

# Study on *N*-Hydroxyphthalimide as Blocking Agent for Isocyanates

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**ABSTRACT:** In this article, *N*-hydroxyphthalimide (NHPH) has been prepared with phthalic anhydride and hydroxylamine hydrochloride. The blocked toluene diisocyanate (NTDI) by NHPH was synthesized also. The effects on the synthesis of NTDI were studied, and the deblocking temperature of NTDI was read by TG-DSC and IR. In the meantime, actual crosslinking reaction conditions on the systems of polyhydroxy compounds were surveyed also. The stability of the mixture of NTDI and polyhydroxy compounds was observed by determining the viscosity of it. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1346–1352, 2002; DOI 10.1002/app.10242

**Key words:** *N*-hydroxyphthalimide; blocking agent; isocyanates

## INTRODUCTION

*N*-Hydroxyphthalimide (NHPH) is a compound with a hydroxy group that bonds with the nitrogen of imide group directly, so it has acidity.<sup>1</sup> Because of this property, NHPH has extensive uses. Many studies have established that NHPH can act as a herbicide,<sup>2–5</sup> a germicide,<sup>6</sup> a catalyst for oxidation of organic compounds,<sup>9,10</sup> a charge-control agent for electrostaographic tones,<sup>11</sup> and an ore floater.<sup>12</sup> However, there are few reports on its uses as blocking agent for isocyanates.

In this article, NHPH has been prepared with phthalic anhydride and hydroxylamine hydrochloride, and the blocked toluene diisocyanate (NTDI) was gained by NHPH and toluene diisocyanate (TDI). The effects on the synthesis of NTDI were studied, and its deblocking temperature was also tested. In succession, the actual crosslinkage factors and the stability of the mixture of NHPH and polyhydroxy compounds were

discussed. Finally, the mechanical property of the coating made by the polyhydroxy compound and NTDI was observed. In this article, we address some basal aspects on the application of NHPH as a blocking agent to the polymer field.

## EXPERIMENTAL

### Materials

Hydroxylamine hydrochloride, pyridine, phthalic anhydride, and dibutyltine dilaurate were obtained from the Shanghai Chemical Reagent Company, and their purities were chemically pure. The polyhydroxy epoxy compound E-12 was obtained from the Shanghai Resin Factory. Trimethylolpropane (TMP) and toluene diisocyanate (the mass ratio of 2,4-TDI with 2,6-TDI is 80/20) were obtained from the Nanjing Rubber Factory.

### Synthesis of NHPH

To a stirred solution of a fixed quantity of hydroxylamine hydrochloride in pyridine, phthalic anhydride was added in portions under heating. At the end of this reaction, parts of the solvent were

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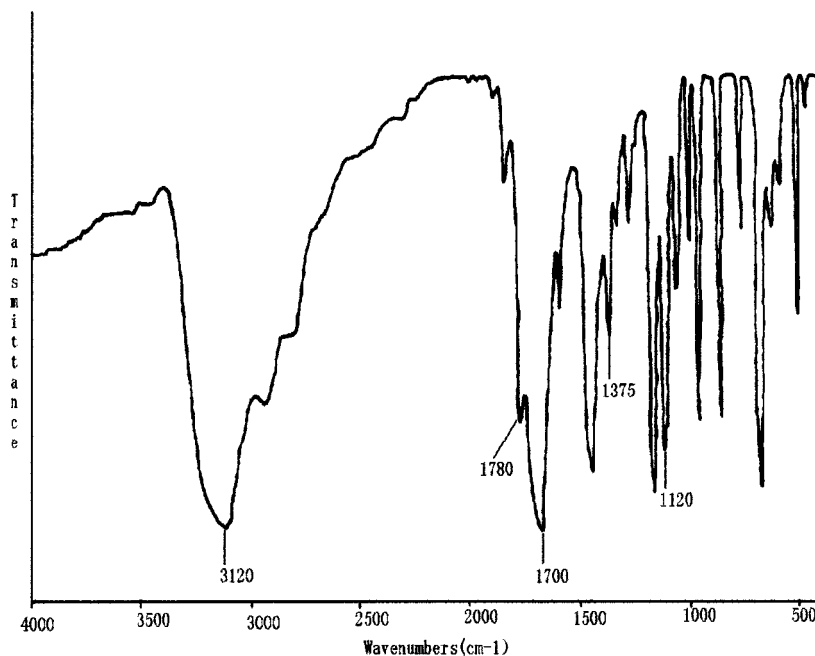


