Three-Group Type Mechanism in the Curing Behavior of Polyacrylate and Blocked Toluene Diisocyanate

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ABSTRACT::   The curing behavior of two resins, five blocked toluene diisocyanate (TDI) crosslinkers and polyacrylate, was studied using Torsional Braid Analysis (TBA) to examine their dynamic mechanical properties. The curing process was clearly divided into two stages. Associated with data from *in situ* FTIR at the molecular level, the first stage was the reaction of deblocked NCO and hydroxyl in polyacrylate. In the second stage, the deblocked NCO attacked the hydrogen in NH group of the urethane bond to conduct deep curing. Computer modeling was used to investigate the lowest-energy configuration of the crosslinker molecule. The space hindrance effect in the molecule causes this type of three-group crosslinking curing mechanism in the blocked TDI crosslinker. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 112–120, 2002

Key words: blocked TDI crosslinker; polyacrylate; TBA; *in situ* FTIR; computer modeling

INTRODUCTION

As the most often used materials in polymer coatings, polyacrylate resin and blocked toluene diisocyanate resin were widely studied for their properties and reactions.[1,2] Polyacrylate and blocked toluene diisocyanates were highly favored to apply in electrodeposition coatings, due to their good performance in both anticorrosion and appearance.

To obtain film with excellent properties, such as hardness and adhesion, it is extremely important to study the curing behaviors of the resins, particularly to understand the curing mechanism.

Little work has been done in this field until recent years. Research was conducted in our laboratory for the curing behaviors of the polymeric material coatings.[3–5] A general scheme of the curing routes of the polyacrylate and blocked toluene diisocyanate was analyzed through Torsional Braid Analysis (TBA) and *in situ* Fourier transform infrared spectroscopy (FTIR). In this article, further studies of the curing behavior of polyacrylate and blocked 2,4-toluene-diisocyanate were performed.

EXPERIMENTAL

Materials

We obtained analytically pure samples of acrylic resin monomers butyl acrylate (BA), N, N-dimethylaminoethyl methacrylate (DM), methyl methacrylate (MMA), 2-hydroxypropyl acrylate (HPA), and initiator 2,2'-azobisisobutyronitrile (AIBN) from Beijing Chemical Co. (Beijing, China). Analytically pure toluene-2, 4-diisocyanate (TDI), diethanolamine (DEA), glycerol (Gly), ethylene glycol
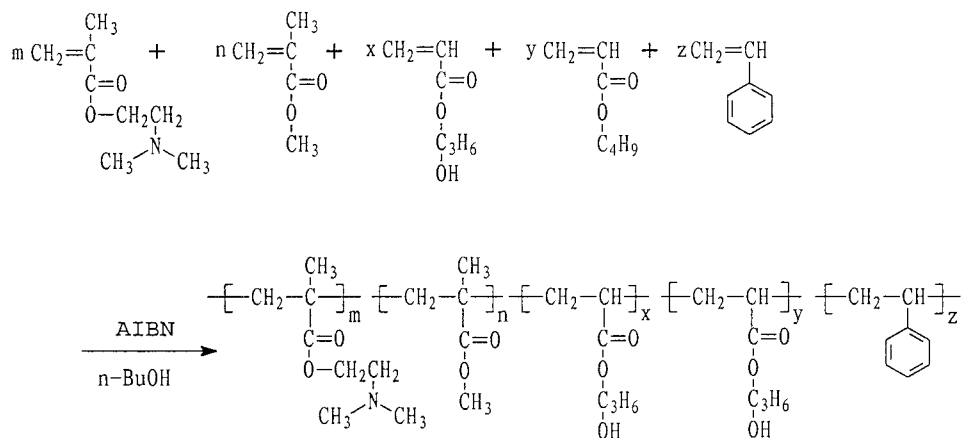
Scheme 1 Synthesis of polyacrylate resin.

monobutyl ether (EGE), butaoxime, and n-butanol samples were also obtained from Shanghai Reagents Factory (Shanghai, China).

Preparation of Polyacrylate Resin

Acrylic resin was prepared by mixing DM (0.2 mol), BA (0.5 mol), MMA (0.3 mol), HPA (0.2 mol), and AIBN (2 g). In a three-necked flask, solvent *n*-butanol was heated to 80°C,and the mixture of monomers and initiator was added. More than 5 h was required to make this random copolymer. The synthesis route is shown in Scheme **1**.

