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SYNTHESIS AND THERMAL DEBLOCKING OF BLOCKED DIISOCYANATE ADDUCTS

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Abstract—Different substituted phenol blocked toluene diisocyanate (TDI) adducts were synthesized. These adducts were characterized by infrared (IR), ^{1}H NMR and mass spectroscopy. The deblocking temperature of these adducts in 2-methoxyethyl ether (diglyme), the effect of different solvent media and different catalysts on the deblocking temperatures were studied by the carbon dioxide (CO_2) evolution method. The solubility of these adducts in polyols of different molecular weights was also determined, as it is an important factor for uniform curing of the adduct with the polyol, at the deblocking temperatures. © 1997 Elsevier Science Ltd

INTRODUCTION

The use of diisocyanates in forming polyurethane coatings and adhesives was always difficult because of their sensitivity before cure towards moisture from high humidity or moisture from solvents, resins, etc. This varied combination of applications has led to the blocked diisocyanate adducts, which can solve or at least reduce these problems and also eliminate toxic hazards associated with the use of some diisocyanates. The highly reactive isocyanate group can be converted to a blocked isocyanate by reacting it with a suitable blocking agent (HO–R).

These adducts are relatively inert at 30°C, they regenerate free isocyanates at a deblocking temperature, which then react with the available nucleophile (hydroxy or amine group) to form stable urethane [1]. The scheme of the reactions is given in Scheme 1.

Step 1. Blocking Reaction

$$\underset{\text{Isocyanate}}{R''NCO} \quad + \quad \underset{\text{Blocking agent}}{HO\text{-}R} \quad \xrightarrow{\text{Catalyst}} \quad \underset{\text{Adduct}}{R''NHCOOR}$$

Step 2. Deblocking Reaction

$$\text{Adduct} \quad \overset{\Delta}{\rightleftharpoons} \quad \underset{\text{Isocyanate}}{R''NCO} \quad + \quad \underset{\text{Blocking agent}}{HO\text{-}R}$$

Step 3. Urethane Formation

$$\underset{\text{Isocyanate}}{R''NCO} \quad + \quad \underset{\text{Hydroxy compound}}{HO\text{-}R'} \quad \rightarrow \quad \underset{\text{Stable Urethane}}{R''NHCOOR'}$$

Scheme 1

The blocked isocyanates are used in several applications, e.g. adhesives, coatings, elastomers and sealants [1–10]. Synthesis of various types of blocked adducts of toluene diisocyanate (TDI) are reported [8–14]. These adducts were characterized by their melting points [12–14], IR [12–16], ^{1}H NMR [13, 14, 16] and mass [14] spectroscopy. The effects of different media [12–14, 17] and different catalysts [18–21] on the deblocking temperature of the adducts are scantily reported. The effects of a few substituent groups in phenols on the deblocking temperature of blocked toluene diisocyanates are reported [12–14].

In this communication we are reporting the synthesis of a series of phenol blocked TDI adducts, using a broad range of substituted phenols, and some of these are used for the first time. These adducts are characterized by their melting points, IR, ^{1}H NMR and mass spectroscopy. D_2O exchange and Nuclear Overhauser Effect (NOE) in ^{1}H NMR are recorded to interpret the structure of the adducts better. The effects of different types of media and solvents and different types of catalysts on the deblocking temperature of these adducts are studied. The deblocking temperatures of these adducts are

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Table 1. Preparation of blocked adducts of TDI

Blocking agents	Solvent mixture	Solvent (washing)	Temperature (°C)	Duration (hr)	Melting points	
					Found (°C)	Reported (°C) (R)
Cyclohexanol ($C_6H_{11}OH$)	a + b	a	45	2.5	154.2	N
Phenol (C_6H_5OH)	a + c	a	30	1.5	148.5	140–150 (13)
o-Cresol ($CH_3C_6H_4OH$)	a + b	a	30	2.0	157.5	150–155 (13)
m-Cresol	a + b	a	35	2.0	118.3	118–120 (13)
p-Cresol	a + b	a	35	2.0	144.3	145–150 (13)
o-Methoxy phenol ($CH_3OC_6H_4OH$)	b + d	b	50	3.0	97.8	95–100 (13)
m-Methoxy phenol	a + b	b	45	3.0	123.4	N
p-Methoxy phenol	a + b	b	45	3.0	143.4	N
p-Tertiary butyl phenol [$(CH_3)_3CC_6H_4OH$]	a + b	a	35	2.5	158.2	N
o-Nitro phenol ($O_2NC_6H_4OH$)	b	b	35	2.5	119.2	118–120 (12)

a = hexane; b = toluene; c = benzene; d = chloroform; N = not reported; (R) = reference. TDI = $CH_3C_6H_3$ $(NCO)_2$.