Figure 1 IR spectrum of NHPH.

distilled, then precipitant was added and a white needle-type crystal was obtained by recrystallization.

Synthesis of NTDI

To a stirred solution of a fixed quantity of NHPH, TDI was dropped in portions with dibutyltine di-

laurate as a catalyst. At the end of this period, parts of the solvent were distilled and precipitant was added. Faint yellow powder was gained by recrystallization.

Analysis and Characterization Techniques

The yield of NTDI was found by the general method for the determination of nitrogen<sup>12</sup>

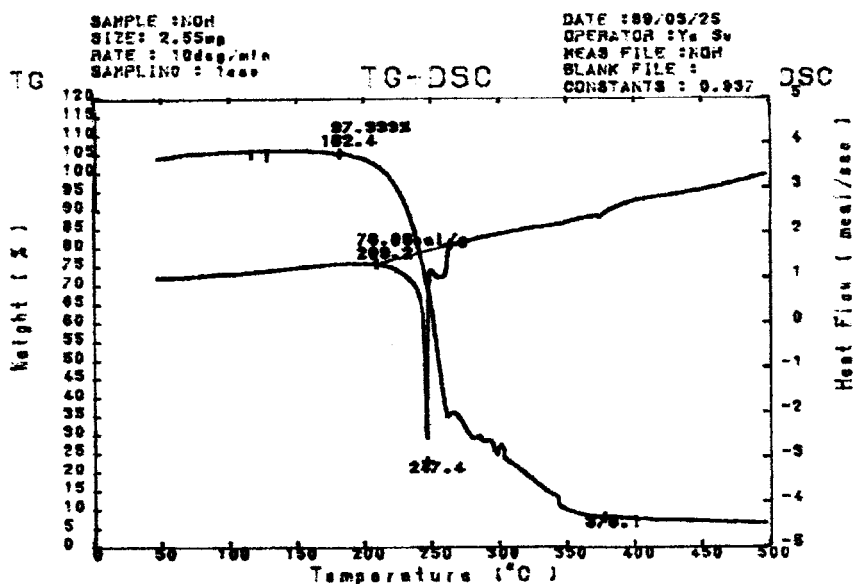


Figure 2 TG-DSC thermogram of NHPH (10°C/min).

