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SYNTHESIS AND PROPERTIES OF PHENOL-BLOCKED TOLUENE DIISOCYANATE CROSSLINKERS

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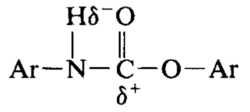
Key Words: Phenol; Toluene diisocyanate; Blocked isocyanate; Thermal dissociation

ABSTRACT

Phenol, 2,4-di-*t*-butylphenol, and 3-methyl-4-nitrophenol blocked TDI adducts were prepared and characterized by elemental analysis and IR and ^{1}H-NMR spectra. The dissociation temperatures were determined by the carbon dioxide evolution method and extrapolation of TG curves. It was found that the adducts based on 2,4-di-*t*-butylphenol and 3-methyl-4-nitrophenol dissociate at a lower temperature than the adduct based on phenol. It was also found that the 3-methyl-4-nitrophenol-blocked TDI adduct shows a low curing time compared to other adducts. The kinetic parameters are reported. The dissolution temperatures of the blocked TDI adducts were determined in four different polyols having different molecular weights.

INTRODUCTION

Blocked isocyanates have been studied and patented for a wide variety of applications including coil coatings, heat-setting adhesives, tirecord-rubber adhesives, and crosslinkings of elastomeric solid rocket propellant binders [1, 2]. The dissociation or deblocking temperature of blocked isocyanate is one of the limiting factors in industrial applications. Almost all heat-cured systems require curing temperatures around 80°C [3]. Since the bond between the isocyanate and the blocking agent is polarizable ( $\mathrm{Ar}-\overset{\mathrm{H}\delta^{-}}{\mathrm{N}}-\underset{\delta^{+}}{\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}}-\mathrm{O}-\mathrm{Ar}$), introduction of an electron-withdrawing substituent on the blocking agent will reduce the dissociation temperature through enhancement of polarization.

In a previous report [4] we described the effect of substituents on the dissociation temperature of phenol-blocked TDI adducts. It was found that substituents at the ortho position favor the dissociation reaction regardless of their nature. It was also found that an electron-withdrawing substituent reduces the dissociation temperature.

In this report we describe the synthesis and thermal dissociation of blocked isocyanates with a sterically hindered phenol and a phenol with a nitro substituent.

EXPERIMENTAL

Materials

Toluene diisocyanate (TDI) (Fluka) containing an 80:20 mixture of 2,4 and 2,6 isomers was distilled at reduced pressure (125°C/10 torr) and used. Solvents were purified by reported procedures [5]. 2,4-Di-*t*-butylphenol (Fluka), 3-methyl-4-nitrophenol (Aldrich), polypropylene glycols (PPG-400, PPG-1000, and PPG-2000), hydroxyl-terminated polybutadiene (HTPB) with a molecular weight of 2500, dibutyltin dilaurate (DBTDL) (Merck), and diazabicyclo[2.2.2]octane (DABCO) (Merck) were used as received.

2,4-Di-*t*-butylphenol–TDI Adduct

An 0.8 M solution of TDI (6.969 g in 50 mL carbon tetrachloride) was added dropwise to a 1.6 M solution of 2,4-di-*t*-butylphenol (16.5 g in 50 mL carbon tetrachloride) over 45 minutes at the reflux temperature. DBTDL (0.2 mL) was used as a catalyst. The addition was carried out in a three-necked flask equipped with a stirrer, condenser, addition funnel, and nitrogen inlet. The supply of nitrogen was stopped before the reflux temperature was reached. After the addition was over, the reaction was continued for 7 hours at the reflux condition. The product was separated as a white precipitate and washed thoroughly with petroleum ether (60–80°C) and dried in air. Yield 60%, mp 155–160°C.

Analysis of $C_{37}H_{50}N_2O_4$ requires C,75.7; H,8.5; N,4.7%. Found: C, 75.1; H, 8.3; N, 4.1%.

3-Methyl-4-nitrophenol–TDI Adduct

A 0.4 M solution of TDI (3.485 g in 50 mL toluene) was added to an 0.8 M solution of 3-methyl-4-nitrophenol (6.125 g in 50 mL toluene) containing 0.2 mL DBTDL at the reflux temperature over a period of 2 hours. After the addition was over, the reaction was continued for 6½ hours. Petroleum ether (60–80°C) was added to the final mass for effective precipitation. Yield 83%, mp 135–138°C.