estimated by the CO_2 evolution method [12]. The curing reaction of these adducts with polyol depends on the homogeneity of the adducts in polyols. This is believed to be a limiting factor. Keeping this idea in mind, the solubility of these adducts in polyols with varied molecular weights at 30°C was determined.

EXPERIMENTAL

The diisocyanate used in this study was a mixture of ~90% toluene 2,4-diisocyanate and ~10% toluene 2,6-diisocyanate. 30 ml of a 1.0 M solution of the blocking agent in mixed solvents (Table 1) was taken in a moisture-free three-necked flask, fitted with a condenser, a dropping funnel, and a nitrogen gas inlet. The contents were heated to 30–50°C with stirring. Catalysts such as triethyl amine (TEA), or di-*n*-butyl tin dilaurate (DBTDL) or diazabicyclo-[2,2,2]octane (DABCO), 0.01 to 0.5% on the weight of the diisocyanate, were added. The mixture was kept under stirring. 30 ml of a 0.5 M solution of TDI in mixed solvents was slowly added dropwise through a dropping funnel. The adduct so formed was washed with toluene or hexane, filtered and dried in a vacuum oven. When cyclohexanol was used as blocking agent, a mixture of catalysts DBTDL and TEA was used, and for *o*-nitrophenol adduct, DABCO was used as catalyst. For other adducts, TEA was used as catalyst. The reaction conditions are given in Table 1. The melting points of these adducts were determined using Buchi 510 melting point apparatus and are also given in Table 1.

CHARACTERIZATIONS OF BLOCKED ADDUCTS

IR spectroscopy

IR spectra of all blocked diisocyanate adducts were recorded using a Nicolet FT-IR 740 units, in KBr pellets, and their IR absorbance bands are given in Table 2. All adducts showed no–NCO absorption band at ~2280 cm^{-1}, and this indicated the complete blocking of isocyanate groups with the blocking agents. A strong stretching vibration band at 1210–1220 cm^{-1} showed the presence of >=O combined with N–H, in all the spectra.

