Synthesis and Thermal Dissociation of Phenol- and Naphthol-Blocked Diisocyanates

H. KOTHANDARAMAN,* A. SULTAN NASAR, and R. KAMAL LAKSHMI

Department of Polymer Science, University of Madras, Guindy Campus, Madras - 600 025, India

SYNOPSIS

Phenol-, 2-naphthol-, and 1-nitroso-2-naphthol-blocked toluene diisocyanate (TDI) and isophorone diisocyanate (IPDI) adducts and their polymers with PPG-1000 were prepared and characterized by nitrogen estimation, IR, and ^{1}H-NMR spectroscopy. The absence of an IR absorption band at 2270 cm^{-1} confirmed the completion of the reaction between the isocyanate and the blocking agents, whereas the presence of a band at 1075–1150 cm^{-1} confirmed the formation of poly(ether urethanes). The deblocking temperatures were determined by the use of DSC and by the carbon dioxide evolution methods. The thermal stabilities of the 2-naphthol-blocked diisocyanates were less than the phenol-blocked diisocyanates. Dissociation temperature was also reduced by the nitroso group in the blocking agent. Mass spectral data confirmed the product analysis. The solubility of the adducts were determined in the different polyols. Adducts based on IPDI showed better solubility than did those based on TDI. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Blocked polyisocyanates have a bright future in the coatings field.[1] They are particularly suitable building blocks for light stable two-component urethane coatings[2] and single-package blocked adduct urethane coatings (ASTM Type 3).[3]

Blocking of the isocyanate is an equilibrium reaction that can be represented as follows:

$$Ar - N = C = O + HO - Ar \rightleftharpoons$$
$$Ar - NH - CO - O - Ar$$
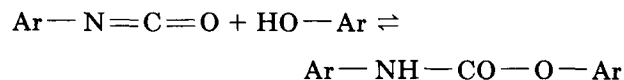
At elevated temperatures, the reaction tends to proceed from right to left.[4]

The temperature of dissociation is an important factor. Blocked isocyanates having dissociation temperatures below 100°C are preferable for industrial applications.[1] The dissociation temperature of the urethane depends upon the chemical nature of the groups adjacent to the urethane linkage. Electronic factors influence the ease with which the ure-

thane bond is dissociated. On account of the possibilities to introduce a number of substituents on the benzene ring, phenol is one of the most studied blocking agents for isocyanates. The substituents having an electron-withdrawing tendency will labilize the urethane linkage and favor the dissociation reactions.[5]

A substantial number of patents cover the use of phenol-blocked isocyanates in various applications.[6–8] Vulcanizing of rubber using phenol- and nitrosonaphthol-blocked isocyanates have been reported.[9] Here, we report the preparation and dissociation temperatures for phenol-, naphthol-, and nitrosonaphthol-blocked toluene diisocyanate and isophorone diisocyanate adducts that may be used as a cross-linker in many thermally curable systems.

EXPERIMENTAL

Materials

Toluene diisocyanate (TDI) (a mixture of isomers containing 80% 2,4-TDI and 20% 2,6-TDI) obtained from Fluka was distilled at reduced pressure and used. Isophorone diisocyanate (IPDI) (Fluka) was used without further purification. Phenol was dis-

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tilled before use. 2-Naphthol and 1-nitroso-2-naph-thol (Koch-Light) were used as received. All solvents were purified by standard procedures.[10] Poly(propylene glycols) (PPG-400, PPG-1000, and PPG-2000) and triol (UB-POL-3000) were obtained from UB Petro Products Ltd. and used as such.

Preparation of Blocked Diisocyanates

A phenol-blocked TDI adduct was prepared by the reported procedure.[5] In a typical synthesis, the blocking agent (2M) was taken in a three-necked flask fitted with a condenser and a magnetic stirrer. Dibutyltin dilaurate (2 drops) was added in all cases except for the 1-nitroso-2-naphthol–TDI adduct where no catalyst was added. Then, the diisocyanate (1M) solution was taken in an addition funnel and fitted into one neck of the flask. Dry nitrogen was passed through the other neck. After 5 min, the flask was closed and the reaction was started. The diisocyanate solution was added drop by drop over a period of 45 min. The reaction mixture was stirred or refluxed for several hours. The product was effectively precipitated by adding petroleum ether (60–80°C) and dried in air. The other details are given in Table I.