Analysis of $C_{23}H_{20}N_4O_8$ requires C, 57.4; H, 4.1; N, 11.6%. Found: C, 57.8; H, 4.5; N, 11.5%.

The phenol-blocked TDI adduct was prepared by a reported procedure [4].

Analytical Methods

Infrared spectra were recorded by the potassium bromide pellet method on a Perkin-Elmer Model 781 spectrophotometer. ^{1}H-NMR spectra were recorded on a Varian EM-390, 90 MHz spectrometer. Chemical shifts were reported relative to the methyl group of toluene. Thermogravimetric analyses were performed using the Metler TA 3000 system at a heating rate of 10°C/min under a nitrogen atmosphere. The sample weight was 4-5 mg, and the gas flow rate was 50 mL/min. The procedure adopted for assessment of the minimum deblocking temperature by the CO_2 evolution method was reported previously [4].

Solubility Tests

This test gives the lowest temperature at which blocked diisocyanate completely dissolves in the polyols. A 0.1 M equivalent dispersion of each adduct in any one of the polyols listed in Table 3 was heated on a temperature-controlled silicone oil bath at a heating rate of approximately 3°C·min^{-1}. Heating was terminated at 160°C. The temperature at which a clear solution was obtained was recorded.

Gelation Tests

A solution of 0.002 M of the adduct dissolved in 20 mL tetrahydrofuran was prepared and added to 9 g HTPB in a beaker and mixed thoroughly. Then the beaker was placed in an oven maintained at 140°C. The gelation time was measured from the time the beaker was placed in the oven until the reaction mixture no longer flowed from the inverted beaker.

RESULTS AND DISCUSSION

The IR spectra (Fig. 1) of phenol-blocked TDI adducts are identical and do not show an absorption peak in the 2270 cm^{-1} range. This indicates that both —NCO groups of the original TDI molecule are completely blocked with phenol. The stretching vibration of the C=O group of the urethane combined with N—H strongly absorbs at 1200-1240 cm^{-1} [6]. The absorption frequencies for N—H stretching, urethane carbamate [7], and C=O stretching vibrations are given in Table 1. ^{1}H-NMR spectra show multiple peaks attributed to aromatic protons at 6.7 to 7.2 ppm. Similarly they show a doublet due to the urethane N—H protons at 7.5 to 9 ppm. However, the peak area is only half of the expected value. This is not surprising because the single N—H proton may be unobservable [8]. The solvents and the chemical shift values for the individual compounds are given in Table 1.

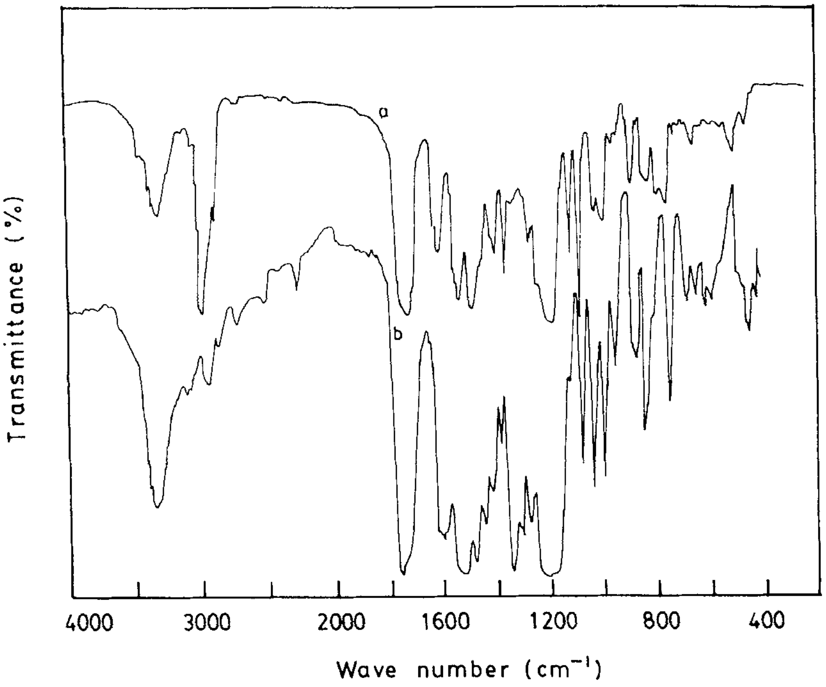
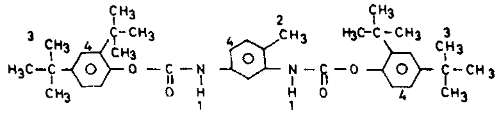
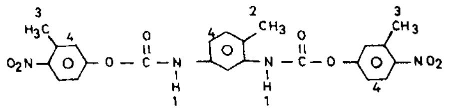