^1H NMR spectroscopy

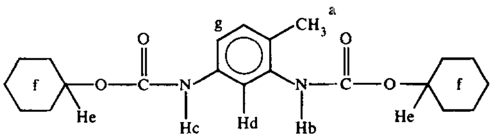
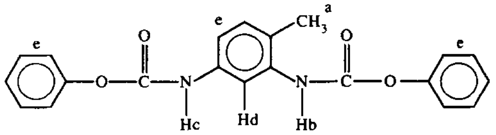
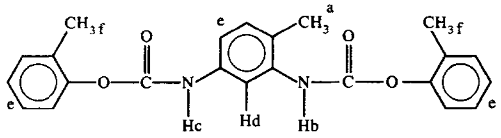
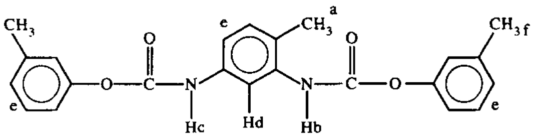
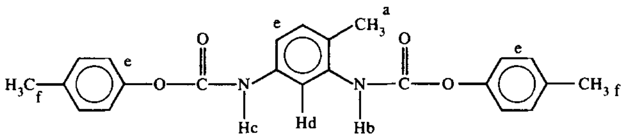
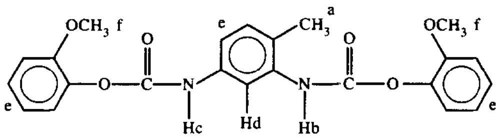
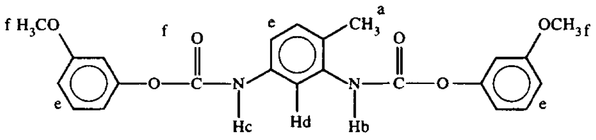
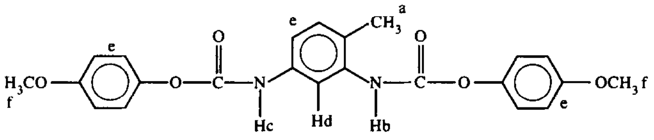
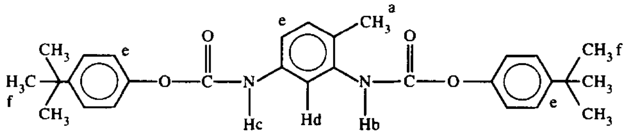
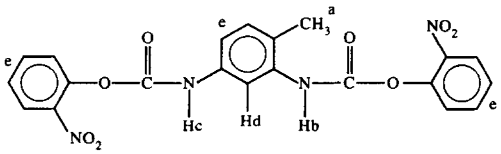
^1H NMR specta of all adducts were recorded using a Gemini 200 MHz unit. The chemical shifts of different adducts and solvents used are given in Table 3. It is observed that all these spectra show a multiplet at δ 6.85 to 7.42 ppm, which is attributed to aromatic ring protons. The singlet peak at δ 2.3 ppm is for the methyl protons of the TDI moiety. The methyl protons of the methoxy group of corresponding adducts appears as a singlet at δ 3.79–3.82 ppm. All protons of *p*-tertiary butyl protons of the *p*-tertiary butyl phenol adduct appear as a singlet at δ 1.15 ppm. All protons of the cyclohexanol part of the corresponding adduct appear as a multiplet in the range δ 1.2–1.9 and 4.7 ppm. Most of the spectra except those of methoxy and nitro phenol adducts show three clear singlets at ~δ 6.70, 6.85 and 7.80 ppm. To understand these three singlets, the spectra with D_2O exchange was taken (Fig. 1). Because of deuterium exchange with the proton of N–H, the intensity of exchanged N–H reduced (Fig. 1, inset). These experiments suggest two N–H groups, appearing at ~δ 6.70 and 6.85 ppm. The other singlet, whose intensity remains unaltered, is the aromatic ring proton (H_d), at ~δ 7.80 ppm (Fig. 1). To differentiate between these two N–H protons, H_b and H_c, the Nuclear Overhauser Effect (NOE) technique was applied during ^1H NMR scanning of phenol–TDI adduct. These experiments further

Table 2. Characteristic IR frequencies of TDI blocked adducts

Blocking agent	Urethane (vs) str. (N–H) (cm^{-1})	Carbonyl (S) >=O Str. (cm^{-1})	Carbonate (S) (–NH–COO–) (cm^{-1})
Cyclohexanol	3275	1700	1569–1584
Phenol	3275–3343	1700–1780	1538–1555
o-Cresol	3258	1703–1739	1533–1557
m-Cresol	3280–3360	1715–1765	1540–1560
p-Cresol	3309	1741–1785	1536–1576
o-Methoxy phenol	3300	1709–1733	1545
m-Methoxy phenol	3246	1709–1741	1545
p-Methoxy phenol	3309–3341	1725–1772	1537–1553
p-Tertiary butyl phenol	3322	1725–1741	1537–1553
o-Nitro phenol	3298	1709–1741	1529–1560

S = strong, VS = very strong.

Table 3

	Blocked adducts	Solvents	Chemicals shifts (δ ppm)
1.		$CDCl_3$	1.2-1.9(m,20H,f);2.15(S,3H,a) 4.7(m,2H,e);6.25(S,1H,b); 6.45(S,1H,c);6.9-7.25(m,2H,g) 7.75(S,1H,d).
2.		$CDCl_3$	2.3(S,3H,a);6.78(S,1H,b);6.85 (S,1H,e);7.15-7.4(m,12H,e);7.89 (S,1H,d).
3.		$CDCl_3$	2.3(S,3H,a);2.4(S,6H,f);6.77(S,1H,b); 6.9(S,1H,c);7.05-7.4(m,10H,e); 7.84(S,1H,d).
4.		$CDCl_3$	2.3(S,3H,a);2.4(S,6H,f);6.75(S,1H,b); 6.8(S,1H,c);6.92-7.4(m,10H,e); 7.84(S,1H,d).
5.		$CDCl_3$	2.3(S,3H,a);2.4(S,6H,f);6.68 (S,1H,b);6.8(S,1H,c);6.85-7.4 (m,10H,e),7.84(S,1H,d).
6.		$CDCl_3$	2.2(S,3H,a);3.89(S,6H,f);6.71(S,1H, b);6.9-7.4(m,11H,d,e);7.95 (S,1H,d).
7.		$CDCl_3$+ DMSO-d_6	2.3(S,3H,a);3.79(S,6H,f);6.6-7.2 (m,12H,b,c,e);7.7(S,1H,d).
8.		$CDCl_3$+ DMSO-d_6	2.3(S,3H,a);3.82(S,6H,f);6.7(S,1H,b); 6.95(S,1H,c);7.0-7.4(m,10H,e); 7.82(S,1H,d).
9.		$CDCl_3$	1.15(S,9H,f);2.3(S,3H,a); 6.65(S,1H,b);6.95(S,1H,c); 7.0-7.2 and 7.3-7.5(m,10H,e); 7.85(S,1H,d).
10.		DMSO-d_6	2.2(S,3H,a);7.1-8.1(13H,m, b,c,d,e).