Preparation of Polyurethanes

A dispersion of 0.001M of the blocked TDI or IPDI adduct in 0.01M of PPG-1000 was prepared in a boiling tube and placed in a thermostated silicone oil bath maintained at 160°C (±0.5°C). The reaction mixture was periodically stirred for 1 h and then

repeatedly washed with petroleum ether (60–80°C) to remove the unreacted polyol and the adduct. The polymer was dried at 80°C.

Characterization Methods of the Blocked Diisocyanates and Their Polymers

IR spectra for all the adducts were recorded by the potassium bromide pellet method in a Hitachi 5879 spectrophotometer. ^{1}H-NMR spectra were recorded on a Varian EM-390, 90 MHz spectrometer. Chemical shifts are reported relative to the methyl group of TDI and IPDI. The nitrogen content was determined by the Kjeldahl–Nessler's method using a Shimadzu UV 160A spectrophotometer.

A Perkin-Elmer Series 7 thermal analysis differential scanning calorimeter (DSC) was used to obtain thermal traces of the blocked diisocyanate adducts. The sample weight was 2–5 mg and the heating rate was 10°C/min.

The mass spectra were recorded using a Finnigan Mat 8230 mass spectrometer operating at 70 eV with an emission current of 0.5 mA. Assessment of minimum dissociation temperatures by the carbon dioxide evolution method and solubility tests were carried out using the procedures already reported.[5,11]

The neat IR spectra for the polymers were recorded in a Perkin-Elmer Model 781 spectrophotometer. ^{1}H-NMR spectra for the polymers were recorded in a Varian EM-390, 90 MHz spectrometer using $CDCl_3$ as a solvent. The relative viscosities of polymers were measured at a concentration of 0.1 g/50 mL of DMF at 30°C by the use of an Ubbelohde viscometer.

Table I   Preparation of Phenol- and Naphthol-blocked Diisocyanates

| Blocking Agent	Isocyanate	Solvent	Reaction Time	Temperature (°C)	Yield (%)	% N Found (Calcd)	mp (°C)
2-Naphthol	TDI	Chlorobenzene	6 h + overnight	60–65	80	7.0 (6.1)	160–164
1-Nitroso-2-naphthol	TDI	Toluene	4 h at 30°C, 5 h at 55°C	—	60	10.3 (10.7)	140–143
Phenol	IPDI	CCl₄	6 h + overnight	Reflux	75	6.3 (6.8)	172–174
2-Naphthol	IPDI	CCl₄	7 h + overnight	Reflux	75	4.8 (5.5)	165–168
1-Nitroso-2-naphthol	IPDI	Toluene	8 h + overnight	60–70	70	9.8 (9.9)	110–114
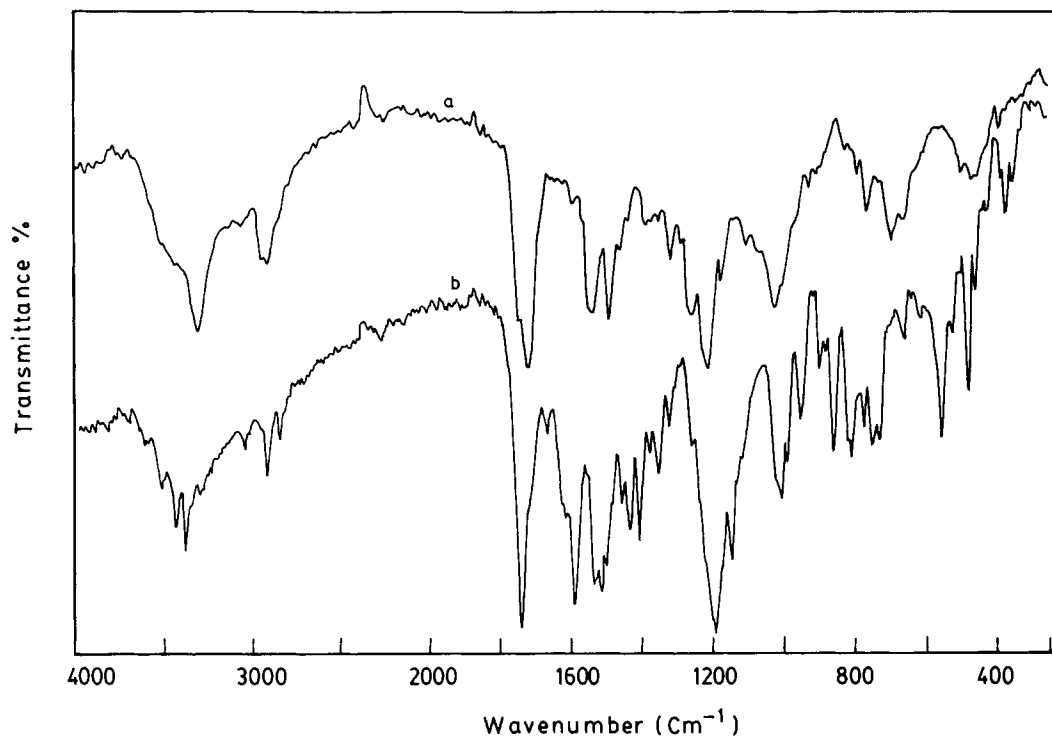
Figure 1   IR spectra of the (a) IPDI–phenol adduct and (b) TDI–2-naphthol adduct.