FIG. 1. Infrared spectrum of (a) 2,4-di-*t*-butylphenol-TDI adduct, and (b) 3-methyl-4-nitrophenol-TDI adduct.

TABLE 1. Spectral Data of Blocked Isocyanates

Blocked isocyanate	^{1}H-NMR Chemical shifts (ppm)	IR frequencies
	$CDCl_3$ 1·1-1·3(s)(36H,3) ; 2·1-2·2(s)(3H,2) ; 6·7-7·2(m)(9H,4) ; 7·5(d)(2H,1)	3300-3340 cm^{-1} (N-H stretching)^s 1680-1720 cm^{-1} (C = O stretching)^{vs} 1530-1540 cm^{-1} (Urethane carbamate)^s
	CD_3COCD_3 : 2·3 (s)(3H,2) ; 2·5(s)(6H,3) ; 7·0-9·0 (m) (9H, 4 and 2H,1)	3340-3380 cm^{-1} (N-H stretching)^{vs} 1710-1730 cm^{-1} (C=O stretching)^{vs} 1510-1540 cm^{-1} (Urethane carbamate)

s = strong, vs = very strong

The minimum dissociation temperatures for the adducts as determined by the carbon dioxide evolution method and by extrapolation of TG curves are given in Table 2. 2,4-Di-*t*-butylphenol-blocked TDI shows a lower dissociation temperature than phenol-blocked TDI. This may be due to the presence of the bulky *t*-butyl group in the ortho position of phenol which facilitates deprotonation of the urethane linkage. 3-Methyl-4-nitrophenol-blocked TDI shows the lowest dissociation temperature due to the electron-withdrawing tendency of the nitro group which labilizes the bond formed between the phenol and the isocyanate. The methyl group at the meta position does not participate in charge distribution in the urethane linkage. When compared to PPG-1000, all the adducts dissociate at relatively lower temperatures in PPG-400. This may be attributed to the poorer solvating power of PPG-1000 compared with PPG-400.

The effect of substituent on the dissociation reaction of blocked TDI adducts is also reflected in the cure (gelation) reaction of HTPB with the adducts. The 3-methyl-4-nitrophenol-blocked TDI adduct requires 105 minutes to give a completely cured elastomer at 140°C, whereas phenol and 2,4-di-*t*-butylphenol-blocked TDI adducts require 270 minutes at identical conditions. A parallel experiment was carried out at room temperature after evaporation of the tetrahydrofuran at 140°C. No cure occurred for 480 minutes, and this confirmed that the solvent does not aid the dissociation reaction of the adduct.

Catalysis is used to reduce the dissociation temperature of blocked isocyanates. In this investigation, catalyzed experiments were carried out in propylene glycol (PG). DABCO was found to catalyze the dissociation reaction, and the results are included in Table 2. Compared to uncatalyzed reactions, all the adducts show lower dissociation temperatures in catalyzed reactions. Griffin and Willwerth [9] found that the *N*-methylmorpholine acts as a deblocking catalyst for a number of blocked TDI adducts. They reported that the deblocking temperature is 85°C in the absence of catalyst and 80°C in the presence of catalyst for the *m*-cresol–TDI adduct. Carlson and coworkers [10] studied the effects of various catalysts on the deblocking of the methylethyl ketoxime-blocked trimerized isophorone diisocyanate. The catalysts chosen were DABCO, tetrabutylammonium chloride, and DBTDL. They reported that neither tetrabutylammonium chloride nor DBTDL catalyzed the deblocking reaction.

