The thermal dissociation of phenol-blocked toluene diisocyanate crosslinkers

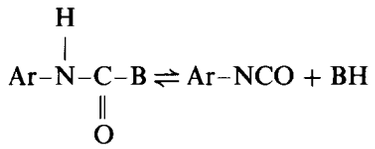
H. Kothandaraman* and A. Sultan Nasar
Department of Polymer Science, University of Madras, Guindy Campus, Madras 600 025, India
(Received 7 October 1991; revised 24 March 1992)

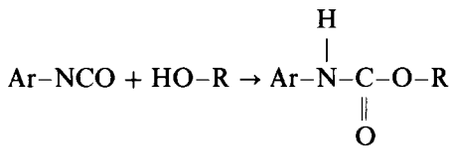
Several toluene diisocyanates blocked with various substituted phenols were prepared. They were characterized by elemental analysis, infra-red and ^1H nuclear magnetic resonance spectroscopy. The deblocking temperatures were determined by use of infra-red spectroscopy and by carbon dioxide evolution methods. The thermal stability of the blocked isocyanate was less for the *ortho*-substituted phenols than for the *para* isomers. Dissociation temperatures were also reduced by electron-withdrawing groups. The dissolution temperatures of the adducts were determined in propylene glycol, poly(ethylene glycol) 400 and hydroxyl-terminated poly(butadiene).

(Keywords: phenols; toluene diisocyanate; blocked crosslinkers; thermal dissociation; solubility behaviour)

INTRODUCTION

A blocked isocyanate is an adduct containing a comparatively weak bond formed by the reaction between an isocyanate and a compound containing an active hydrogen atom. At elevated temperatures the reaction tends to proceed in such a way as to regenerate the isocyanate and the blocking agent[1–3]. The regenerated isocyanate can react with a substrate containing the hydroxyl functional group to form thermally stable bonds. The overall reaction can be seen as:





where BH is the blocking agent. Phenol is the most popular blocking agent[4], particularly for aromatic isocyanates, since the urethane linkage formed from the aromatic reactants is unstable at elevated temperatures.

Blocked polyisocyanates have a bright future in the coatings field[5]. They are particularly suitable building blocks for light-stable two-component urethane coatings[6] and single-package blocked adduct urethane coatings (ASTM type-3)[4].

Wicks[7,8] has reviewed the blocked isocyanates, in which a number of blocking agents were described. A substantial number of patents cover the use of phenol-blocked isocyanates in various applications[9–11].

Several investigators[12–15] have studied the thermal dissociation of aryl *N*-arylurethanes. One-component urethane coatings with blocked isocyanate groups, which on heating regenerate free isocyanate groups and cure fast, have led to the acceptance of these coatings as wire enamels in the electrical industry. Here we report the preparation and dissociation temperatures for some phenol-blocked toluene diisocyanates, which may be useful as replacements for toluene diisocyanate used as a crosslinker in many thermally curable systems.

EXPERIMENTAL

Materials

The diisocyanate used for the preparation of adducts was a mixture of isomers containing 80% 2,4-toluene diisocyanate and 20% 2,6-toluene diisocyanate (TDI) obtained from Riedel-AG. Phenol, *o*-cresol, *m*-cresol (Merck), *p*-cresol, *o*-chlorophenol (Merck), propylene glycol and triethylamine were distilled before use. Guaiacol (Fluka), 2,6-dimethylphenol (Fluka), *p*-chlorophenol (Fluka), poly(ethylene glycol) 400 (PEG) and 1,4-diazabicyclo[2.2.2]octane (DABCO) (Merck) were used as received. All solvents were purified by standard procedures[16]. Diethylene glycol diethyl ether (Fluka) was purified by drying with potassium hydroxide, gently refluxed with sodium metal and then distilled under reduced pressure. Hydroxyl-terminated poly(butadiene) (HTPB) was obtained from the Vikram Sarabhai Space Centre.

Preparation of blocked diisocyanates

In a typical synthesis, 50 cm^3 of a 1.6 M solution of the blocking agent was taken in a two-necked flask fitted with a magnetic stirrer. Triethylamine (0.1 cm^3) was

*To whom correspondence should be addressed

0032-3861/93/030610-06
© 1993 Butterworth-Heinemann Ltd.

added in all cases except for the reaction with 2,6-dimethylphenol where 0.12 g of DABCO was added as the catalyst. Then 50 cm^3 of a 0.8 M solution of toluene diisocyanate 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 toluene diisocyanate solution was added drop by drop over 45 min. In some cases, at the end of the reaction, the adduct separated as a white precipitate. In other cases the final mass was a fully or a partially homogeneous liquid. In such cases a non-solvent was added to precipitate the adduct. Other details are summarized in *Table 1*.