RESULTS AND DISCUSSION

Typical IR spectra for phenol- and naphthol-blocked TDI and IPDI are given in Figure 1. The characteristic absorption frequencies for the N — H stretching, C═O stretching, and urethane carbamate vibrations are identical for all the adducts. The stretching vibration of the C═O group of the urethane combined with N — H absorbs strongly at 1200–1220 cm^{-1} and confirms the presence of the urethane linkages.[12] Absence of absorption at 2250–2270 cm^{-1} indicates that both isocyanate groups in TDI and IPDI are completely blocked. The absorption frequencies for individual adducts are given in Table II.

The ^{1}H-NMR spectra shows multiple peaks at 6.8–7.6 ppm, which are attributed to aromatic protons. Similarly, all spectra show a peak at 7.2–8.5 ppm, which is due to the urethane N — H protons. But the peak area is less than the calculated value. This is not surprising because the single N — H proton may be unobservable.[13] The solvents and the chemical shifts for the individual compounds are given in Table III.

The nitrogen contents were found to agree well with the calculated values. The melting points for all the adducts were determined and the values are given in Table I. Except for phenol-blocked TDI, all other values are reported for the first time.
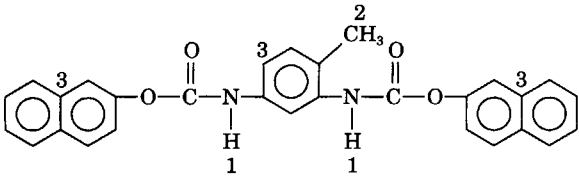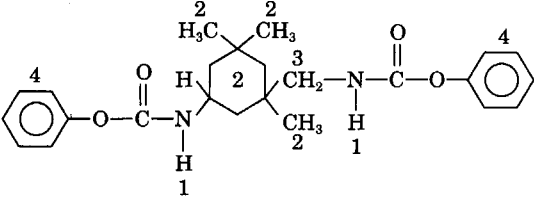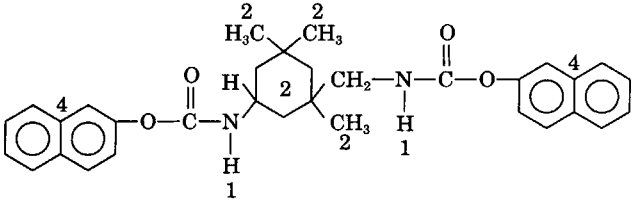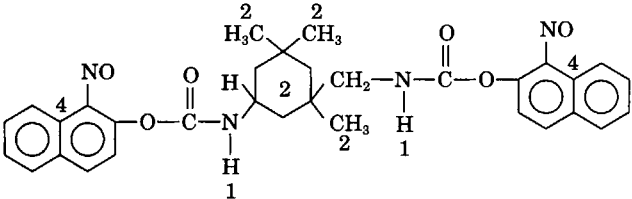
The minimum temperatures at which the adducts