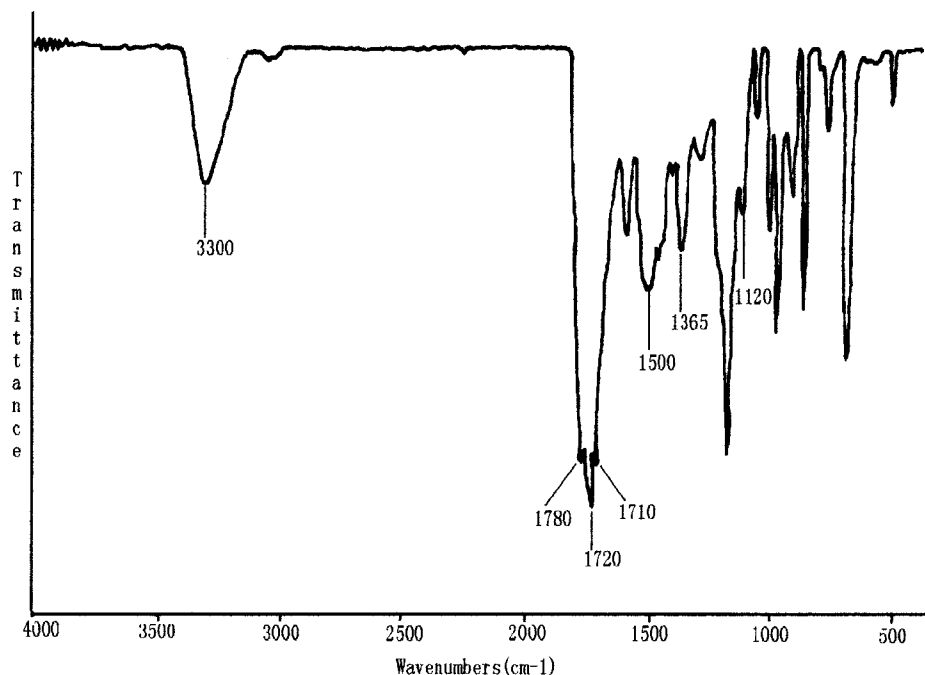


Figure 3 IR spectrum of the synthesis of NHPH and TDI.

spectrometer (Nicolet Company, USA) and TG-DSC analyzer (Rigacu Company, Japan). A NQJ-79 rotary-type viscometer was used to trace the variation of the viscosity of the polyhydroxy compound mixed with NTDI. The mechanical properties (hardness, shock strength flexibility, and adhesive power) of the coating made from the polyhydroxy compound with NTDI were determined in accordance with GB/T1730-93, GB/T1732-93, and GB1720-79, respectively.

## RESULTS AND DISCUSSION

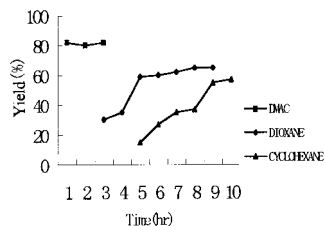
### Results of the Synthesis of NHPH

The white needle-type crystal gained by the reaction of phthalic anhydride and hydroxylamine hydrochloride was pressed into a tablet with potassium bromide to determine its IR spectrum, which was shown in Figure 1. Compared with the Sadtler<sup>13</sup> standard IR spectrum, it can be seen that the IR spectrum of synthesized NHPH con-

Table I Effects of Reaction Conditions on Yield of NTDI

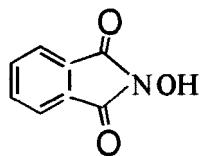
	A	B	A × B	C	D	E	Yield
1	1	1	1	1	1	1	80%
2	1	1	1	2	2	2	82%
3	1	2	2	1	1	2	80%
4	1	2	2	2	2	1	81%
5	2	1	2	1	2	1	Little
6	2	1	2	2	1	2	Little
7	2	2	1	1	2	2	65%
8	2	2	1	2	1	1	65%
$K_1^a$	3.23	1.62	2.92	2.25	2.25	2.26	—
$K_2$	1.30	2.91	1.61	2.28	2.28	2.27	—
$K_3$	1.93	1.29	1.31	0.03	0.03	0.01	—

<sup>a</sup>  $K_1$  sum of the yield to level 1.  $K_2$  sum of the yield to level 2.  $K_3$  the difference of the yields between level 1 and level 2. All the solvents were refined under reduced pressure and dried by molecular sieves.



**Figure 4** The effects of solvents and reaction time on the yield of blocked compounds (catalyst amount: 0.1 mL) dripping rate of TDI: 6 mL/min, the mol ratio of reactants is 1 : 1.

tains absorption peaks in 1780, 1720, 1375, and 1120  $\text{cm}^{-1}$ , which can be assigned to cyclic imide, and in 1700  $\text{cm}^{-1}$ , which belongs to the carbonyl group. At 3120  $\text{cm}^{-1}$ , this corresponds to the hydroxy group. As a result, the structure of the compound can be concluded.