Characterization methods of the blocked diisocyanates

Infra-red spectra for all the adducts were recorded by the potassium bromide pellet method at room temperature in a Perkin–Elmer model 781 spectrophotometer. ^1H n.m.r. spectra were recorded on a varian EM-390, 90 MHz spectrometer. Chemical shifts are reported relative to the methyl group of toluene. Elemental analysis (C, H, N) was determined by the Analytical and Spectroscopy Division, Vikram Sarabhai Space Centre, Trivandrum. All samples were reprecipitated in toluene and dried before they were analysed. The melting point for all compounds was determined in a Toshniwal melting-point apparatus.

Assessment of minimum deblocking temperatures

The experimental procedure adopted for the determination of the minimum deblocking temperature was based on the CO_2 evolution method of Griffin and Willwerth[12]. Specially fabricated glassware was used. The deblocking reaction was carried out in two different glycols. The results are shown later in *Table 5*.

Assessment of the minimum and the 50% deblocking temperature of blocked diisocyanate

The deblocking reaction was carried out in a thermostated silicone oil bath, which was maintained to an accuracy of ± 0.5°C. The reaction tube containing 5 cm^3 of diethylene glycol diethyl ether was placed in the oil bath for 20 min to attain constant temperature. Then the weighed quantity (equivalent to 0.05 M) of the adduct was added and closed immediately. After 5 min the tube was shaken. After 10 min, the tube was taken out and cooled suddenly. The i.r. cell was filled with this solution and the spectrum was scanned exactly 10 min later, over the range of 4000–1500 cm^{-1}. A Perkin–Elmer model 700 instrument was used. The temperature at which detectable absorption appeared at 2270 cm^{-1} (correspondingly, the intensity of urethane carbonyl group decreased) was taken as the minimum deblocking temperature (see *Figure 3*).

Below the dissociation temperature, the spectrum shows an absorption peak for the C=O group in the urethane at 1700–1760 cm^{-1} and does not show any band for the isocyanate functionality. A number of spectra were recorded over a wide temperature range. The temperature at which the spectrum lost 50% of the absorption intensity of urethane C=O was taken as the 50% deblocking temperature.

Solubility tests

This test[12] gives the lowest temperature at which blocked diisocyanate completely dissolves in the glycols. A 0.1 M equivalent dispersion of each adduct in any one of the glycols listed in *Table 6* was heated on a temperature-controlled silicone oil bath at a rate of heating of approximately 3°C min^{-1}. Heating was terminated at 160°C. The temperature was recorded at which a clear solution was obtained.

RESULTS AND DISCUSSION

Characterization of the blocked diisocyanates

A typical infra-red spectrum for the phenol-blocked toluene diisocyanate is given as *Figure 1*. All the i.r. spectra are identical and do not show absorption in the

Table 1 Preparation of blocked toluene diisocyanates

Blocking agent	Solvent	Non-solvent	Reaction time	Temperature (°C)	Yield (%)	Elemental analysis (%)			
							C	H	N
Phenol	Benzene	None	6 h + overnight + ½ h at 30°C	40–50	80	Found	69.2	5.1	7.9
						Calc.	69.6	5.0	7.73
o-Cresol	Toluene	Petroleum ether, 60–80°C	8½ h + overnight + ½ h at 30°C	50–55	85	Found	70.6	5.6	7.7
						Calc.	70.75	5.6	7.17
m-Cresol	Benzene	Petroleum ether, 60–80°C	6½ h + overnight + ½ h at 30°C	50–60	82	Found	70.7	5.6	7.3
						Calc.	70.75	5.6	7.17
p-Cresol	Benzene	Petroleum ether, 60–80°C	5 h + overnight + ½ h at 30°C	50–60	77	Found	70.7	5.6	7.3
						Calc.	70.75	5.6	7.17
Guaiacol	Chloroform	Petroleum ether, 60–80°C	6½ h + overnight + ½ h at 30°C	40–45	92	Found	64.9	5.3	6.8
						Calc.	65.39	5.25	6.63
2,6-Dimethyl-phenol	Benzene	None	7 h + overnight + ½ h at 30°C	50–60	88	Found	71.4	6.3	6.8
						Calc.	71.74	6.26	6.69
o-Chlorophenol	Chloroform	Petroleum ether, 60–80°C, for maximum yield	7 h + overnight + ½ h	30	71	Found	58.2	3.8	7.1
						Calc.	58.48	3.74	6.5
p-Chlorophenol	Chloroform	Petroleum ether, 60–80°C, for maximum yield	7 h + overnight + ½ h	30	78	Found	58.2	3.5	6.6
						Calc.	58.48	3.74	6.5