Table II   IR Frequencies for Blocked Isocyanate Adducts

Adduct	N — H (Stretching) (cm^{-1})	C═O (Stretching)^{vs} (cm^{-1})	Urethane Carbamate[s] (cm^{-1})
2-Naphthol–TDI	3350[s]	1720	1565
1-Nitroso-2-Naphthol–TDI	3200–3400[b]	1760	1565
Phenol–IPDI	3300–3350[s]	1720	1540–1550
2-Naphthol–IPDI	3350[s]	1720	1500–1540
1-Nitroso-2-naphthol–IPDI	3300–3500[b]	1760	1500–1540

s, strong; b, broad; vs, very strong.

Table III ¹H-NMR Chemical Shifts of Phenol- and Napthol-blocked Diisocyanates

Blocked Isocyanate	Solvent and Chemical Shift (ppm)
	DMSO-D₆, 2.1–2.3 (S) (3 H,2); 6.8–8.2 (m) (19 H, 1 and 3)
	CDCl₃, 0.8–1.8 (m) (16 H, 2); 2.7–2.9 (d) (2 H, 3); 6.7–7.2 (m) (10 H, 4); 7.2–7.4 (d) (2 H, 1)
	CDCl₃, 0.8–1.8 (m) (16 H, 2); 2.7–2.9 (d) (2 H, 3); 6.8–7.6 (m) (14 H, 4); 7.8–8.0 (b) (2 H, 1)
	CDCl₃, 0.8–1.9 (m) (16 H, 2); 2.8–3.0 (d) (2 H, 3); 6.7–7.3 (m) (12 H, 4); 8.3–8.5 (b) (2 H, 1)

dissociate to regenerate an appreciable amount of free isocyanate were determined by the Griffin and Willwerth[11] method. The experiments were conducted in propylene glycol (PG) and PPG-400. The results from the DSC method are given in Table IV.

The dissociation temperatures found in PPG-400 are relatively lower than in PG. This is due to the presence of additional ether oxygen atoms in PPG-400, which may facilitate the deprotonation of the adduct. This solvent-assisted deprotonation may

Table IV Dissociation Temperature of Blocked Diisocyanate Adducts

	Carbon Dioxide Evolution Method			
Adduct	In Propylene Glycol (PG)	In PGª (Catalyzed)	In PPG-400	DSC Method
Phenol–TDI	78	72	69	170
2-Naphthol–TDI	80	72	67	155
1-Nitroso-2-naphthol–TDI	68	68	61	—
Phenol–IPDI	100	94	95	180
2-Naphthol–IPDI	90	85	90	160
1-Nitroso-2-naphthol–IPDI	87	83	87	—

ª 0.005 g of diazabicyclo[2.2.2]octane was used as a catalyst.

Table V   Mass Spectra (70 eV) of the Blocked Diisocyanate Adducts

Adduct	Fragments Found (Assignment)					
	m/z	I[a]	m/z	I[a]	m/z	I[a]
Phenol–TDI (mol wt = 362.37)	93 (C_6H_5O phenol–H)	2	94 (C_6H_6O phenol)	100	174 ($C_9H_6N_2O_2$–TDI)	44
2-Naphthol–TDI (mol wt = 462.52)	143 ($C_{10}H_7O$ naphthol–H)	3	144 ($C_{10}H_8O$ naphthol)	100	174 ($C_9H_6N_2O_2$–TDI)	50
1-Nitroso-2-naphthol–TDI (mol wt = 520.50)	172 ($C_{10}H_6NO_2$ nitrosonaphthol–H)	3	173 ($C_{10}H_7NO_2$ nitrosonaphthol)	26	174 ($C_9H_6N_2O_2$–TDI)	42
Phenol–IPDI (mol wt = 410.51)	93 (C_6H_5O) phenol–H)	5	94 (C_6H_6O phenol)	100	222 ($C_{12}H_{18}N_2O_2$–IPDI)	0.5
2-Naphthol–IPDI (mol wt 510.65)	143 ($C_{10}H_7O$ naphthol–H)	4	144 ($C_{10}H_8O$ naphthol)	96	222 ($C_{12}H_{18}N_2O_2$–IPDI)	1.0
1-Nitroso-2-naphthol–IPDI (mol wt = 568.63)	172 ($C_{10}H_6NO_2$ nitrosonaphthol–H)	4	173 ($C_{10}H_7NO_2$ nitrosonaphthol)	92	222 ($C_{12}H_{18}N_2O_2$–IPDI)	Nil