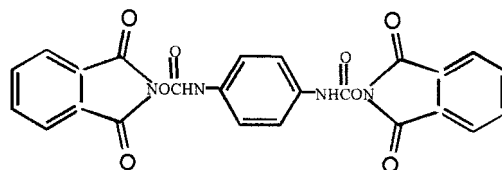


In addition, Figure 2 is the TG-DSC thermogravimetric curve of NHPH. An endothermic peak at  $D_T = 247.4^\circ\text{C}$  (range of 209.2–270°C)

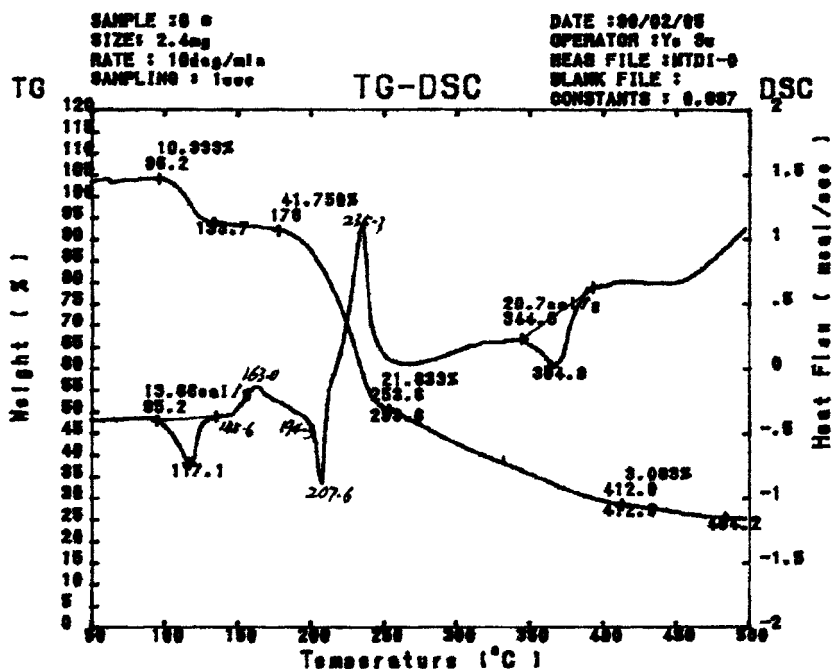
and its corresponding TG curve showed the weight loss was 87.3%, so a decision can be drawn that this is the heat decomposition peak of NHPH.