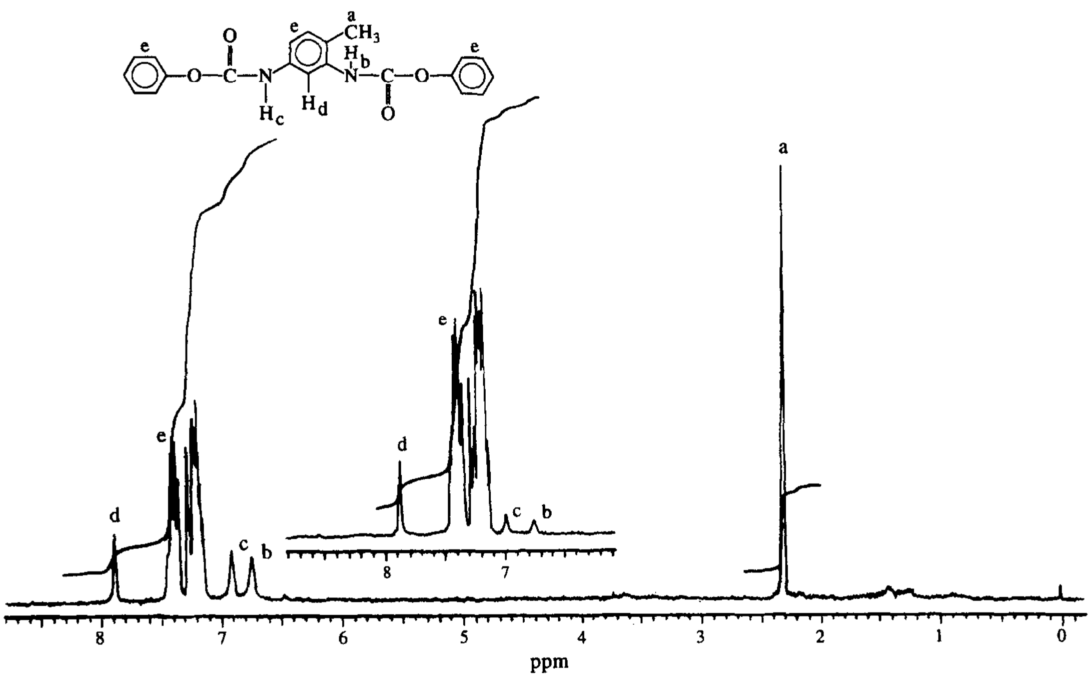


Fig. 1. ^1H NMR of phenol blocked TDI adduct. Inset D_2O exchange.

differentiated N–H protons as H_b and H_c at $\sim\delta$ 6.70 and 6.85 ppm, respectively (Fig. 1).

Mass spectroscopy

Mass spectra of all these blocked adducts of TDI were recorded using a Micromass VG 7070, U.K. The mass spectra of a few substituted phenol blocked TDI adducts were reported [14]. The mass fragmentation pattern of a series of adducts is given in Table 4. Attempts are now made to understand the fragmentation pattern, in a lucid manner, of the adducts by the chemical ionization (C.I.) technique in acetone, except for cyclohexanol-based adduct. It is seen that all adducts show a characteristic peak which is equal to the molecular mass of the adduct (MA) minus the molecular mass of the blocking agent (MB). Even when mass spectra at 20 eV energy were taken, the molecular mass ion could not be detected. This is believed to be due to scission of the one blocking agent. Cyclohexanol blocked TDI gave a molecular ion peak, which may be due to its aliphatic nature. The mass spectra of diisocyanate blocked adducts with phenol, *p*-methoxy and *p*-tertiary butyl phenol are given in Fig. 2 for ready reference.

