

Synthesis and Characterization of Butan-1-ol Modified Toluene Diisocyanate Trimer

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ABSTRACT: Butan-1-ol modified toluene diisocyanate trimer (TDI-trimer) was synthesized and characterized with Fourier transform infrared spectroscopy, gel permeation chromatography, and thermal gravimetry analysis techniques. The modified TDI-trimer showed good dissolvable ability with hydroxy resin and can be used to produce paints with acrylic polyol resin. The thermal stability of the modified

TDI-trimer was improved by simply increasing both the amount of catalyst and the ratio of —NCO/—OH, less depended on the kind of catalyst. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4958–4962, 2006

Key words: toluene diisocyanate; compatibility; thermal stability

INTRODUCTION

Polyurethanes (PUs) are used in a wide range of industrial applications such as foams, adhesives, leathers, and elastomer.^{1,2} As raw materials for PUs industry, toluene diisocyanate (TDI) is the most important and commercially available one. In the presence of catalyst, TDI takes part in the reaction as described in Scheme 1, and polymerize into isocyanurate ring, which is termed trimer.

Because of the strong electron withdrawal effect of isocyanurate ring, it can then increase the reactivity of —NCO groups, which can quickly react with hydroxyl group containing resin. As expected, isocyanurate ring has a high decomposition temperature of 377°C³ showing high thermal stability when compared with other polyurethane materials. However, the rigid and polar isocyanurate ring is soluble only in strong polar solvents. In this case, TDI-trimer exhibits poor compatibility with acrylic polyol resin, which usually uses toluene or dimethylbenzene as solvent.

Here, in this work, a highly compatible TDI-trimer modified with butan-1-ol was synthesized in the pres-

ence of the organic catalyst or 2,4,6-trisdimethylamino-methyl-phenol (DMP-30) or lithium acetate (LiAc), and its properties were characterized and discussed.

EXPERIMENTAL

Materials

The chemicals used for the synthesis of toluene diisocyanate (TDI)-trimer are listed in Table I. All the chemicals are reagent grades and are used as received. Butyl acetate was distilled before use to remove trace water.

Synthesis of TDI-trimer

All the reactions were carried out in a 1000-mL four-necked round-bottomed glass vessel at isothermal conditions in a bath. The reactor was equipped with a mechanical stirrer, a nitrogen inlet, and a thermometer. In the first step, a calculated quantity of TDI, butan-1-ol, and butyl acetate was introduced into the reactor and heated at 60°C for 1 h. DMP-30 was then slowly added dropwise into the reactor at the constant temperature. When —NCO group in the resulting mixture decreased to about 9%, a calculated quantity of benzoyl chloride was quickly added and the addition of DMP-30 was also stopped. The reaction was kept for another 1 h at this temperature, followed by cooling down. It should be noted that the reaction system was purged with nitrogen all the time. The reaction conditions and the results of the synthesized TDI-trimer are tabulated in Table II.

SEM observation

Unmodified TDI-trimer and modified TDI-trimer were used to prepare paint films with acrylic polyol resin,

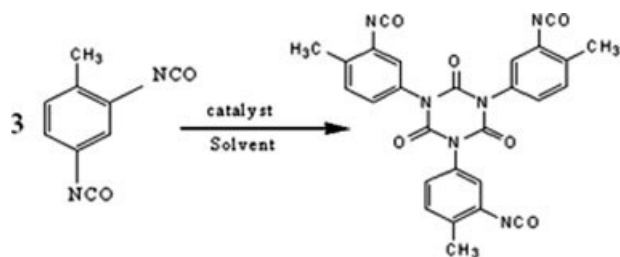
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Scheme 1 The formation of isocyanurate ring (trimer).

respectively. The paint films were then examined with a Philips-30 scanning electron microscope (SEM).

FTIR spectroscopy analysis

FTIR spectra of the modified TDI-trimer samples was performed on a PerkinElmer 1730 spectrophotometer in the mid-IR range from 4000 to 400 cm^{-1} and with a resolution of 4 cm^{-1} using KBr pellets.

