Synthesis, deblocking and cure reaction studies of secondary alcohol-blocked isocyanates

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Abstract
A series of 1,3-dichloro-2-propanol-blocked diisocyanates, based on diisocyanates including 4,4'-methylene di(phenyl isocyanate), toluene-2,4-diisocyanate, isophorone diisocyanate and 1,6-diisocyanatohexane, were prepared and characterized thoroughly by Fourier transform infrared, 1H-NMR, 13C-NMR spectroscopic methods and elemental analysis (CHN). The blocking reaction of 1,3-dichloro 2-propanol with aromatic diisocyanates occurs faster than with the aliphatic isocyanates. The deblocking temperature of blocked isocyanates was determined by thermogravimetric analysis, differential scanning calorimetry and the CO2 evaluation method. Cure reactions of blocked isocyanates with hydroxyl-terminated polybutadiene were also followed to establish the structure–property relationship of the 1,3-dichloro-2-propanol-blocked isocyanates. The deblocking studies reveal that the aromatic isocyanates undergo deblocking more easily than aliphatic isocyanates. The dissolution behavior of 1,3-dichloro-2-propanol-blocked isocyanates in Terathane-2000, polypropylene glycol-2000, polycaprolactone diol-2000 and hydroxyl-terminated polybutadiene-2500 was also studied, and it was found that all adducts are soluble in these polyols.

Keywords
Synthesis, secondary alcohol-blocked isocyanates, deblocking temperature, cure-reaction with HTPB

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. The regenerated isocyanate can react with a co-reactant that contains hydroxyl functional groups to form urethane with more thermally stable bonds. The overall reaction in a typical polyurethane heat-curable system is

where BH is the blocking agent.

The deblocking temperature of the blocked isocyanates is an important factor, and it should be close to 120 °C. For example, a blocked isocyanate that can be deblocked at temperatures below 160 °C is suitable for heat-curable systems such as organic powder coatings. Furthermore, there are certain applications for which it is necessary to use a blocking agent that should be cleaved off at temperatures less than 100 °C (e.g. solid rocket propellant, which contains explosive material).1

The deblocking temperature of blocked isocyanates depends on the structures of the blocking agents and structures of the isocyanates.2 Several compounds, namely, phenols, oximes, amides, imides, imidazoles, amidines and related compounds, pyrazoles, 1,2,4-triazoles, hydroxamic acid esters, and active methylene compounds, have been reported as blocking agents.3–11 Several alcohols have also been reported as blocking agents;12–14 however, there is no report on halogenated secondary alcohol as a blocking agent. Thus, it was decided to synthesis a series of
substituted 1,3-dichloro-2-propanol blocked isocyanates and to study their deblocking reaction in detail.

**Experimental**

**Materials**

The 1,3-dichloro 2-propanol (Fluka), 4,4′-methylenedi(phe- ny1 isocyanate) (MDI) (Lancaster), toluene 2,4-diisocyanate (TDI) (Aldrich), 1,6-diisocyanatothexane (HMDI) (Fluka), isophorone diisocyanate (IPDI) (Aldrich), poly (tetrahydrofuran) Terathane, $M_n = 2000$ (Aldrich), poly (propylene glycol) (PPG, $M_n = 3300$) (Aldrich), poly (ε-caprolactone diol) (PCL, $M_n = 2000$) (Aldrich), and hydroxyl-terminated polybutadiene (HTPB, $M_n = 2500$) (Aldrich) were used as received. Toluene (Merk), methanol (Merk) and dimethyl formamide (DMF; Merck) were purified according to standard procedures.

**Measurements**

Fourier transform infrared (FTIR) spectra for the monomers and polymers were recorded on a Perkin-Elmer 2000 FTIR spectrophotometer by the KBr pellet method. $^1$H-NMR and $^{13}$C-NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. Differential scanning calorimetric (DSC) analyses were performed on a Perkin-Elmer DSC7 series in a nitrogen atmosphere. A heating rate of $10 \, ^\circ \text{C} \, \text{min}^{-1}$ was applied. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer TGA7 series. The measurements were performed in a nitrogen atmosphere with a heating rate of $20 \, ^\circ \text{C} \, \text{min}^{-1}$.