Preparation of Blocked Polyurethane

A half-blocked TDI was prepared by slowly adding the single-group blocking reagent EGE (0.2

mol) to TDI (0.2 mol) over a period of 40 min in a reactor kept below 20°C. Subsequently, the mixture was heated to 40°C and maintained at that temperature for 1 h. Three-group blocking reagent DEA (0.2 mol) was then added. The whole mixture reacted below 100°C until no free isocyanate groups were shown in the infrared spectrum.

The other kinds of blocked polyurethane resins were made in a similar fashion. A total of five kinds of crosslinking resins were obtained, as shown in Scheme **2**.The compounds C1, 2-EC-4-Gly-blocked toluene diisocyanate, and C2, 2-EC-blocked-4-Gly-blocked toluene diisocyanate are isomers, which named order isomers in polymers. Compounds C3 and C4 also are order isomers.
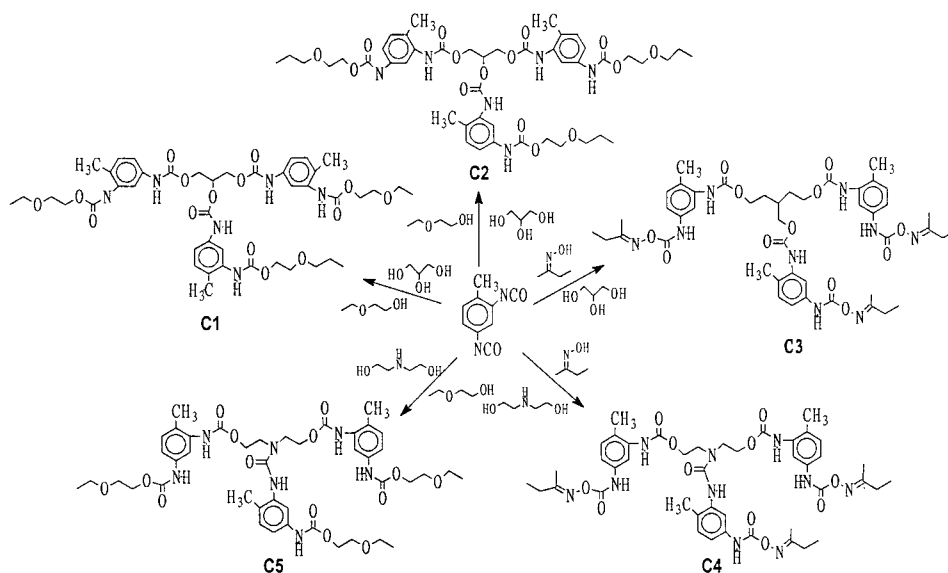
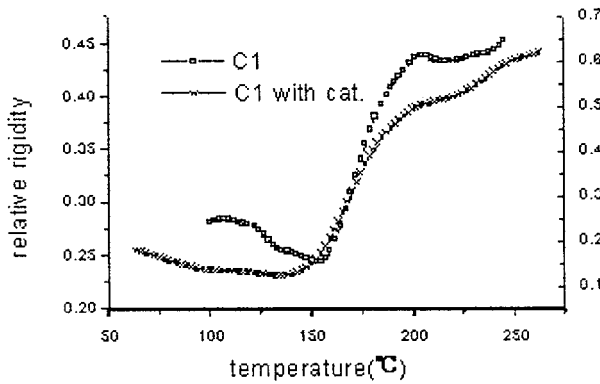**Scheme 2** Syntheses of blocked TDI crosslinkers.

Figure 1 Curing curve of C1 and polyacrylate.

TBA

A GDP-2 polymer material dynamic TBA apparatus, made in Jilin University, China, was employed. Polyacrylate resin and one of the blocked polyurethanes, in a 4:1 weight ratio, were combined at room temperature with and without a dibutyltin dilaurate catalyst. Acetone was used to reduce the viscosity of the mixture. The mixture was used to prepare specimens for TBA. The polymer-braid composite specimens were prepared by impregnation of multifilament fiberglass braids with the mixture and dried at 50°C for 5 h. The specimen was then mounted in the fully automated TBA apparatus, that was maintained at predetermined conditions. In the TBA test with heating, the heating rate was 2°C/min.