[a] I represents the intensity of the peak.

also be a reason for differences in the dissociation temperatures found by the carbon dioxide evolution method and the DSC method. Wagener and Murla[14] studied the thermal dissociation behavior of phenol-blocked phenyl isocyanates and found that the physical state of the blocked isocyanate also is an important factor in determining the temperature at which dissociation begins. The 2-naphthol-blocked TDI and IPDI deblock at lower temperatures than do those blocked with phenol. Also, it is found that
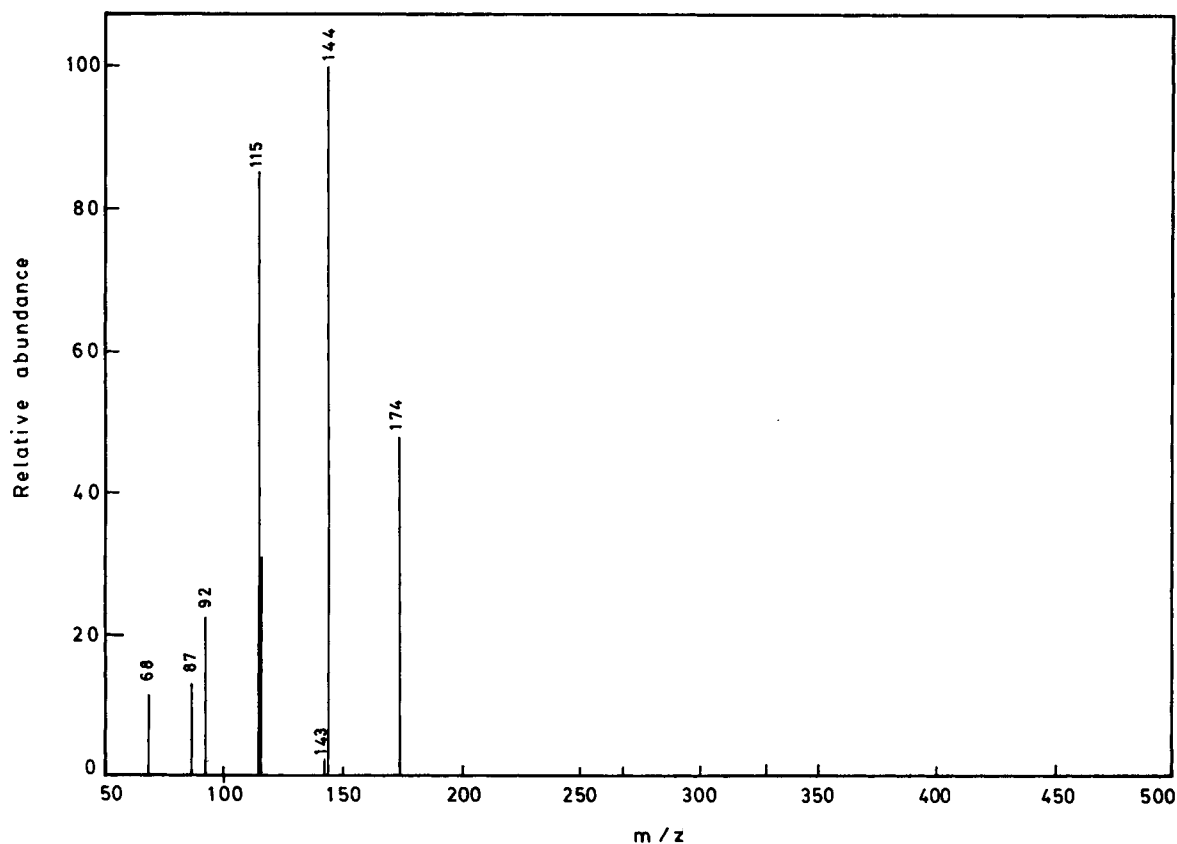
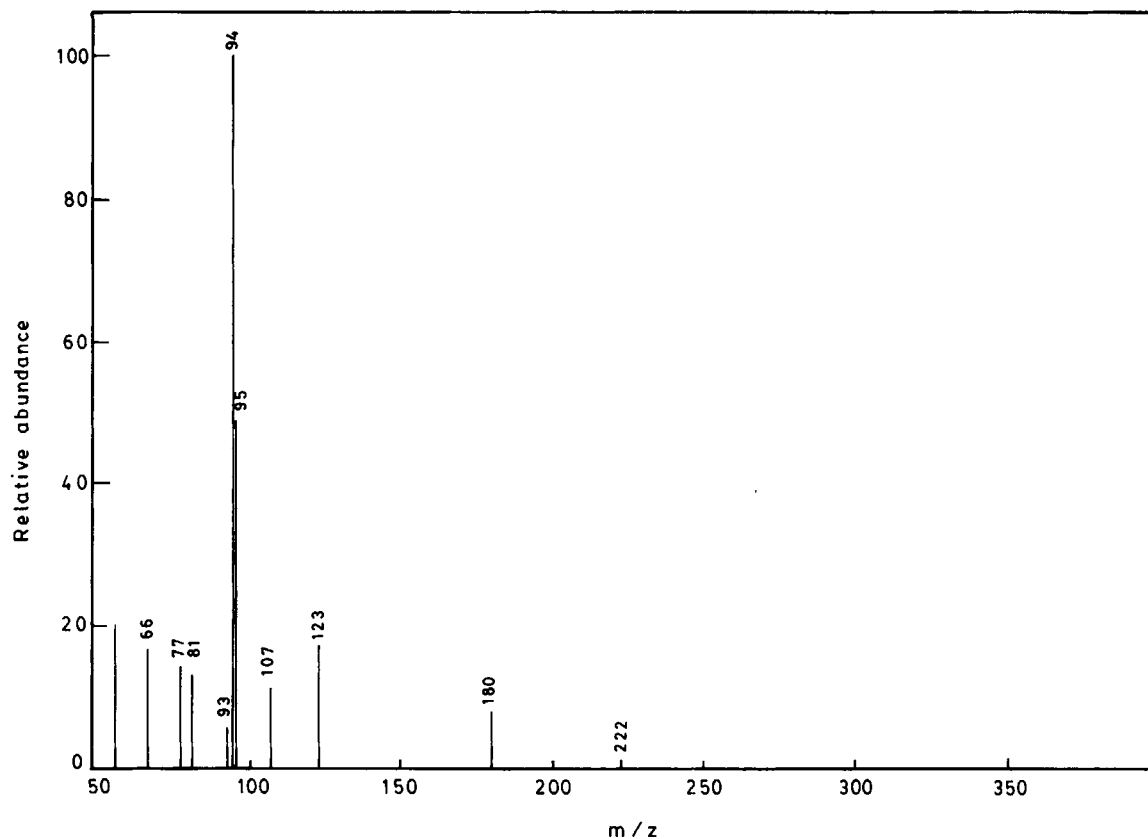**Figure 2**   Electron impact mass spectrum of TDI–2-naphthol adduct.