In the thermogravimetric experiments, all the adducts dissociate in a single-stage reaction and show only one DTG curve (Fig. 2). This is not surprising because the volatility of the precursors of the adducts is very high at the temperature at which the dissociation reaction starts. The kinetic parameters were calculated from the TG curves by the Coats and Redfern [11] method using linear regression analysis (Table 2). The dissociation reaction follows first-order kinetics. 2,4-Di-*t*-butylphenol and 3-methyl-4-nitrophenol-blocked TDI adducts have lower activation energies than the phenol-blocked TDI adduct. As previously discussed, this is due to steric and electronic effects of the substituents, respectively.

Since polyols are the main coreactants for blocked isocyanates in urethane coatings and other industrial processes, the solubility of blocked isocyanates in hydroxy compounds acquires greater importance. The solubility tests were carried out in four polyols having different molecular weights, and the results are given in Table 3. PPG-400, PPG-1000, and PPG-2000 are polyether diols, and UB-POL-

TABLE 2. Dissociation Temperatures and Kinetic Parameters for Blocked TDI Crosslinkers

	Dissociation temperature, °C							
	CO_2 evolution method					Kinetic parameters		
Adduct	In PG[a]	In PG (catalyzed)[b]	In PPG-400	In PPG-1000	TGA	n	E_a, kJ·mol^{-1}	InA
Phenol–TDI	78	72	69	79	175	1.2	133	25
2,4-Di-*t*-butylphenol–TDI	78	72	70	76	172	1.0	106	15
3-Methyl-4-nitrophenol–TDI	75	60	55	60	160	1.2	70	7

[a] PG = propylene glycol.

[b] In the presence of 0.005 g DABCO.

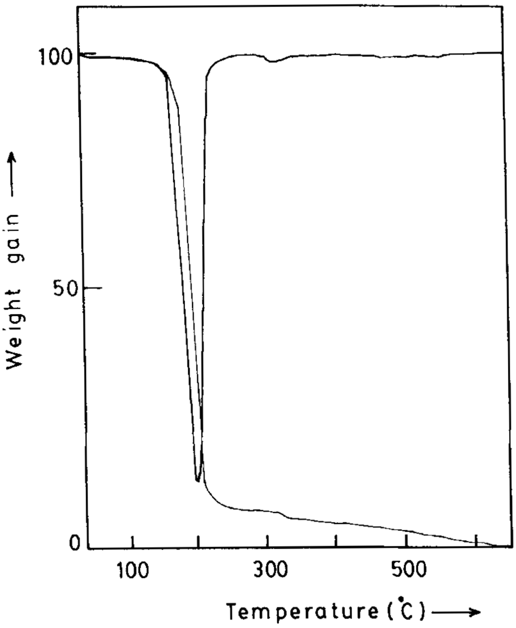


FIG. 2. TG and DTG curves of phenol-blocked TDI adduct.

3000 is a glycerol-based triol. In all the polyols, the phenol-blocked TDI adduct shows poor solubility. Methyl and *t*-butyl groups improve the solubility of the adducts. The adduct with 3-methyl-4-nitrophenol shows better solubility even though it contains a nitro group. This may be due to dissociation rather than dissolution of the adduct in polyols. It is also found that solubility decreases with an increase in the molecular weight of the polyols.

TABLE 3. Dissolution Temperature of the Adducts in Polyols

Adduct	In PPG-400, °C	In PPG-1000, °C	In PPG-2000, °C	In UB-POL-3000,[a] °C
Phenol–TDI	160	Partially soluble at 160	Partially soluble at 160	Partially soluble at 160
2,4-Di-*t*-butylphenol–TDI	85	115	130	130
3-Methyl-4-nitrophenol–TDI	72	105	125	160

[a] UB-POL-3000 is a glycerol-based triol.

CONCLUSION

This report establishes for the first time that di-*t*-butyl and methyl substituents increase the solubility of adducts, thus extending the applicability of polyurethane products as coatings and elastomers.

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