DISSOCIATION TEMPERATURE

Minimum deblocking temperature

The deblocking temperatures of the adducts were determined according to the procedure followed by Griffin and Willwerth [12]. But, we have modified it to suit to our convenience in the following manner. 0.2 to 0.3 g of adduct was taken in 10 ml 2-methoxyethyl ether (diglyme) along with 2.5 g of molecular sieves (Linde 4 Å saturated with moisture ($\sim$24%) by weight at 30°C, in a 155 × 20 mm^2 test tube having a side arm. The side arm was connected to a glass sparge tube which was immersed into a saturated solution of barium hydroxide. Provision was also made so that the system continuously sparged with a slow stream of carbon dioxide-free

Table 4. Characteristic mass fragments of blocked TDI adducts

TDI adduct	Molecular mass (MA)	MA–MB		MA–2MB		MB		MB + 1	
		m/z	*I* (%)	*m/z*	*I* (%)	*m/z*	*I* (%)	*m/z*	*I* (%)
Cyclohexanol	374[a]	274	15.0	174	50.4	100	—	55a	100.0
Phenol	362	268	3.7	174	64.2	94	100.0	—	—
o-Cresol	391	282	100.0	174	22.3	108	—	—	—
m-Cresol[b]	391	283	100.0	174	17.9	108	—	—	—
p-Cresol[b]	391	283	58.2	174	4.4	108	—	—	—
o-Methoxy phenol[b]	422	299	6.6	174	13.4	124	90.2	125	100.0
m-Methoxy phenol[b]	422	299	8.9	174	46.0	124	64.2	125	100.0
p-Methoxy phenol[b]	422	299	6.0	174	31.3	124	100.0	125	37.3
p-Tertiary butyl phenol[b]	475	325	2.2	174	46.2	150	37.3	135a	100.0
o-Nitrophenol[b]	452	—	—	174	82.5	139	63.0	—	—

[a] Molecular mass ion detected.

[b] By chemical ionization (C.I.) technique.

MA = molecular mass of adduct, MB = molecular mass of blocking agent, *I* = intensity of the peak, (a) = peak with highest intensity.