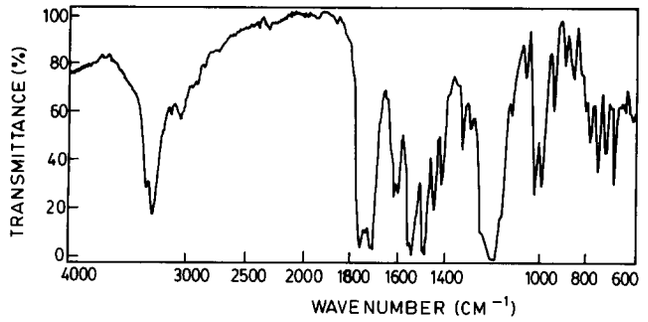


Figure 1 I.r. spectrum of the toluene diisocyanate–phenol adduct

2270 cm^{-1} range. This indicates that both the –NCO groups of the original toluene diisocyanate are completely blocked with phenol. In the 1700–1775 cm^{-1} range, absorption by carbonyl groups shows two bands for all compounds, which provides additional evidence. The stretching vibration of the C=O group of the urethane combined with N–H absorbs strongly at 1210–1220 cm^{-1} (ref. 17). The absorption frequencies for N–H stretching, urethane carbamate[15] and C=O stretching vibrations are given in *Table 2*.

Recently, Lonikar *et al.*[15] reported ^1H n.m.r. spectra for some masked isocyanates. However, data for phenol-blocked toluene diisocyanates have not been reported in the literature. *Figure 2* gives the ^1H n.m.r. spectra for toluene diisocyanate blocked with a series of substituted phenols. All the spectra show multiple peaks at 6.5–7.2 ppm, which are attributed to aromatic protons. Similarly, all spectra show a doublet at 7.4–7.6 ppm, which is due to the urethane N–H protons. But the peak area is only half of the expected value. This is not surprising because the single N–H proton may be unobservable[18]. The singlet at 2.2 ppm is ascribed to the methyl protons in the isocyanate moiety. The methoxy protons appear as a singlet at 3.6–3.7 ppm. The solvents and the chemical shifts for the individual compounds are summarized in *Table 3*.

The elemental analyses data for the blocked isocyanates are given in *Table 1*. The results agree well with the calculated values, indicating that the compounds are pure.

Table 4 shows the melting points for the adducts. The data for *m*-cresol, guaiacol and *p*-chlorophenol-toluene diisocyanate adducts coincide with the reported values[12]. Differential scanning calorimetric results[19] also confirm the data.