In situ Fourier Transform Infrared Spectroscopy (FTIR)

A Nicolet-170SX FTIR and temperature controller were employed. The samples without catalyst were analyzed by averaging 15 scans in the tem-
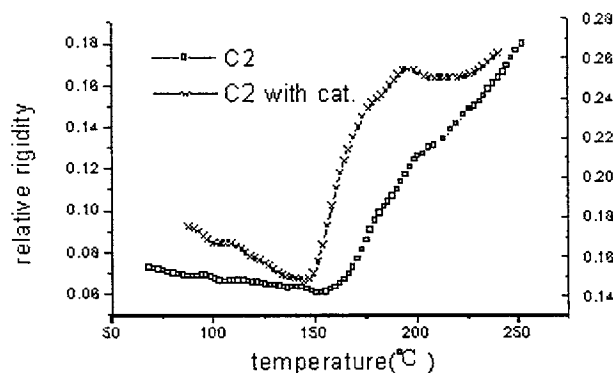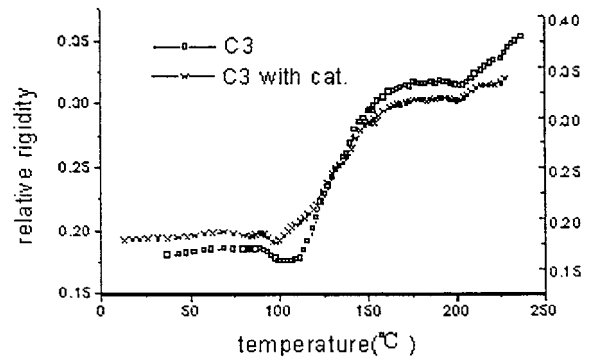

Figure 3 Curing curve of C3 and polyacrylate.

perature range between 100 and 250°C. The heating rate was 2°C/min and the analytical wavelength range was between 400cm^{-1} and 4000 cm^{-1}.

RESULTS AND DISCUSSIONS

TBA with Heating: a View from Molecular Mechanics

The heating and curing processes of the two-component complex was investigated through the change of relative rigidity of the samples in the TBA tests. As shown in Figures 1–5, the curing process was divided into two stages. If we define the sudden change of the curve as a curing temperature, there are two main curing temperatures demonstrated by these graphs.

The deblock/block mechanism[6] of the curing reaction of the polyacrylate and polyurethane is the commonly accepted explanation for curing studies. The free —NCO group would be released from the polyurethane with an increase of the heating temperature, that was named the de-
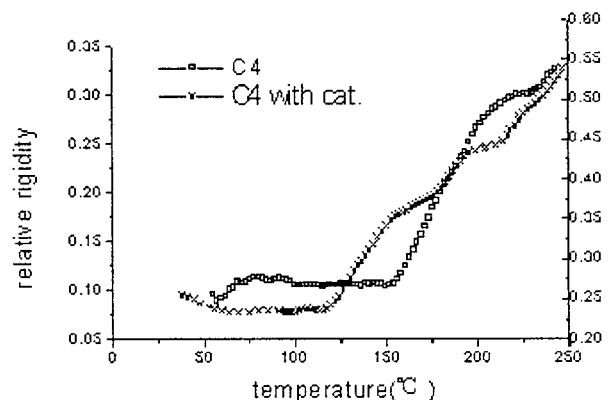

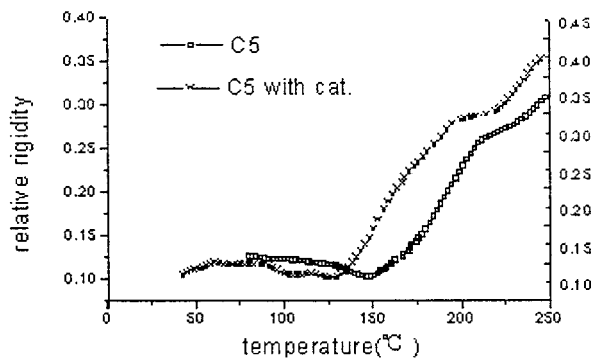**Figure 2** Curing curve of C2 and polyacrylate.