GPC analysis

The molecular weight and the polydispersity of the modified TDI-trimer and unmodified TDI-trimer were measured with a Waters-515 gel-permeation chromatograph (GPC) analyzer, which was equipped with Waters 410 refractometric detector and Ultrastaygel 10³ A capillary column. The eluent was tetrahydrofuran, and the flow velocity was 1.0 mL/min. Experiments were performed at 40°C.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out on a PerkinElmer TGA7 analyzer, which was calibrated with calcium oxalate. Ten milligrams of TDI-trimer sample was used. The experiment was performed at a temperature range of 30–800°C at a heating rate of 10°C/min under a static air atmosphere. The samples were reacted at 120°C for 2 h before subjecting for scanning.

RESULTS AND DISCUSSION

Unmodified TDI-trimer and modified TDI-trimer with butan-1-ol were mixed with acrylic polyol resin,

respectively. The mixture was then poured onto a glass substrate to prepare paint films. Figure 1 shows the morphology of the paint films prepared by unmodified TDI-trimer (A) and modified TDI-trimer with acrylic polyol resin (B). It can be clearly seen that paint film (A) has much bigger particles than paint film (B). The unmodified TDI-trimer tends to be agglomerated due to its poor compatibility with acrylic polyol resin, resulting in the formation of the bigger particles when the paint is prepared. It is obvious that the modified sample has better compatibility with acrylic polyol resin than the unmodified sample.

The difference in compatibility between modified and unmodified samples was confirmed by dimethylbenzene tolerance experiment. In the tolerance experiment, dimethylbenzene was added into the container with a certain amount of the sample till the sample turned to be turbid. The dimethylbenzene tolerance was indicated by the ratio of the weight of the added dimethylbenzene to that of the sample, which is called tolerance index. It is higher than 2.3 for the modified sample, but lower than 1.5 for the unmodified sample.

Figure 2 shows the FTIR spectrum of modified TDI-trimer sample. Isocyanurate ring is characterized by the absorption peaks at 1714, 1415, and 757 cm^{-1} , indicating the produced trimer. The isocyanate group is characterized by the absorption peak at 2275 cm^{-1} . There are some dimers in product as evidenced by the absorption peak at 1592 cm^{-1} . Urethane bond can also be observed in the absorption peaks at 3292, 1542, and 1222 cm^{-1} ,^{4,5} indicating that there appear various alkyl structures on the isocyanurate ring due to the presence of butyl groups. In the far-IR range, three coupling absorption peaks at 2960, 2931, and 2872 cm^{-1} corresponded to the $\nu_{\text{C-H}}$ in the methyl and methylene. In the finger range, the absorption peak at 561 cm^{-1} and the absorption peak at 609 cm^{-1} , respectively, are assigned to the inner face and the outer face deformative vibration of $-\text{NCO}$ group.⁶

Figure 3 shows the molecular weight and the polydispersity of unmodified TDI-trimer sample. The number-average molecular weight (M_n) of the unmodified TDI-trimer is 2181 g/mol and the polydispersity (M_w/M_n) of the unmodified TDI-trimer is 1.98. In general, properties of polymer will become better if M_w/M_n is smaller. Figure 4 shows the molecular weight and the

TABLE I
Chemicals Used for the Synthesis of TDI-Trimer

Chemicals	Specifications
Toluene diisocyanate (TDI)	Molecular weight: 174.16 g/mol; purity: 99.7%: $\frac{2,4\text{-TDI}}{2,6\text{-TDI}} = \frac{80}{20}$
Butan-1-ol	Molecular weight: 74 g/mol; purity: >99.2%
Butyl acetate	Molecular weight: 116 g/mol; purity: >99.6%
DMP-30	Molecular weight: 225 g/mol; purity: >99.5%
Lithium acetate (LiAc)	Molecular weight: 102.2 g/mol; purity: >99.00%
Benzoyl chloride	Molecular weight: 140.5 g/mol; purity: >99.00%

TABLE II
The Appearance of the Synthesized TDI-Trimer

Sample	r(NCO/ OH)	Catalyst concentration (wt %)	Appearance
A	7.5	0.1	Colorless and viscous liquid
B	7.5	0.05	Colorless and viscous liquid
C	7.5	0.2	Yellowish and viscous liquid
D	10	0.1	Colorless and viscous liquid
E	14	0.1	Colorless and viscous liquid
F	18	0.1	Colorless and viscous liquid
G	7.5	0.1	Yellowish and viscous liquid

All samples except G were catalyzed with DMP-30, and sample G was catalyzed with LiAc. Catalyst concentration was the weight ratio of catalyst to TDI.