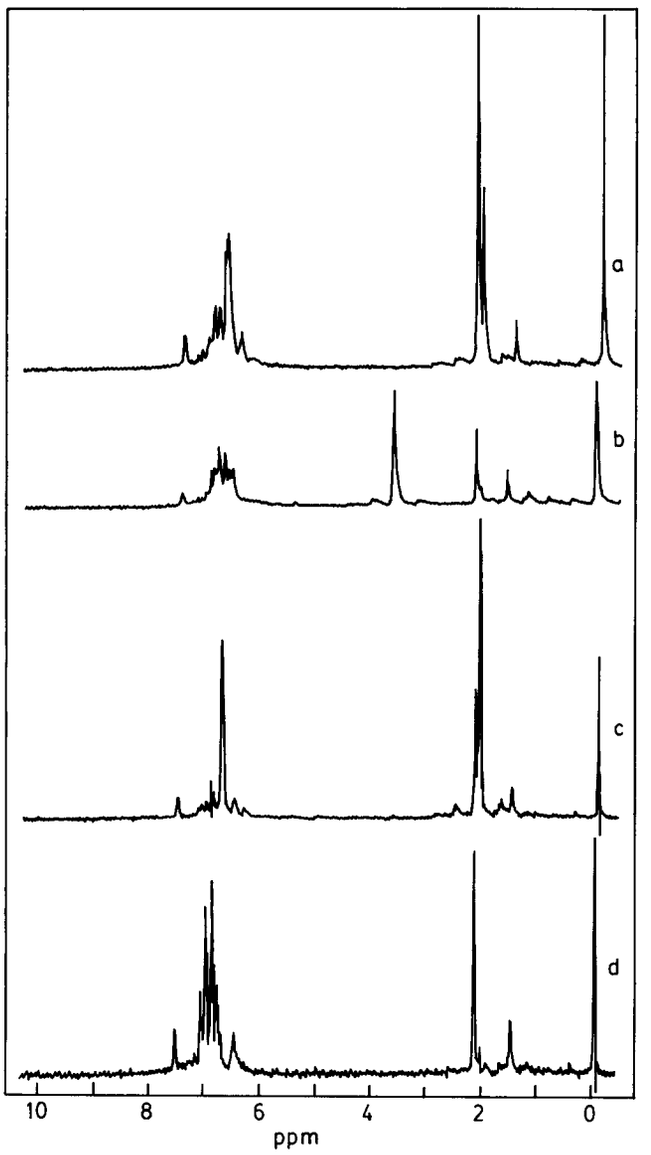


Figure 2 ^1H n.m.r. spectra of blocked toluene diisocyanates: (a) No. 3, (b) No. 5, (c) No. 6, (d) No. 8 (solvent, $CDCl_3$)

Dissociation temperature – effect of substituents on the blocking agent

In the blocked isocyanates, the bond between the carbonyl carbon atom and the blocking agent is thermally labile. Substituents on the blocking agent will affect the stability of this bond. The urethane carbonyl

Table 2 I.r. frequencies for blocked isocyanates

Adduct	N–H stretching[VS] (cm^{-1})	C=O stetching[S] (cm^{-1})	Urethane carbamate[S] (cm^{-1})[15]
Phenol–TDI	3280–3350	1700–1760	1540–1560
o-Cresol–TDI	3260	1710–1740	1540–1560
m-Cresol–TDI	3280–3360	1715–1765	1540–1560
p-Cresol–TDI	3300	1710–1770	1545–1570
Guaiacol–TDI	3280–3300	1715–1775	1545–1565
2,6-Dimethylphenol–TDI	3260	1710–1740	1540–1560
o-Chlorophenol–TDI	3260	1725–1750	1545–1565
p-Chlorophenol–TDI	3260–3280	1725–1755	1550–1560