Figure 4 Curing curve of C4 and polyacrylate.
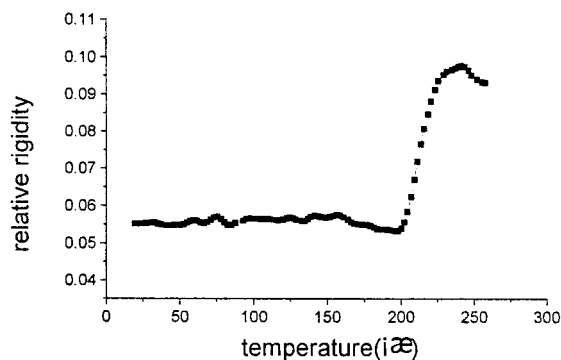
Figure 5 Curing curve of C5 and polyacrylate.

Figure 6 Self-curing curve of C5.

blocking step. The free —NCO will then immediately react with another compound containing active hydrogen; consequently one more stable urethane bond was formed, that was defined as the blocking step. Thus, an effective curing process was accomplished and a useful polymeric crosslinking film was obtained.

From the above graphs, we can infer that in the first curing stage, the original polyurethane molecule was deblocked and subsequently blocked with another molecule to make a more stable structure, a crosslinking polymer structure, that greatly increased the relative rigidity of the specimen. The second stage should be the delocking of urethane bond in the crosslinking polymers. Blocking is done to form a more compact polymer crosslinking structure, as the relative rigidity of the complex continued to increase in these graphs. The second curing temperature was the same for all of these five crosslinking resins. We extrapolate that the second stage has no relation to the blocking reagents used in the polyurethane, either the single-group reagent or the three-group reagent.

Moreover, we found that dibutyltin dilaurate catalyst could lower the first curing temperature efficiently, while having little effect on the second step. Britain and Ggemeihardt[7] have shown that dibutyltin dilaurate is a special catalyst for the reaction of NCO and OH groups. So we can deduce that the first curing stage comprises the curing reactions between NCO, within polyacrylate resin, and OH of the polyacrylate resin. In this complex system, there is only reactive hydrogen from the NH group, except for that from the OH group. We can conclude that the second stage is the curing reaction between the NCO group and the NH group.

To further verifiy our deduction, we studied the curing behavior of the crosslinking resin alone. The experimental result was shown in Figure 6. Only one curing stage appeared in the graph, and the curing temperature is consistent with the second curing temperature that emerged in the curing behaviors of the other polyurethanes and of polyacrylate. Considering the only active hydrogen of NH group in the crosslinking resin, this

Table I   Curing Temperatures from Different Curing Systems

Figures	Crosslinkers Used	First Curing Temperature (°C)	Second Curing Temperature (°C)
1	C1	154	203
	C1 with catalyst	144	203
2	C2	154	203
	C2 with catalyst	145	203
3	C3	119	203
	C3 with catalyst	98	203
4	C4	120	203
	C4 with catalyst	105	203
5	C5	154	203
	C5 with catalyst	130	203

crosslinking process should be the deblocking/blocking reaction between NCO and NH within the polyurethane, or the self-crosslinking of the crosslinker. There is good evidence from mechanical dynamics to prove our conclusion about the second stage in the curing behavior of the polymer complex.

In the first curing stage, the behavior becomes more complicated. In the single group blocking reagents used in the tests, butaoxime shows lower deblocking or blocking temperature with the NCO group than does ethylene glycol monobutyl ether. This can be attributed to the carbon-nitrogen double bond in the butaoxime, which leads to the conjugated structure in the molecule, and increases the activity of the hydrogen connected to the oxygen atom. Consequently, the reaction of the OH with the NCO group is more easily conducted in the oxime than that of the ethylene glycol monobutyl ether. Thus, butaoxime is a practical low-temperature curing reagent in polymer coatings. The curing temperature could be decreased to approximately 100°C, 50°C lower than the crosslinker blocked by the ethylene glycol monobutyl ether (Fig. 3).

While comparing Figures 1 and 2, or Figure 3 with Figure 4, we find no differences in the curing behavior of the blocking order isomers. The range of curing temperatures, between 100 and 250°C is high enough to eliminate the electrical effect of the 1-methyl group in the benzene. Therefore, no significant difference of reactive activity between ortho- and para- positions was shown in either the deblocking or blocking steps.