**General procedure for the synthesis of 1,3-dichloro 2-propanol-blocked diisocyanate adducts (1–4)**: A solution of 0.0325 eq of 1,3-dichloro-2-propanol dissolved in 20 mL of dry DMF was placed in a 250 mL three-necked, round-bottomed flask fitted with a magnetic stirrer and a nitrogen inlet. A solution of 0.0325 eq of diisocyanate in 20 mL of dry DMF was placed in an addition funnel and fitted with the flask. The diisocyanate solution was added drop wise to the 1,3-dichloro 2-propanol solution over a period of 30 min with stirring under a nitrogen atmosphere. The reaction was monitored using FTIR, and the procedure was stopped after complete disappearance of the absorption of the –NCO group. The blocked isocyanate adduct was precipitated by the addition of the reaction mixture to 200 mL of methanol, dried in air and recrystallized from toluene.

$1,3$-dichloro 2-propanol-MDI adduct (1): FTIR (KBr, cm$^{-1}$) 3300 (urethane NH stretching), 1725 (urethane C=O stretching), 1510 (urethane NH bending); $^1$H-NMR [dimethyl sulfoxide (DMSO)-d$_6$, δ] 3.7 (–CH$_2$ of 1,3-DCP protons), 3.95 (–CH$_2$ of MDI moiety), 4.5 (–CH of 1,3-DCP moiety), 9.10 (urethane NHCN), 7.47–6.98 (aromatic protons); $^{13}$C-NMR (DMSO-d$_6$, δ) 45.30 (–CH$_2$ of 1,3-DCP protons), 43.95 (–CH$_2$ of MDI moiety), 78.60 (–CH of 1,3-DCP moiety), 135.86–122.36 (aromatic carbons), 156.36 (urethane C=O); Anal. Caled for C$_{21}$H$_{22}$Cl$_2$N$_2$O$_4$: C, 49.63%. Found: 50.24; H, 4.36%. Found: 4.56; N, 5.51%. Found: 5.60%.

$1,3$-dichloro 2-propanol-TDI adduct (2): FTIR (Neat, cm$^{-1}$) 3320 (urethane NH stretching), 1707 (urea C=O stretching), 1519 (urea NH bending); $^1$H-NMR (DMSO-d$_6$, δ) 2.67 (Ar-Me), 3.87 (–CH$_2$ of 1,3-DCP protons), 4.59 (–CH of 1,3-DCP moiety), 9.17 and 8.97 (urethane NH protons), 7.40–6.88 (aromatic protons); $^{13}$C-NMR (DMSO-d$_6$, δ) 16.25 (Ar-Me), 45.33 (–CH$_2$ of 1,3-DCP protons), 78.70 (–CH of 1,3-DCP moiety), 142.55–118.36 (aromatic carbons), 153.21 and 153.12 (urea C=O); Anal. Caled for C$_{31}$H$_{18}$Cl$_4$N$_2$O$_4$: C, 41.69%. Found: 42.24; H, 4.20%. Found: 4.26; N, 6.48%. Found: 6.65%.

$1,3$-dichloro 2-propanol-IPDI adduct (3): FTIR (KBr, cm$^{-1}$) 3349 (urethane NH stretching) 1698 (urea C=O stretching), 1506 (urea NH bending); $^1$H-NMR (CDCl$_3$, δ) 0.70–0.9 (CH$_3$ protons of isocyanate moiety), 1.27–1.47 (–CH$_2$ protons of isocyanate moiety), 2.96 (–CH$_2$–proton of isocyanate moiety), 7.04 and 7.10 (urethane NH), 4.48 (–CH of 1,3-DCP moiety), 3.70 (–CH$_2$Cl– moiety); $^{13}$C-NMR (CDCl$_3$, δ) 34.20, 29.78, and 26.62 (CH$_3$ of isocyanate moiety), 46.19, 45.62 and 41.24 (–CH$_2$ of isocyanate moiety), 43.47 (–CH of isocyanate moiety), 22.51 (–C of isocyanate moiety), 53.43 (–CH$_2$ of isocyanate moiety), 72.32 (–CH of 1,3-DCP moiety), 45.10 (–CH$_2$Cl of 1,3-DCP moiety), 156.46 and 155.87 (urethane C=O); Anal. Caled for C$_{18}$H$_{33}$Cl$_2$N$_2$O$_4$: C, 45.02%. Found: 44.40; H, 6.30%. Found: 6.26; N, 5.83%. Found: 5.35%.