S, strong; VS, very strong

Table 3 ^{1}H n.m.r. chemical shifts of phenol-blocked toluene diisocyanates

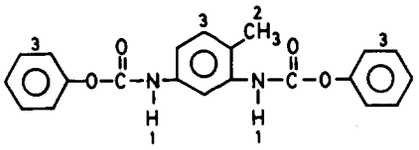
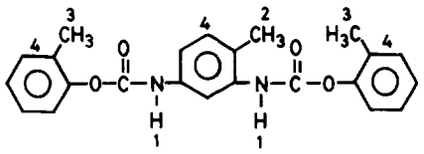
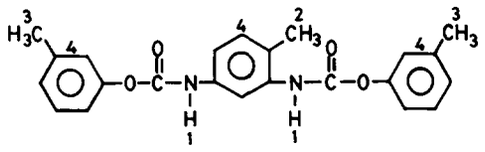
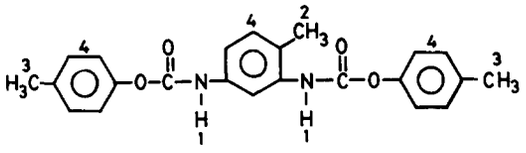
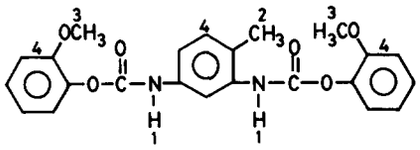
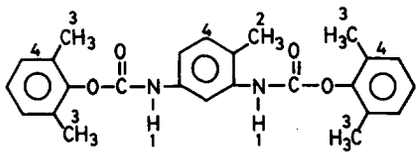
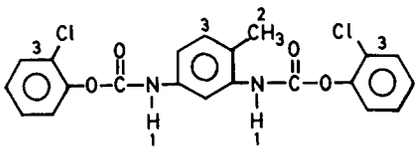
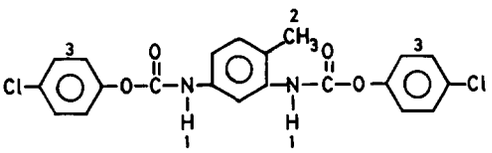
Blocked isocyanate		Solvent and chemical shift (ppm)
1		DMSO-d_6 2.1–2.2 (s, 3H, 2); 6.7–7.2 (m, 14H, 3); 7.4 (d, 2H, 1)
2		$CDCl_3$ 2.1–2.2 (m, 9H, 2 and 3); 6.6–7.0 (m, 11H, 4); 7.5–7.6 (d, 2H, 1)
3		$CDCl_3$ 2.1 (s, 3H, 2); 2.2 (s, 6H, 3); 6.5–7.2 (m, 11H, 4); 7.4–7.5 (d, 2H, 1)
4		$CDCl_3$ 2.1 (s, 3H, 2); 2.2 (s, 6H, 3); 6.6–7.0 (m, 11H, 4); 7.4 (d, 2H, 1)
5		$CDCl_3$ 2.2 (s, 3H, 2); 3.6–3.7 (s, 6H, 3); 6.5–7.0 (m, 11H, 4); 7.4–7.5 (d, 2H, 1)
6		$CDCl_3$ 2–2.2 (m, 15H, 2 and 3); 6.6–7.0 (m, 9H, 4); 7.5 (d, 2H, 1)
7		$CDCl_3$ 2.2 (s, 3H, 2); 6.7–7.2 (m, 11H, 3); 7.5 (d, 2H, 1)
8		$CDCl_3$ 2.2 (s, 3H, 2); 6.7–7.1 (m, 11H, 3); 7.5 (d, 2H, 1)

Table 4 Melting points for phenol-blocked toluene diisocyanates

Adduct	M.p. (°C)	Lit. m.p. (°C)[12]
Phenol–TDI	145–150	–
o-Cresol–TDI	150–155	–
m-Cresol–TDI	118–120	115–116
p-Cresol–TDI	145–150	–
Guaiacol–TDI	95–100	103–105
2,6-Dimethylphenol–TDI	155–160	–
o-Chlorophenol–TDI	150–155	–
p-Chlorophenol–TDI	133–136	125–127

carbon has a partial positive charge. Electron-donating substituents will increase the negative charge density at the blocking group. The greater the charge difference, the greater will be the strength of the bond[12]. Conversely, electron-withdrawing substituents will reduce the negative charge density and make the bond more labile. This is reflected in the results obtained. The minimum dissociation temperature for the eight adducts was determined by the carbon dioxide evolution and infra-red methods (*Table 5*). In the first method, two different dihydroxy compounds are used. Poly(ethylene glycol) 400

Table 5 Dissociation temperatures of phenol-blocked toluene diisocyanates

Blocking agent	Dissociation temperature (°C)			
	Carbon dioxide test method		Infra-red method	
	In poly(ethylene glycol) 400	In propylene glycol	Initial dissociation	50% dissociation
Phenol	71	78	110	130
o-Cresol	88	87	120	150
m-Cresol	78	85	120	140
p-Cresol	88	88	165	>180
Guaiacol	85	83	70	130
2,6-Dimethylphenol	92	93	125	155
o-Chlorophenol	68	66	75	95
p-Chlorophenol	70	69	80	–

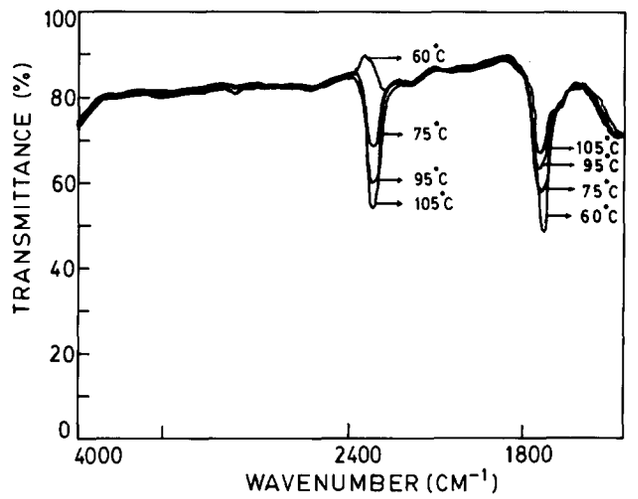


Figure 3 I.r. spectra of the TDI–*o*-chlorophenol adduct at different temperatures

has much practical utility. It has already been studied with the adducts of ethyl methyl ketoxime, ε-caprolactam and benzotriazole blocked 4,4′-diphenylmethane diisocyanate (DMDI) in coatings[20].