In contrast to the second stage, the curing temperature was obviously associated with the blocking reagents in the first stage. In comparing Figure 3 with Figure 4, this temperature only related
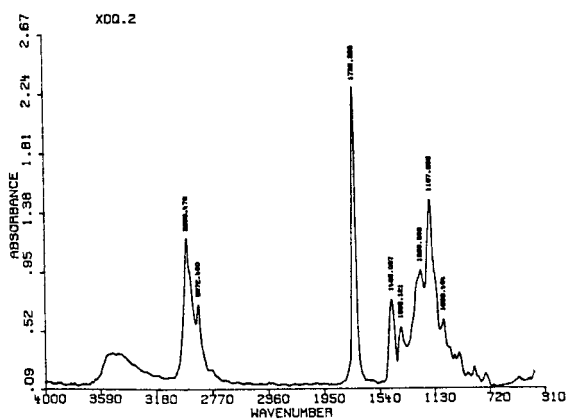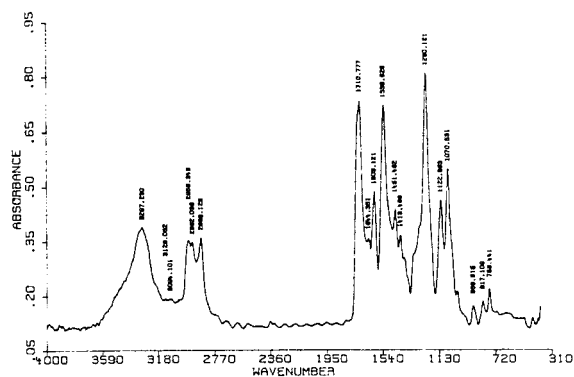

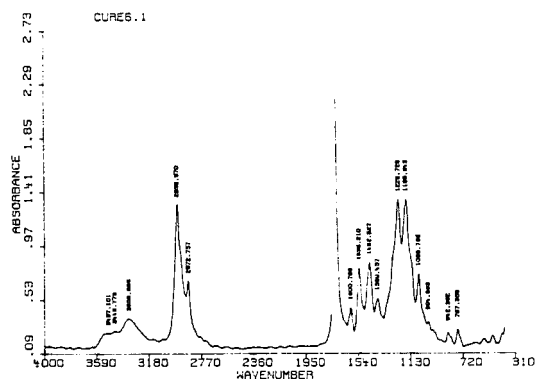**Figure 8**   IR spectrum of crosslinker C5 resin.

to the single-group blocking reagents in the polymer complex. In Figure 3, three-group blocking reagent is glycerol. Three-group blocking reagent in Figure 4 is diethanolamine. They are all blocked with the same single-group blocking reagent, butaoxime. And the first curing temperature is almost the same as that observed from the curves. In addition, when different single-group reagents were employed, but with the same three-group in the polyurethane resins, two distinct first curing temperatures were presented (Figs.1 and 3). This is a surprising phenomenon encountered in the curing behavior. In general views, the single group blocking reagents and three-group reagents should have the same chance to cause blocking and deblocking reactions. Why this happened is unclear. We need more information to prove our preliminary conjecture for the curing behavior of the polymer complex of polyacrylate and polyurethane.

In situ FTIR: Evidence at the Molecular Level

Though we have some facts about the curing behavior through the results of the polymer mechanics tests, the TBA experiment.The heating process of polyacrylate and polyurethane C5 was traced by the *in situ* FTIR study to further understand the curing reactions involved in the process. More evidence at the molecular level was obtained from the following experimental results.

Figure 7 and Figure 8 represent, respectively, the IR spectra of the polyacrylate and crosslinker C5. Figure 9 is the spectrum of the complex of these two resins. The attribution of the IR characteristic vibration[8] is described in Table 2. Figure 10 shows the *in situ* FTIR spectra of the complex.

Figure 7   IR spectrum of polyacrylate resin.

Figure 9 IR spectrum of mixture of polyacrylate and crosslinker C5.