polydispersity of the modified TDI-trimer. The number-average molecular weight (M_n) is 616 g/mol and the polydispersity is 1.62, smaller than those of the unmodified TDI-trimer. It is well-known that there is difference between the reactivity of 2,—NCO group and 4,—NCO group in TDI. When TDI-trimer is modified with butan-1-ol, butan-1-ol will react with 4,—NCO group first to consume some 4,—NCO groups and reduce its activity. Consequently, the residual 4,—NCO group begins to polymerize under ca-

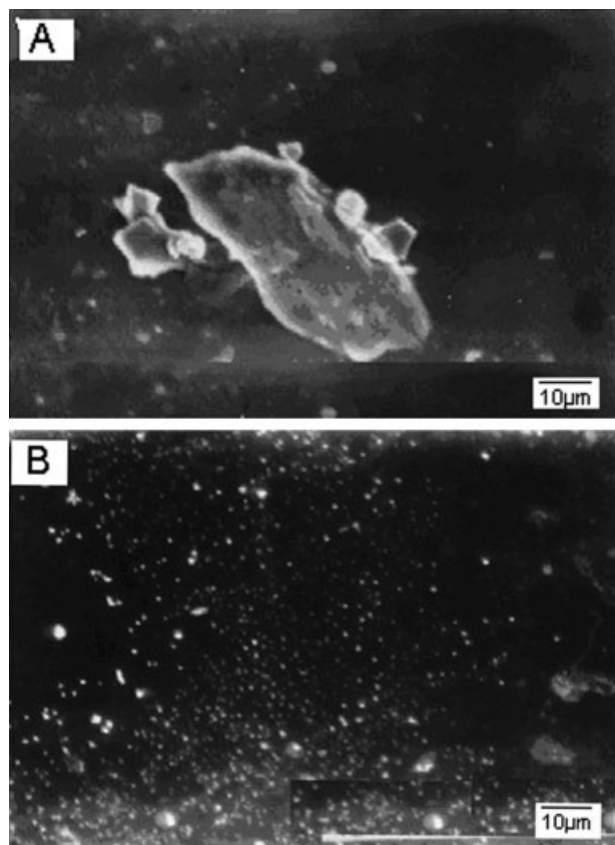


Figure 1 Scanning electron micrographs of paint films prepared with unmodified (A) and modified (B) TDI-trimer.

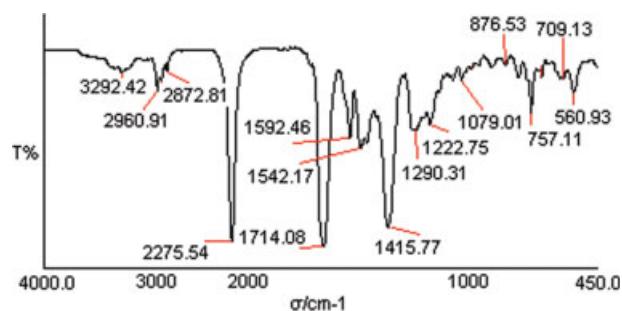


Figure 2 FTIR spectrum of TDI-trimer modified by butan-1-ol. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

talysis at a lower rate, and lower molecular weight of polymer with smaller polydispersity can be obtained. This resulted in the modified TDI-trimer with better compatibility with acrylic polyol resin.

The thermal degradation behavior and the pyrolysis mechanism of urethane-derived polymers have been studied in detail elsewhere in literature.^{4,7-14} The mechanism of thermal decomposition of these polymers involves at least three overlapping steps, as can be seen from their TGA curves. Urethane bonds decompose and produce the starting compounds (such as diisocyanates and polyols) at about 200°C. When the temperature reaches 300°C, the decomposition of urethane bonds is almost completed. Thus, first step decomposition from 150 to 350°C corresponds mainly to the decomposition of urethane bonds. During this step, the resulted products such as amines, olefins, and carbon dioxide can be found as evidenced by gas chromatography/mass spectrometry (GS/MS) analysis. Under the atmosphere of static air, the diisocyanate formed during the thermal decomposition may be dimerized to carbodiimide, which in turn can react with hydroxy groups to form a crosslinked structure. The isocyanurate ring scission occurs at about 377°C,³ so the second stage at the temperature range of 370–495°C corresponds to the thermal decomposition of isocyanurate rings. The final step over 500°C is the