### Effects on the Synthesis of NTDI

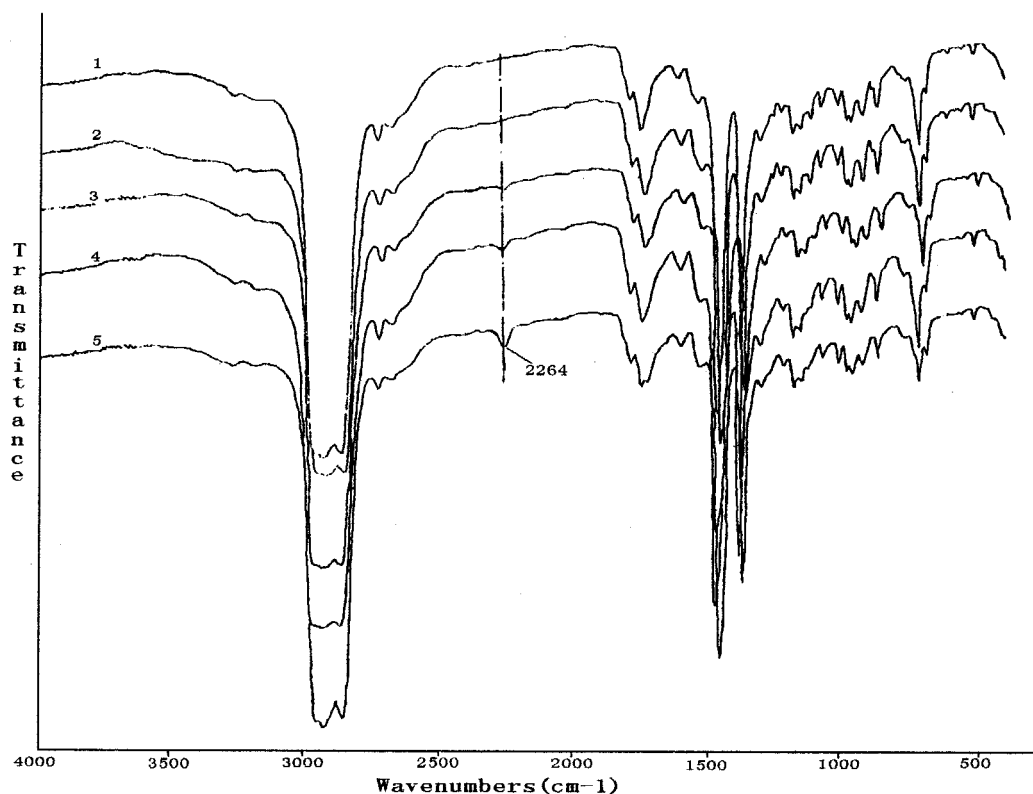
Figure 3 showed the IR spectrum<sup>13,14</sup> of the results of NHPH and TDI, from which it can be seen that the absorption peaks in 1780, 1710, 1365, and 1120  $\text{cm}^{-1}$  were the characteristic peaks of cyclic imide, and the peaks in 3300, 1720, and 1500  $\text{cm}^{-1}$  belonged to the urethano group. However, the characteristic peak of the NCO group of TDI in 2260  $\text{cm}^{-1}$  and the hydroxyl group of NHPH in 3120  $\text{cm}^{-1}$  disappeared. So it can be concluded that the resultant is blocked by toluene diisocyanate NTDI:



It is obviously important to get a high yield on the synthesis of NTDI. In this article, five factors were chosen with two levels per each factor as follow: (1) kind of solvent (*N,N*-dimethyl, acet-



**Figure 5** DSC-TG thermogram of NTDI (10°C).



**Figure 6** IR spectrum of NTDI at different temperatures for 10 minutes: 1.50, 2.10, 3.120, 4.140, and 5.160°C.

amide); (2) reaction time (2 h, 6 h); (3) catalyst amount (0.1 mL, 0.25 mL); (4) dripping rate of TDI (1.5 mL/min, 6 mL/min); (5) mixture ratio of reactants (1 : 1, 1 : 1.2). Orthogonal Table  $L_8$  ( $2^7$ )<sup>15</sup> was taken, and the interaction of the solvent and time was listed in the third row. The experimental data were shown in Table I, which indicated that solvent and reaction time were main factors; the other three were secondary factors. On the above basis, fixing the three secondary factors, effects of solvent, and reaction time on yield were studied further, and the experimental data was shown in Figure 4, which indicated that

using *N,N*-dimethyl acetamide as the solvent and reaction time was 1 h with the yield 80%; however, it took 9 h to get a yield of 95% with dioxane and 10 h to get yield 57% with cyclohexane. The evidence indicated that the polarity of the solvents is the key factor in the yield of NTDI: the stronger the polarity of the solvent, the faster the reaction rate with the higher yield.

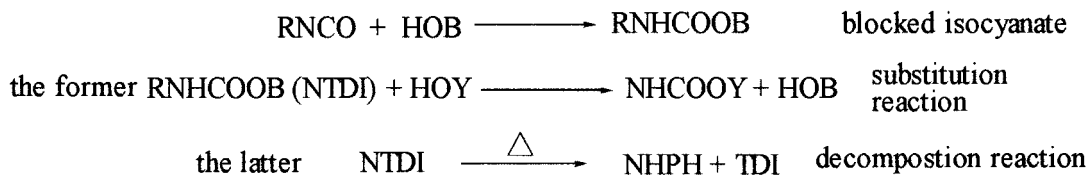
#### Deblocking Temperature of NTDI

Figure 5 shows the TG-DSC thermogravimetric curve of NTDI. An endothermic peak at  $D_T$