To verify that the first curing is the most effective curing, as previously discussed, the change of the character peaks of ether bond was examined. Because the ether bond exists only in the ethylene glycol monobutyl ether in the whole complex; and the ethylene glycol monobutyl ether can be deduced in a variation of the TBA tests, deblocking and blocking reaction with NCO should occur, starting at 154°C.Thus, the peak 1069 cm^{-1}, the special peak of ether bond, together with peak 842 cm^{-1}, a stable peak of methyl group connected to carboxylic group in MMA, was chosen as reference. The change of the relative absorbance area of the two peaks is plotted against the temperature in Figure 11. From the graph, no significant change is shown before 154°C. After that, a continuous decreasing of the ether bond was observed. At the temperature of 154°C ethylene glycol monobutyl ether begins to escape from the complex. As the temparature increases, it is continuously released, which is in accord with the mechanism outlined above. Finally, a sharp de-
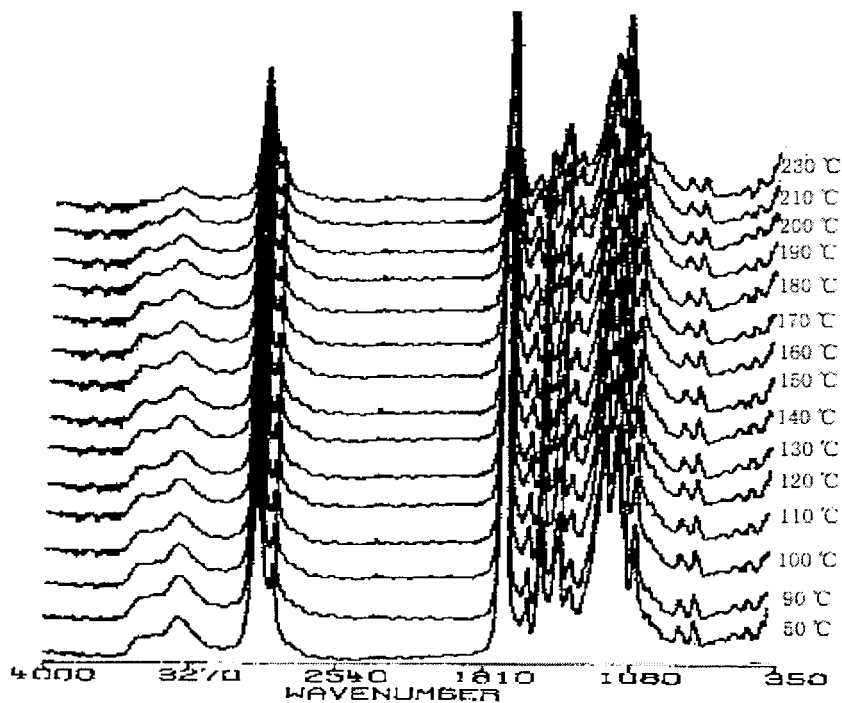
crease can be seen from the graph, which is probably caused by the quick evaporation of the molecule, due to the high temperature.

We used the peak 3369 cm^{-1}, the characteristic peak of O═H and N—H stretch vibration, although we originally planned to use only the OH vibration peak, the overlap of these two peaks make us think about them together. Similarly, the absorbance area rate of 3369cm^{-1} to 842cm^{-1} was plotted against the temperature (Fig. 12). The area decreased from temperature range of 154°C until approximately 200°C, and a steep drop occurred after 203°C. The OH group belongs to the polyacrylate in this system, and the OH will react with the deblocked NCO group during the curing process. The NH group contributes to the urethane, which may come from the material crosslinker or from the urethane formed at the time of curing. The decreasing of the curve between 154°C and 203°C should result from the consumption of OH reacted by the free NCO groups, as described in the first curing stage mechanical experiments. The steep drop in the graph after 203°C is caused by the total amount of the OH and NH groups disappearing; at that temperature NH can easily react with the NCO, as represented above.