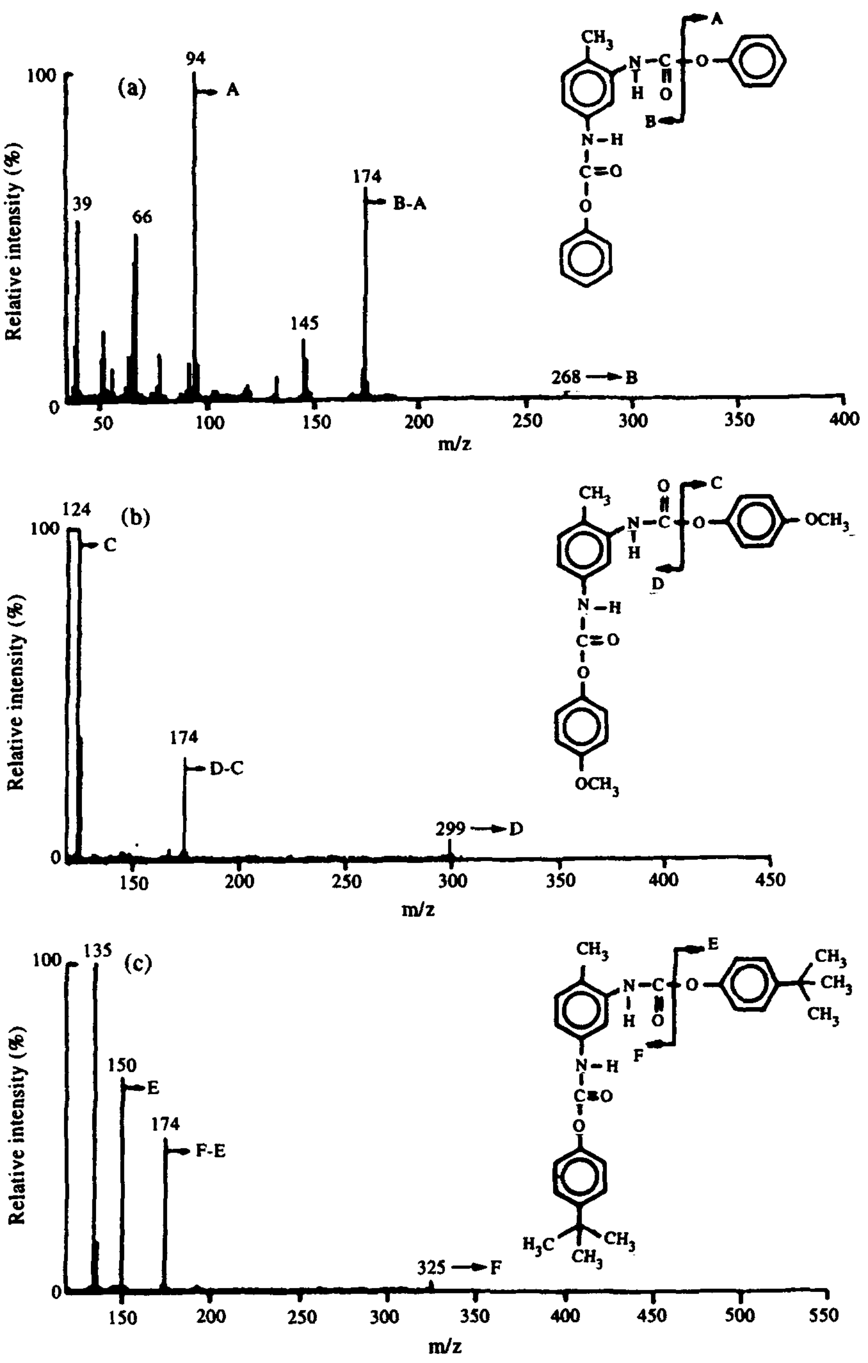


Fig. 2. Mass spectra of: (a) phenol, (b) *p*-methoxy phenol, (c) *p*-tertiary butyl phenol blocked TDI adducts.

nitrogen gas. The test tube was heated in a silicone oil bath, at a rate of 3°C/min. As the deblocking takes place the regenerated isocyanates (NCO) react with moisture available from the molecular sieves, liberating carbon dioxide. This carbon dioxide reacts with the saturated solution of barium hydroxide, to cause turbidity, due to the formation of insoluble barium bicarbonate. The minimum temperature at which detectable turbidity appears was taken as the minimum deblocking temperature, and these results are given in Table 5. It is observed that cyclohexanol based adduct did not deblock even at 120°C, which may be due to the higher bond strength in adduct formation with it. It is found that adducts having high electron releasing groups (–CH_3 and –OCH_3) deblocked at higher temperature than those unsubstituted or substituted with electron withdrawing group (–NO_2) [12, 22, 23]. Also, *o*-substituted adducts

Table 5. Deblocking temperature of adducts

Adducts	Temperature (°C)
TDI–cyclohexanol	> 120
TDI–phenol	51
TDI–*o*-cresol	53
TDI–*m*-cresol	52
TDI–*p*-cresol	57
TDI–*o*-methoxy phenol	54
TDI–*m*-methoxy phenol	53
TDI–*p*-methoxy phenol	59
TDI–*p*-tertiary butyl phenol	58
TDI–*o*-nitro phenol	36

Table 6. Effect of different media on deblocking temperature of TDI–phenol adduct

Medium	Solubility (w/w) % at 30°C	Deblocking temperature (°C)
Glycerol	0.23	85
Propylene glycol	2.00	62
Diethylene glycol	4.99	60
Polypropylene glycol-400	8.50	57
Polyethylene glycol-400	13.82	55
Diglyme	28.00	51
Dimethylsulphoxide (DMSO)	H.S.	45
Dimethylformamide (DMF)	H.S.	43
Diethyl malonate (DEM)	H.S.	42

H.S. = highly soluble.

Table 7. The effect of catalysts on deblocking temperature of TDI–phenol adducts in propylene glycol

Catalyst	Deblocking temperature (°C)
No catalyst	62.0
Triethanol amine	54.0
DABCO	52.5
DBTDL	48.0

deblocked at lower temperature than their *p*-isomers. Higher electron releasing groups ($-OCH_3$) deblocked at higher temperature than lower electron releasing groups ($-CH_3$). Adducts of *o*-nitro phenol having strong electron withdrawing group ($-NO_2$) deblocked at the lowest temperature.