**Table II** Relations between Viscosity and Time (at 100°C)<sup>a</sup>

Serial Number	Mixture Ratio	0 h	2 h	4 h
T1	NTDI and E-12 (NCO/OH = 1 : 1)	15mp × s	60mp × s	70mp × s
T2	NTDI and E-12 (NCO/OH = 1.5 : 1)	15mp × s	cured	cured
T3	NTDI and TMP (NCO/OH = 1 : 1)	15mp × s	71mp × s	85mp × s
T4	NTDI and TMP (NCO/OH = 1 : 1)	15mp × s	cured	cured

<sup>a</sup> No solvent volatilization during the determination. Concentration: 25%.



**Scheme 1** Two different reacting mechanisms of NTDI.

= 117.1°C (range of 95.2–145.6°C) and its corresponding TG curve showed the weight loss was 10%, so it was considered as the cause of volatile impurity; the exothermal peak at  $D_T = 163.0^\circ\text{C}$  (range of 145.6–194.3°C) and its corresponding TG curve showed there was no distinct weight loss, so it should be the deblocking peak of NTDI. Compared with the TG-DSC thermogravimetric curve of NHPH (Fig. 2), the endothermogram peak at  $D_T = 207.6^\circ\text{C}$  can be regarded as the deblocking peak of NHPH. When the temperature elevated more, TDI was oxidated ( $D_T = 235.5^\circ\text{C}$ ). With an even more elevated temperature, the deblocking peak of the other substance can be seen ( $D_T = 380.9^\circ\text{C}$ ).

The IR spectra of NTDI mixed with paraffins treated at different temperatures for 10 min are shown in Figure 6, which indicated the characteristic peak of NCO ( $2264 \text{ cm}^{-1}$ ) at  $120^\circ\text{C}$  and more distinct at  $140^\circ\text{C}$ , which means that NTDI began deblocking at  $120^\circ\text{C}$  or more. In addition, the initial deblocking temperature of NTDI obtained from IR spectrum ( $120^\circ\text{C}$ ) is lower than that obtained from the TG-DSC thermogravimetric curve ( $145^\circ\text{C}$ ) and the difference is attributed to a relatively fast scanning temperature of TG-DSC.

### Conditions of Cure of NTDI and Polyhydroxyl Compounds

Tables II and III showed a viscosity amplitude of variation of the one-pack system composed by

**Table III** Variation of Viscosity at  $120^\circ\text{C}^{\text{a}}$

Serial Number	Mixture Ratio	0 h	1 h
T <sub>2</sub>	NTDI and E-12 (NCO/OH = 1.5 : 1)	18mp × s	cured
T <sub>4</sub>	NTDI and TMP (NCO/OH = 1 : 1)	19mp × s	cured

<sup>a</sup> No solvent volatilization during the determination. Concentration: 25%.

NTDI and the polyhydroxy compound E-12 as well as trimethylol propane (TMP). When NTDI and the polyhydroxy compound (NCO/OH = 1 : 1) coexisted at  $100^\circ\text{C}$ , viscosity of the system began rising (Table II). It indicated that partials of NTDI started deblocking, and the deblocking result of TDI reacted with the polyhydroxy compound. However, the system of NCO/OH = 1.5 : 1 has an even more reactionary rate at  $100^\circ\text{C}$  and the system was wholly cured after 2 h. Even with a match of NCO/OH = 1 : 1, the systems cured entirely at  $120^\circ\text{C}$  after an hour. It is obvious that the initial deblocking temperature, when NTDI coexists with the polyhydroxy compound, is lower than that obtained from the IR spectrum and TG-DSC thermogravimetric curve. That is because of the different mechanism of reaction.<sup>16,17</sup>

From the scheme above, it is obvious that the latter needed higher energy than the former.