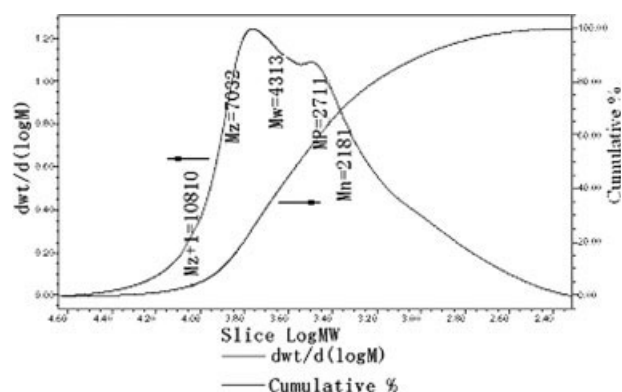


Figure 3 GPC trace of unmodified TDI-trimer.

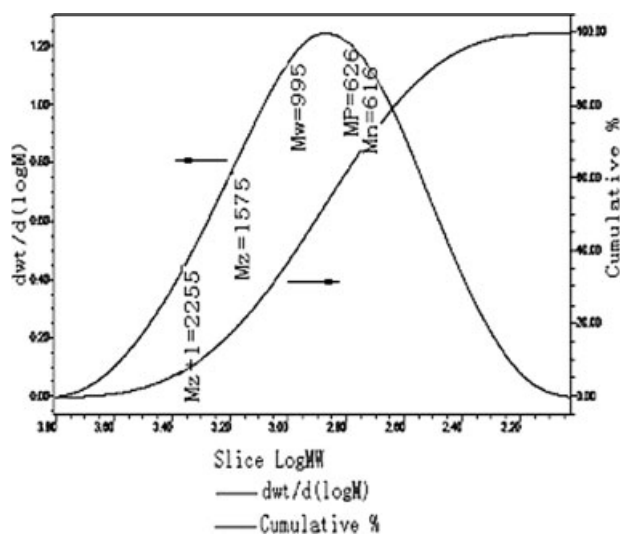


Figure 4 GPC trace of modified TDI-trimer.

decomposition of carbodiimide linkages formed in the first step, which yields CO_2 and char.^{10,14} Because the experiments were carried out under a static air atmosphere, the content of residue is usually higher than 20%.

Figure 5 shows the TGA curves of samples with different NCO/OH ratio (r). Sample A ($r = 7.5$) shows lower thermal stability. More $-\text{OH}$ groups will consume more NCO groups and reduce the number of isocyanurate rings, which in turn result in the decrease of the thermal stability. Moreover, the thermal stability increases with the increasing NCO/OH ratio, and the content of residue also increases with the increase.

For different PUs, varying backbone structures, such as isocyanurate ring, urethane, biuret, allophanate, etc., can be obtained under different synthetic conditions. For above-mentioned structures, the polyurethane with isocyanurate ring exhibits the best thermal stability. The onset weight loss temperature of isocya-

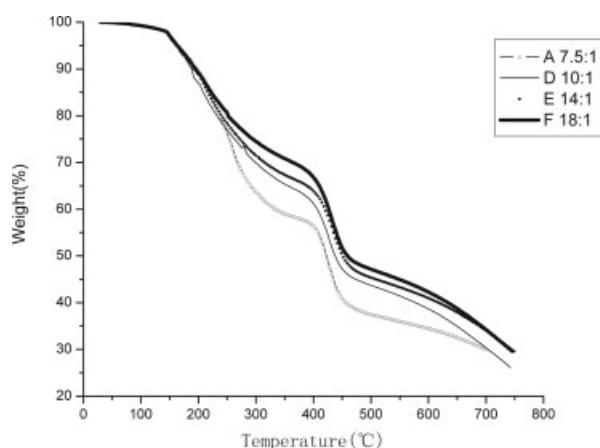


Figure 5 Effect of $-\text{NCO}/-\text{OH}$ ratio on the thermal stability of TDI-trimer.