The deblocking temperatures obtained with the carbon dioxide evolution method were lower than those obtained from the i.r. spectral studies, except in the cases of the guaiacol and *o*-chlorophenol blocked adducts (*Figure 3*). This may be due to the solvent-assisted deprotonation of the adduct. Anagnostou and Jaul[20] have reported that Carbowax-400 (poly(ethylene glycol) 400 (PEG)) lowers the deblocking temperature from 120°C in the absence of PEG to 107°C in PEG for the ethyl methyl ketoxime–DMDI adduct. Sal'nikova[21] and his coworkers reported that the dissociation of aryl *N*-arylurethanes in hexanol proceeds at a reasonable rate at a lower temperature than when the phenylurethane alone is taken. The dissociation temperatures determined in the poly(ethylene glycol) and propylene glycol are approximately close. This may be due to the same nucleophilicity of the glycols. In poly(ethylene glycol) the number of available hydroxyl groups is less, but it has the additional ether oxygen atoms.

In both methods, the electronic effect on the deblocking reaction is clearly established. The electron-releasing substituents such as the methyl group retard the dissociation whereas the electron-withdrawing substituents such as the chlorine atom favour the reaction.

The third column of *Table 5* shows the initial dissociation temperature of the adducts determined by the infra-red method. Phenols with *ortho* substituents dissociate at lower temperatures than do those with *para* substituents. This is attributed to steric effects. Mukaiyama and Iwanami[22] have reported that the *ortho* substituents accelerate the dissociation regardless of their nature, and facilitate the deprotonation of the urethane linkage. In contrast with the methyl group at the *ortho* position, the *m*-cresol–toluene diisocyanate adduct dissociates to the same extent as does the *o*-cresol–toluene diisocyanate adduct at the same temperature. This may be due to resonance effects, i.e. the methyl group at the *meta* position does not increase the negative charge density on the phenolic oxygen atom as does the methyl group at the *ortho* and *para* positions. The dissociation temperature of the 2,6-dimethylphenol–toluene diisocyanate adduct is higher than that of the *o*-cresol–toluene diisocyanate adduct. It can be concluded that the electronic effect predominates over the steric effect. The adduct with *o*-chlorophenol starts to dissociate at a low temperature due to the electronic effect on the deprotonation of the urethane –N–H group. The methoxy group at the *ortho* position reduces the decomposition temperature, indicating the predominance of the steric effect over the electronic effect. Griffin and Willwerth[12] observed the same trend with the guaiacol–TDI adduct and the *m*-cresol–TDI adduct.

The fourth column of *Table 5* shows the temperature at which half of the isocyanate is regenerated. These data acquire greater importance owing to the different reactivity of the isocyanate group in toluene diisocyanate[22,24]. This confirms that both functionalities may be regenerated at that temperature. The results show some discrepancy. For example, the adducts with phenol and guaiacol start to dissociate at 110°C and 70°C respectively. However, the 50% conversion temperature is the same for both the adducts.

Solubility of the adducts in glycols

For polyurethane heat-cured systems, the degree of crosslinking and uniformity between regenerated isocyanate and hydroxy co-reactant depends upon the solubility of the blocked isocyanate in the hydroxy compound. The solubility test for phenol-blocked toluene diisocyanate is carried out separately in three different glycols. Propylene glycol is a simple hydroxyl compound

Table 6 Temperature of dissolution of the adducts in glycols

Adduct	In propylene glycol (°C)	In poly(ethylene glycol) 400 (°C)	In hydroxyl-terminated poly(butadiene) (°C)
Phenol–TDI	160	56	Part. soluble at 160
o-Cresol–TDI	76	50	Not completed at 160
m-Cresol–TDI	72	57	132
p-Cresol–TDI	79	62	150
Guaiacol–TDI	67	67	150
2,6-Dimethylphenol–TDI	135	118	Not completed at 160
o-Chlorophenol–TDI	86	58	Not completed at 160
p-Chlorophenol–TDI	109	78	Part. soluble at 160