### Stability and Coating Performance of NTDI and Polyhydroxyl Compounds

The system was prepared by a solution of NTDI and TMP in DMAC with a prorated of NCO/OH = 1.5 : 1, and the viscosity of the solution was measured periodically at room temperature. It could be seen from the data of Table IV that the viscosity of the solution was kept basically unchangeable for 200 days. This indicates that the system of NTDI and TMP is stable at room temperature.

Table V showed the coating performance of the one-pack system of NTDI and E-12. The determination of the coating mechanical properties indi-

**Table IV** Effects of Shelf Life on Viscosity<sup>a</sup>

Shelf life (day)	10	30	50	80	110	150	200
Viscosity (map × s)	20	21	22	24	25	27	28

<sup>a</sup> Solution of NTDI and TMP (NCO/OH = 1.5 : 1). Concentration: 25%.

**Table V The Mechanical Properties of the Coatings<sup>a</sup>**

Mixture Ratio	Adhesive Power (Grade)	Shock Strength (kg × mm)	Flexibility (mm)
NTDI and E-12 (NCO/OH = 1.5 : 1)	2	50	0.5

<sup>a</sup> The sample was dried for 2 h at 100°C and another 3 h at 120°C.

cated this kind of coating mixture could cure relative wholly at 100 and 120°C with good coating performance.

## CONCLUSION

During the synthesis of NTDI by NHPH and TDI, the kind of solvent has a significant effect on the yield: the stronger the polarity of the solvent, the faster the reaction rate, with the higher yield. Studies on the IR spectrum and TG-DSC thermogravimetric curve of NTDI indicated the initial deblocking temperature was in the range of 120–145°C; however, when it coexisted with polyhydroxyl compounds, the initial deblocking temperature was about 100°C, and the system showed a fast deblocking and curing reaction rate at 120°C. The solution of NTDI and polyhydroxyl compounds performed good coating mechanical properties after baking at 100 and 120°C; the system composed of NTDI and polyhydroxyl compounds had a long shelf life at room temperature.

## REFERENCES

1. Keisuke, K. *J Polym Sci Polym Chem Ed* 1979, 17, 1619.
2. Franz, J. E. U.S. Pat. 368,794 (1977).
3. Misslitz, U.; Meyer, N.; Kast, J. DE Pat. 4,204,206.
4. Kast, J.; Meyer, N.; Misslitz, U. DE Pat. 4,222,261.
5. Hagen, H.; Nilz, G.; Roetsh, T. DE Pat. 4,126,999.
6. Takeychi, T.; Kondo, S. JP Pat. 03,232,891.
7. Keisuke, K. *J Org Chem* 1978, 17, 2919.
8. Yasutaka, I. *J Org Chem* 1995, 60, 3934.
9. Yasutaka, I. *J Org Chem* 1996, 61, 4520.
10. Wilson, J. L.; Bonser, S. M.; Osterhandt, H. W. U.S. Pat. 5,332,637 (1994).
11. Ren, J. *J Metal (Chinese)* 1993, 29, 241.
12. Zhang, Z. X.; Zhang, R. G. *Qualitative Analysis for Organic Group (Chinese)*; Chemistry Industry Press: Beijing, 1990, p 437.
13. Wang, Z. X. *Analysis for IR Spectra of Polymers (Chinese)*; Chemistry Industry Press: Beijing, 1989.
14. Ma, X. S. *Paints Coating Indust* 1997, 6, 14.
15. Chinese Academic of Science. *Probability and Statistics*; Science and Technology Press: Beijing, 1979.
16. Yu, Z. N. *Coatings Technology (in Chinese, Book 2)*; Chemistry Industry Press: Beijing, 1993.
17. Guise, G. B. *J Appl Polym Sci* 1979, 23, 353.
18. Liu, Y. K. *Paints Coating Indust* 1982, 4, 35.