$1,3$-dichloro 2-propanol-HMDI adduct (4): FTIR (KBr, cm$^{-1}$) 3345 (urethane NH stretching), 1685 (urea C=O stretching), 1508 (urea NH bending); $^1$H-NMR (CDCl$_3$, δ) 1.29 (–CH$_2$–CH$_2$–CH$_2$–CH$_2$–CH$_2$–CH$_2$– of isocyanate moiety), 1.50 (–CH$_2$–CH$_2$–CH$_2$–CH$_2$–CH$_2$–CH$_2$– of isocyanate moiety), 3.08 (–CH$_2$–CH$_2$–CH$_2$–CH$_2$–CH$_2$– of isocyanate moiety), 7.12 (urethane NH protons), 3.7 (–CH$_2$–Cl of 1,3-DCP moiety), 4.2 (–CH of 1,3-DCP moiety); $^{13}$C-NMR (CDCl$_3$, δ) 26.24 (–CH$_2$–CH$_2$–CH$_2$–CH$_2$–CH$_2$– of isocyanate moiety), 28.51 (–CH$_2$–CH$_2$–CH$_2$–CH$_2$–CH$_2$– of isocyanate moiety), 39.47 (–CH$_2$–CH$_2$–CH$_2$– of isocyanate moiety), 72.20 (–CH of 1,3-DCP moiety), 45.0 (–CH$_2$–Cl of 1,3-DCP moiety), 156.90 (urea C=O); Anal. Caled for C$_{14}$H$_{24}$Cl$_4$N$_2$O$_4$: C, 39.46%. Found: 40.24; H, 5.68%. Found: 5.26; N, 6.57%. Found: 6.65%.

**CO$_2$ evaluation method**

The CO$_2$ evaluation method was used to determine the minimum de-blocking temperatures of the blocked diisocyanate adducts. In a typical experiment, 0.2–0.3 g of blocked isocyanate adduct was placed in 10 mL of DMSO together with 2.5 g of molecular sieves saturated with moisture at 25 °C in a 25 mL two-neck, round-bottom flask.
with a magnetic stirrer. One neck of the flask was connected to a supply of dry, carbon dioxide-free nitrogen, and the other neck was connected to a purging tube, which was immersed in a saturated solution of barium hydroxide. The system was continuously purged with a slow stream of carbon dioxide-free, dry nitrogen gas. The flask was heated in a silicone oil bath at a rate of 3 \degree C \text{ min}^{-1}. As de-blocking occurs, regenerated NCO reacts with the available moisture from the molecular sieves, liberating carbon dioxide. This carbon dioxide then reacts with the saturated solution of barium hydroxide, causing turbidity due to the formation of insoluble barium bicarbonate. The minimum temperature at which detectable turbidity appeared was taken as the minimum de-blocking temperature.

**Cure-time studies**

A sample of 2.5 g (0.002 eq) of HTPB was taken separately in four beakers, each of diameter 30 mm. To each one, 0.002 equivalent of blocked diisocyanate was added and mixed thoroughly. Then, the beakers were placed in an air circulated oven maintained at 140 \degree C. The beakers were inverted at regular time intervals to observe the flow behavior of the mixture. The time at which the mixture ceased to flow was taken as the cure-time. A duplicate experiment was conducted for each blocked isocyanate to ensure the accuracy of the data collected. The cure reaction of blocked diisocyanate adducts (1–4) is given in Scheme 2.

**Solubility test**

This test gives the lowest temperature at which blocked diisocyanate adducts or blocked polyisocyanates completely dissolve in different polyols. A 0.1 equivalent dispersion of each blocked isocyanate in any one of the polyol was heated on a temperature controlled oil bath at a heating rate of 3 \degree C \text{ min}^{-1}. The temperature at which a clear solution was obtained was recorded as the dissolution temperature.
Result and discussion

Synthesis of blocked isocyanate adducts

The diisocyanates were blocked with 1,3-dichloro-2-propanol. The blocking reactions were monitored using FTIR spectroscopy, and the reactions were stopped when the –NCO absorption peak at 2270 cm\(^{-1}\) completely disappeared. The temperature and time required for the blocking reaction are given in Table 1. The reaction of 1,3-dichloro-2-propanol with isocyanates was not catalyzed. However, a catalyst, excess of blocking agent and long reaction time are needed for reactions involving IPDI. In the case of aromatic isocyanates, the carbonyl carbon of the –NCO group is more electropositive because the aromatic ring drains the electron density of the nitrogen atom, which facilitates the blocking reaction. In the case of the aliphatic isocyanates, the carbonyl carbon is less electropositive, and the nucleophile is attacked by the 1,3-dichloro-2-propanol. Therefore, the use of a catalyst is inevitable for the preparation of blocked isocyanates.