Figure 3   Electron impact mass spectrum of IPDI–phenol adduct.

the adducts based on TDI show lower dissociation temperatures than those based on IPDI. This is due to the aromaticity of naphthol and TDI. Since the carbonyl carbon of the urethane group has a partial positive charge, the bond between the carbon and oxygen of the blocking agent will be labilized by the reduction of the negative charge density through

resonance in the aromatic ring. Bayer[15] reported that the dissociation temperature decreased from 200 to 180°C on introducing an aryl component instead of the alkyl component in the blocking agent. He also observed that the introduction of an aryl isocyanate reduces the dissociation temperature from 180 to 120°C. Introduction of an electron-

Table VI   Temperature of Dissolution of the Adducts in Polyols

	Dissolution Temperature (°C) in				
Adduct	PPG-400	PPG-1000	PPG-2000	UB-POL-3000	HTPB
Phenol–TDI	160	Not completed at 160	Partly soluble at 160	Partly soluble at 160	Partly soluble at 160
2-Naphthol–TDI	100	136	155	160	Not completed at 160
1-Nitroso-2-naphthol–TDI	110	125	150	Not completed at 160	Not completed at 160
Phenol–IPDI	80	97	110	110	125
2-Naphthol–IPDI	83	108	115	127	143
1-Nitroso-2-naphthol–IPDI	67	90	115	123	145

PPG, poly(propylene glycol): UB-POL-3000, a glycerol-based triol.

Table VII Polyurethanes Prepared from PPG-1000 and Blocked Diisocyanates

Polymer	IR Absorption of $-CH_2-O-CH_2-$ (cm^{-1})	^{1}H-NMR Chemical Shift of $-O-CH_2-$ (ppm)	Relative Viscosity η_r
PPG–Phenol-blocked TDI	1075–1125	3.4–3.5	1.016
PPG–naphthol-blocked TDI	1075–1125	3.4–3.5	1.025
PPG–phenol-blocked IPDI	1150	3.4–3.5	1.004
PPG–naphthol-blocked IPDI	1100	3.4–3.5	1.004
PPG–nitrosonaphthol-blocked IPDI	1100	3.4–3.5	1.064

withdrawing group like the nitroso group in naphthol will further labilize the bond and result in the lowest dissociation temperature. Diazabicyclo-[2.2.2]octane (DABCO) was found to catalyze the deblocking reaction and the results are listed in Table IV.

Since urethane scission takes place on applying heat, there should be an endothermic transition in the DSC curve. Phenol-blocked TDI and IPDI show two endothermic transitions. The first transition is very sharp due to the melting of the compound. Naphthol-blocked TDI and IPDI showed a single transition. It may be concluded that the melting temperature and initial dissociation temperature are the same for those adducts.

The common fragments found in the electron impact mass spectra are listed in Table V. In all cases, the molecular ion (M^+) peak is very insignificant. As previously discussed, this is due to the scission of the $-NH-CO-O-$ linkage in the adduct. Since two molecules of the blocking agent could be generated by one molecule of the adduct dissociated, the base peak corresponds to the phenols or naphthols (Figs. 2 and 3). Accordingly, TDI ($m/z = 174$) appeared with 50% intensity. Because of the complex fragmentation usually observed in cycloalkanes, the peak for IPDI ($m/z = 222$) was very weak and no peak was observed in the case of the 1-nitroso-2-naphthol adduct. The branching in the IPDI molecule will also increase the breaking of the skeleton of the IPDI.[16]

Solubility of the blocked diisocyanates is a limiting factor for uniform curing with the hydroxy co-reactants. The solubility test for blocked TDI and IPDI were carried out separately in five different polyols. The results are summarized in Table VI. Adducts based on IPDI show better solubility than that of those based on TDI due to the presence of the aliphatic component. The authors[5] reported that the methyl substituent on the benzene ring improves the solubility of the adduct. Also, it is found that

the solubility of the adducts decreased with increasing molecular weights of the polyos. Naphthol- and nitrosonaphthal-blocked diisocynates show better solubility than that of the phenol-blocked diisocyanates. This may be due to the dissociation rather than to the solvation of the adducts by the polyos.

The spectroscopic results and the relative viscosities for the polyurethanes derived from blocked diisocynates and PPG-1000 are given in Table VII. When compared to IR and ^{1}H-NMR spectra for the blocked diisocynate adducts, the IR absorption bands for $-CH_2-O-CH_2-$ at 1075–1125 cm^{-1} and the ^{1}H-NMR signals for $-CH_2-$ protons attached to oxygen ($-O-CH_2-$) at 3.4–3.5 ppm indicated the formation of poly(ether urethanes). Polymers derived from naphthol- and nitrosonaphthol-blocked diisocynates show slightly higher relative viscosity than that of those derived from phenol-blocked diisocynates. This may be due to higher molecular weight of the polymer, because naphthol and nitrosonaphthol reduce the dissociation temperature and thus favor the polymerization reaction with the polyol.

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