In addition, the amount of NH doesn't increase after 154°C. No arising tendency is shown in Figure 12. Any increase would mean that the diethanolamine is deblocked from the system, because it is the only way for the increase of NH to occur. We conclude that the three-group blocking reagent doesn't participate in the delocking/blocking reactions in the curing process. From the *in situ* FTIR, our conclusions about the mechanism of curing behaviors are supported. However, a method is still needed to understand the behavior

Table II   Attribution of IR Vibration Peaks

Polyacrylate (cm^{-1})	Crosslinker C5 (cm^{-1})	Mixture (cm^{-1})	Vibration Mode
3600–3180	3287	3337	ν (O—H), ν (N—H)
2950, 2872	2958, 2868	2958, 2872	ν (C—H)
1730	1710	1720	ν (C═O)
	1536, 1290	1536	δ (N—H)
1456, 1365	1451	1452, 1369	δ (C—H)(methyl)
	1230	1226	δ (N—H)
1167	1122	1160	ν (C—O)(fatty ester)
	1070	1070	ν (C—O)(ether)
842	842	842	δ (C—H)(methyl)

**Figure 10**   IR spectra of polyacrylate and C5 at various temperatures during curing process.

of the three-group blocking reagent in the curing process, which has shown an abnormal phenomenon in view of its chemical reaction.

### Molecular Modeling: An Explanation Through Molecular Configuration

For the second stage curing reaction, some clues can be investigated through the behavior of the three-group blocking reagents in the chemical mechanism. A computer molecular model was performed.

The deblocking/blocking reaction of NCO is the nucleophilic reaction occurring to the carbon of the carboxylic group. The charge deficiency of the carbon makes this reaction proceed easily. Any electricity withdrawal connected with the carbon atom will benefit the reaction, and any electricity donor will hamper it. The urethane bond is one stable structure in the compound, due to the unshared electrons in the nitrogen atom, which make the three-group blocking frame exist steadily in a higher temperature.
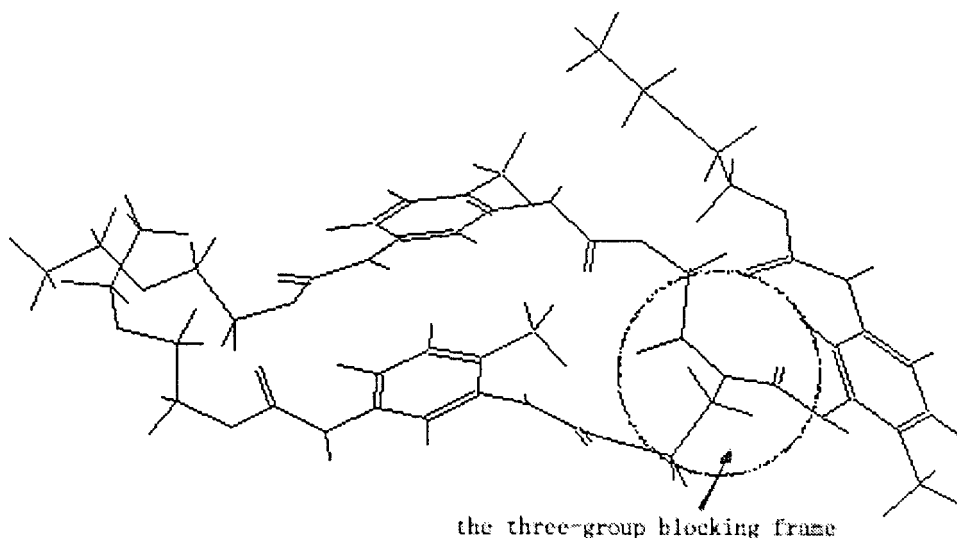
In addition, those blocking reagents usually have high boiling points and low volatility. Even
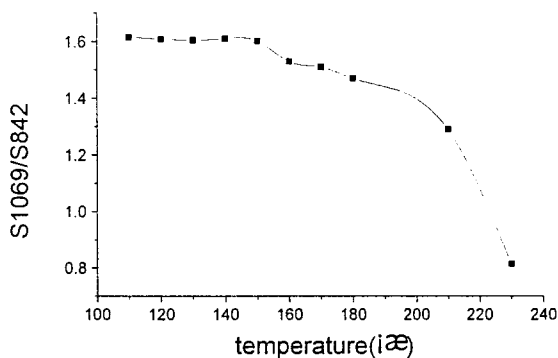
Figure 11   Change of characteristic peak of ether during curing process.
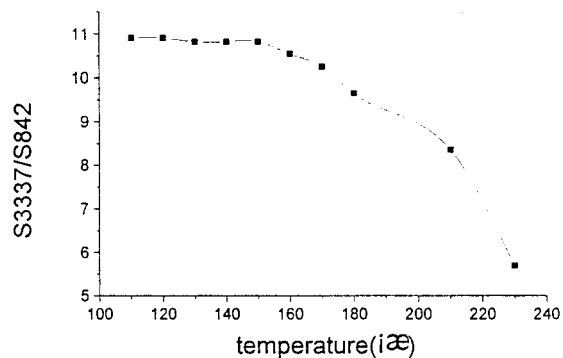
Figure 12   Change of characteristic peak $3337 cm^{-1}$ during curing process.

