst for the case of an excess of isocyanate (r=2), % of BDMA by weight of total mixture.

Influence of the stoechiometric ratio r on the Tg

In order to determine the change in the glass-transition temperature with the stoechiometric ratio (that is the relative amount of isocyanurate and oxazolidone rings), a second DSC experiment with the materials already polymerized was carried out. Five different ratios from 0.5 to 4 were investigated. When the ratio is higher than 4, the recrystallization of the MDI is too fast and we cannot obtain homogeneous mixtures. All these reactions were catalyzed with 0.5% BDMA by weight of the total mixture. Figure 7 shows that an excess of isocyanate higher than   r=3 leads to the highest glass-transition temperature which reaches almost 300 °C.
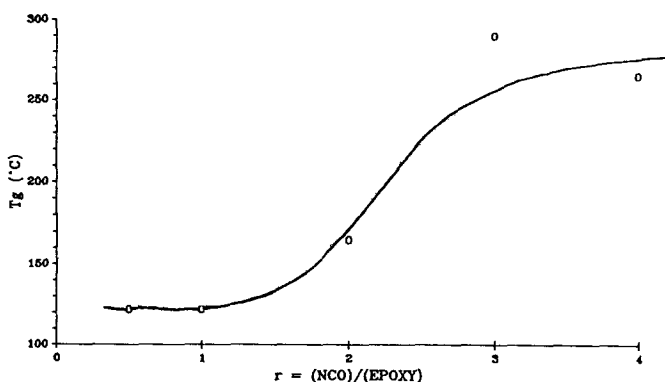

Figure 7 : Tg of isocyanate-epoxy networks versus the ratio r (r = [NCO]/[EPOXY])

When the ratios are lower than 1, the materials have a glass-transition temperature of 120 °C. This experiment confirms that the higher r gives the higher cross-linking density because of the greater amount of formed isocyanurate rings. If there are many oxazolidone divalent rings, the cross-linking density is lowered and the mobility of the network is increased.

These experiments also confirm the excellent thermal properties of these materials as predicted and observed in other papers (1,2,4,10,12,13).

CONCLUSION

This work confirms that a tertiary amine such as benzyl dimethylamine is a very effective catalyst for the reaction between a diepoxide and a diisocyanate to give copolymers having trivalent isocyanurate and divalent oxazolidone rings in their structure. Increasing the amount of BDMA favours the isocyanurate formation and leads to gel times which could be as short as a few seconds. The glass-transition temperature of these materials can reach 300 °C when a high excess of isocyanate is introduced. The cross-linking density is very high because many trivalent rings are formed. If the amount of oxazolidone rings increases, which can be achieved with an excess in epoxy functions, the T_g decreases to 120 °C. The cross-linking density is lowered and the mobility of the network is higher.

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