Effect of different media on deblocking temperature

The effect of different media on deblocking temperature of phenol–TDI adduct was studied as per the procedure described above. The deblocking temperature and the solubility of the adduct in the media are reported in Table 6.

The deblocking temperature is believed to depend on the presence of ether oxygen and highly polar groups present in the medium. In our experiment also, it was found that the ether oxygen linkages and polar solvents facilitate the deprotonation process during deblocking of the adducts. Solubility of the adducts in the media also plays a vital role. It is also observed that the higher the solubility of the adduct, the lower the deblocking temperature (Table 6).

Catalytic effect on deblocking temperature

The effect of catalysts on the deblocking temperature of TDI–phenol adduct in propylene glycol medium was studied while maintaining all other conditions the same as described above. The catalysts used and the deblocking temperatures of the phenol–TDI adducts are given in Table 7. The amount of catalyst (0.005 g) used was maintained constant in each experiment. Organometallic catalyst DBTDL was found to be the most suitable of all the catalysts tried, for deblocking TDI–phenol adduct at the lowest temperature (48°C).

SOLUBILITY OF THE BLOCKED DIISOCYANATE ADDUCTS

The homogeneity of the diisocyanate adducts in polyols is an important limiting factor for its uniform curing. Thus attempts were made to determine the maximum percentage solubility (w/w) of adducts in different molecular weight polyols at 30°C. No qualitative solubility data of adducts in polyols are reported so far. The percentage solubility (w/w) before forming dispersion of various blocked adducts of TDI in polypropylene glycols having molecular weights in the range 400–2000 and glycerol were determined, and the results are given in Table 8. It is noticed that methyl substituted phenol blocked TDI adducts are more soluble in polyols than in unsubstituted phenols. It is found that the solubility of the adducts with methyl substituted phenols is in the following decreasing order: "*ortho* < *meta* < *para*". It is also noticed that the adducts are less soluble in *o*-methyl substituted phenol than in unsubstituted phenol. This may be due to less solvation of the *ortho* isomer due to its steric hindrance with the NHCOO– group. As the distance between urethane linkage and substituted groups increases, the solubility increases.

It is also observed that the solubility of the blocked adducts decreases with increase in the molecular weight of the polypropylene glycols. This observation is in agreement with the reported [14] qualitative results. It is understood that as the molecular weight of the polypropylene glycol increases, the chain length of this polyol also increases, but the freedom of chain movement decreases. Thus, solvation of the adduct's NHCOO– group becomes more hindered for the solvation sites of polyol (ether linkage). This causes less solvation of adducts in higher molecular weight polypropylene glycols.

CONCLUSIONS

The thermal dissociation of substituted blocked phenol–TDI adducts depends on several factors, such

Table 8. The solubility (w/w) % of different blocked TDI adducts in polypropylene glycol of different molecular weights

Adducts	PPG-400	PPG-725	PPG-1200	PPG-2000	Glycerol
TDI–phenol	8.5	5.4	4.5	2.6	0.23
TDI–*o*-cresol	3.6	2.6	1.6	1.2	0.22
TDI–*m*-cresol	10.7	7.2	5.2	3.2	0.27
TDI–*p*-cresol	13.5	9.5	6.7	3.9	0.27
TDI–*p*-tertiary butyl phenol	8.5	5.5	4.4	2.5	0.26

as: (a) the type of catalyst; (b) the type of medium; (c) the substituent groups in the phenol blocking agent; and (d) the solubility of blocked diisocyanate adducts in the medium. It is observed that an organometallic catalyst DBTDL is better than organic catalysts such as triethanolamine and DABCO in deblocking diisocyanate blocked adducts at much lower temperatures. The media having more ether linkages and those with high polarity facilitate deblocking of the adducts at lower temperatures. This observation is further reinforced by their high capacity to solubilise the blocked diisocyanate adducts. *Ortho* substituted phenols are found to be better blocking agents than the *para* substituted phenols on the basis of deblocking temperature. The cyclohexanol is not a suitable blocking agent as its deblocking temperature is pretty high.

The solubility of the blocked diisocyanate in various polyols is very important for the uniform curing of the deblocked isocyanate with them. Therefore, the solubility of these adducts in various polyols was determined for this purpose.

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