Figure 13 Lowest energy configuration of C5 computed by software *hyperchem* with semiexperience method.

if they are deblocked from the molecule, they won't leave the system at a lower temperature, and they can reform the urethane bonds again rapidly. This can also explain why they seem not take part in the curing reactions.

When the computing molecular configuration of the crosslinker is studied, surprisingly, there is some significant space hindrance effect involving this polyurethane molecule. The three-group blocking frame is wrapped by the three benzene rings around it, (Fig.13), and even the upper space is enclosed by other carbon chains, which decrease the possibility of the frame bumping into other active hydrogen containing groups, thus lessening chance of devastation of the structure.

Based on the above facts, no three-group blocking reagent will escape from the curing system, and the three-group will exist steadily in the poly-
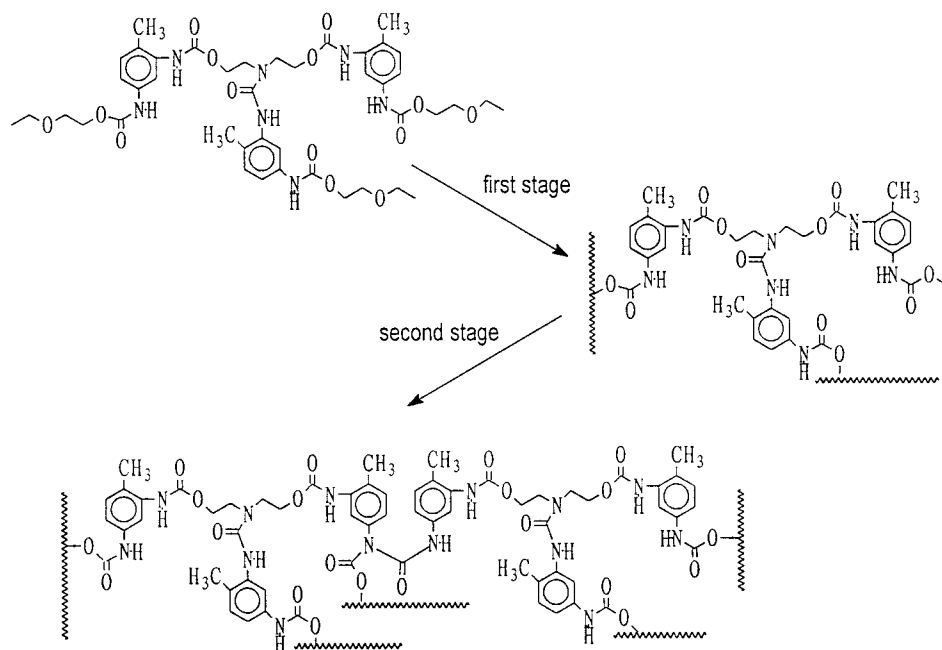
Scheme 3 Three-group type curing mechanism with C5.

mer resins to keep the extent of crosslinking of the materials. For this reason, an expected high performance film is obtained through the curing process of polyacrylate and polyurethane resins. The mechanism of the curing is conducted as shown in Scheme **3**.

CONCLUSIONS

From this article, the complete curing behavior of polyacrylate and blocked toluene diisocyanate can be understood, and a full mechanism of the curing process is provided. The curing process is divided into two stages in the reaching ranges test through the TBA.

The first stage is mainly the deblocking/blocking of the single group reagent used in polyurethane verified by *in situ* FTIR. The three-group blocking reagent exists steadily throughout the curing process, chiefly due to space hindrance effect, which is observed in molecular configuration through computer modeling.

The second stage of the curing behavior is the reaction of free NCO group with the NH group due to the urethane. This is the deep curing of the polymer resins, and it brings about damage to the film performance, which should be avoided in the application.

Through this article, we understand that the three-group type of curing mechanism proceeds with blocked toluene diisocyanate. This result is valuable in the practical application of polyurethane coatings.

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