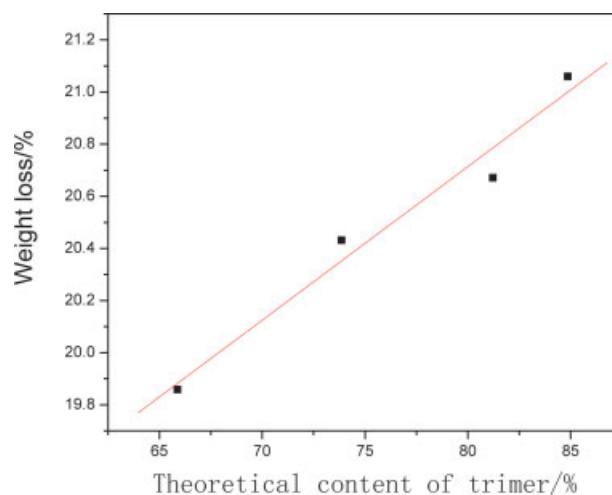


Figure 6 Weight loss content at 370–495°C versus theoretical trimer content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

nurate containing PU is higher than 370°C, at which other polyurethanes almost decompose. Thus, the weight loss at temperature range of 370–495°C may represent the trimer content. In this connection, the trimer content can be easily obtained from TG analysis. Figure 6 shows the result together with the theoretical calculation result (dash line). The theoretical content of trimer (ω) is calculated according to eq. (1).

$$\omega = \frac{(n_1 - n_2) \times M_1}{n_1 M_1 + n_2 M_2} \times 100\% \quad (1)$$

where n_1 the mole of TDI, M_1 molar mass of TDI, n_2 the mole of butan-1-ol, and M_2 molar mass of butan-1-ol.

From Figure 6, it is evident that there is a satisfied linear relationship between the weight loss at 370–495°C and the theoretical content of trimer in the prod-

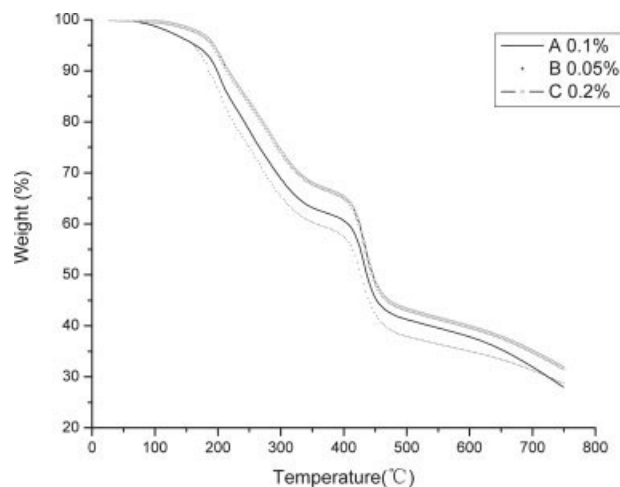


Figure 7 TG traces of TDI-trimer prepared with different DMP-30 contents.

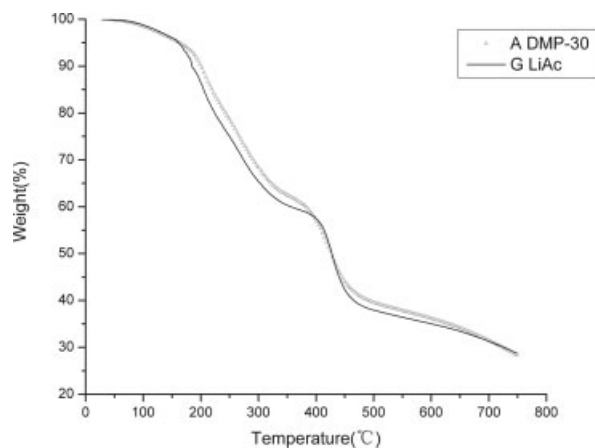


Figure 8 TG traces for TDI-trimer prepared with different catalysts.

ucts. In other words, TG analysis can be used to quantitatively predict the trimer content.

The TGA curves of samples A, B, and C with the same —NCO/—OH ratio but different DMP-30 concentrations are shown in Figure 7. It is apparent that the thermal stability increases with the increasing DMP-30 content.

The TGA curves of the samples prepared with both DMP-30 (A) and LiAc (G), respectively, under the same ratio ($r = 7.5 : 1$) are shown in Figure 8. There is no significant difference in the weight loss at 370–495 °C between the two samples. This implies that the catalyst can only affect the polymerization but not the content of isocyanurate rings.

CONCLUSIONS

Highly compatible TDI-trimer can be readily synthesized by the modification of butan-1-ol and using 2,4,6-trisdimethylaminomethyl-phenol as catalyst. With the modification, the molecular weight and polydispersity of TDI-trimer become smaller. The thermal stability of the modified TDI-trimer can be improved with increasing —NCO/—OH ratio.

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