and poly(ethylene glycol) 400 is a low-molecular-weight hydroxyl-terminated polyether. Hydroxyl-terminated poly(butadiene) is a low-molecular-weight polymer with a long hydrocarbon chain. The results are summarized in *Table 6*. Methyl and chloro substituents on the blocking agent improve the solubility of the adduct in the propylene glycol. All adducts give complete solution in poly(ethylene glycol) 400 at relatively lower temperatures than does the propylene glycol. This is due to the presence of the ether linkages. The temperatures of dissolution of the adducts were uniformly low in poly(ethylene glycol) 400 with the exception of the adduct with 2,6-dimethylphenol. All adducts show poor solubility with the hydroxyl-terminated poly(butadiene). This is attributed to the long-chain hydrocarbon in the polymer.

CONCLUSIONS

A number of phenol-blocked toluene diisocyanates were prepared with good yields. The results reveal that the deblocking temperature is reduced by electron-withdrawing substituents and increased by electron-donating substituents. One interesting observation concerns the low deblocking temperature of guaiacol and *o*-chlorophenol based adducts. There may be many practical applications for hydroxyl-terminated polyethers when used as a co-reactant in relatively low-temperature curing systems.

ACKNOWLEDGEMENT

ASN thanks the Indian Space Research Organization for financial support.

REFERENCES

1 Mukaiyama, J. and Hoshino, Y. *J. Am. Chem. Soc.* 1956, **78**, 1946
2 Bayer, O. *Angew. Chem.* 1947, **59**, 257
3 Petersen, S. *Liebigs Ann. Chem.* 1949, **562**, 205
4 Damusis, A. and Frisch, K. C. 'Treatise on Coatings' (Eds R. R. Myers and J. S. Long), Marcel Dekker, New York, 1967, Vol. 1, Part 1, pp. 435–516
5 Potter, T. A., Rosthauser, J. W. and Schmeler, H. G. 'Blocked isocyanate in coatings', presented at the Eleventh International Conference in Organic Coating Science and Technology, July 1985, Athens
6 Rosthauser, J. W. and Williams, J. L. *Prep. Polym. Mater. Sci. Eng.* 1984, **50**, 344
7 Wicks Jr, Z. W. *Prog. Org. Coat.* 1975, **3**, 73
8 Wicks Jr, Z. W. *Prog. Org. Coat.* 1981, **9**, 3
9 Henry, R. A. and Martin, E. C. *Chem. Abstr.* 1979, **91**, 59635t
10 Mitsubishi Electric Corp., Japan. Pat. 80 139 421; *Chem. Abstr.* 1981, **94**, 67020r
11 Ivanov, M. G., Golov, V. G., Vodopyanov, V. G., Rodinov, Yu. A. and Moler, I. I. *Chem. Abstr.* 1984, **100**, 52172k
12 Griffin, G. R. and Willwerth, L. J. *Ind. Eng. Chem. Prod. Res. Dev.* 1962, **1**, 265
13 Lateef, A. B., Reeder, J. A. and Rand, L. *J. Org. Chem.* 1971, **36**, 2295
14 Wagener, K. B. and Murlo, M. A. *Polym. Prepr.* 1989, **30**, 287
15 Lonikar, S. V., Rangsimuntakaul, N., Gilbert, R. D. and Fornes, R. E. *J. Polym. Sci. (A) Polym. Chem.* 1990, **28**, 759
16 Vogel, V. I. 'Practical Organic Chemistry', ELBS, London, 1971
17 Hartz, R. E. *J. Appl. Polym. Sci.* 1975, **19**, 795
18 Kemp, W. 'NMR in Chemistry', Macmillan, London, 1986, p. 214
19 Kothandaraman, H. and Sultan Nasar, A. unpublished results
20 Anagnostou, T. and Jaul, E. *J. Coat. Tech.* 1981, **53**, No. 673, 35
21 Sal'nikova, Yu. C. A., Schmidt, A. and Voladorskaya, Yu. I. *Dokl. Akad. Nauk SSSR* 1968, **181**, 669
22 Mukaiyama, T. and Iwanami, M. *J. Am. Chem. Soc.* 1957, **79**, 73
23 Burkus, J. and Eckert, C. F. *J. Am. Chem. Soc.* 1958, **80**, 5948
24 Britain, J. W. and Gemeinharut, P. G. *J. Appl. Polym. Sci.* 1960, **4**, 207