FTIR spectroscopy was successfully employed to characterize the blocked diisocyanate adducts. FTIR spectra of all 1,3-dichloro-2-propanol-blocked diisocyanate adducts are identical and show no absorption in the 2270 cm\(^{-1}\) range, which indicates that the –NCO groups of the diisocyanate molecules are completely blocked by the blocking agent. The formation of a urethane linkage is easily identified by two main characteristic bands: the strong bands at 3300–3349 cm\(^{-1}\) correspond to the stretching vibrations of urethane –NH, and the absorption bands at 1685–1725 cm\(^{-1}\) correspond to the stretching vibrations of urethane carbonyl (–C=O) groups in all spectra. The formation of a urethane linkage and the disappearance of bands at 2270 cm\(^{-1}\) are strong evidence for the blocking of isocyanate groups of the diisocyanates. The spectra of blocked diisocyanate adduct BI (1–4) are shown in Figure 1.

Similar to FTIR spectra, \(^1\)H-NMR and \(^13\)C-NMR spectra of 1,3-dichloro-2-propanol-blocked diisocyanate are also almost identical. A typical \(^1\)H-NMR spectrum of 1,3-dichloro-2-propanol-blocked diisocyanate (BI-1) is given in Figure 2, which shows the –CH\(_2\) and –CH– protons of the 1,3-dichloro-2-propanol moiety at 3.7 and 4.5 ppm, respectively, and the urethane proton at 9.10 ppm. The \(^13\)C-NMR spectrum has a urethane carbonyl carbon at 156.69 ppm, which confirms the formation of amine-blocked isocyanates and their structures. In addition, Figure 2 shows the proton peaks for the BI (2–4), whereas Figure 3 shows the \(^13\)C-NMR for BI (1–4).

Deblocking temperature

The deblocking temperatures of 1,3-dichloro-2-propanol-blocked isocyanates were determined using TGA, DSC and
the CO₂ evaluation method. The minimum deblocking temperatures of 1,3-dichloro-2-propanol-blocked isocyanates are given in Table 2, and the TGA and DSC thermograms of blocked isocyanates are given in Figures 4 and 5, respectively. The decomposition of blocked isocyanate occurs upon applying heat; therefore, there should be an endothermic transition in the DSC curve of blocked diisocyanate adducts. The DSC thermogram of 1,3-dichloro-2-propanol-\textit{MDI} shows two endothermic transitions at 140 and 192 °C. The first sharp transition corresponds to the melting point of the adduct; the second transition at 192 °C corresponds to the de-blocking of the blocked adduct. The de-blocking temperature of the blocked diisocyanate adducts determined by DSC are in the following order: 1,3-dichloro-2-propanol-\textit{HDI} > 1,3-dichloro-2-propanol-\textit{IPDI} > 1,3-dichloro-2-propanol-\textit{MDI} > 1,3-dichloro-2-propanol-TDI.

The low deblocking temperature of 1,3-dichloro-2-propanol-blocked isocyanates is due to the presence of two bulky chloro groups in the blocked isocyanate moiety. The bulky chloro groups accelerate the deblocking reaction; at the same time, the highly electro-negative character of the chloro group present in the blocking agent drains the electron density present oxygen atom of blocking agent. Thus, the bond formed between the blocking agent and isocyanate become more labile.

Similar to the structure of the blocking agent, the isocyanate structure can also strongly affect the strength of the labile bond formed during the blocking reaction and hence the deblocking temperature. If the blocked isocyanate is based on aromatic isocyanate, the aromatic ring drains the electron density of the nitrogen atom of isocyanate moiety and makes the labile bond formed between the isocyanate and blocking agent more labile. The opposite is true for the cases of blocked isocyanates based on aliphatic isocyanates. According to this argument, the results obtained are consistent with the isocyanate structures. The low deblocking temperatures of the blocked isocyanate series 1 and 2 are due to the presence of aromatic rings in the structures, and the high deblocking temperature of the blocked isocyanate series 3 and 4 is due to the use of aliphatic isocyanates. Among the isocyanate used, TDI-based blocked isocyanate (BI-2) undergoes deblocking at the lowest temperature due to the methyl group present in the isocyanate moiety, which accelerates the deblocking reaction through the steric factor.

**Cure-time studies**

To study the structure–property relationship of the blocked isocyanates synthesized, they were treated with HTPB,

<table>
<thead>
<tr>
<th>Compound no.</th>
<th>Blocked isocyanate adducts</th>
<th>Debloking temperature (°C)</th>
<th>Cure-time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>TGA</td>
<td>DSC</td>
</tr>
<tr>
<td>BI-1</td>
<td>MDI-DCP</td>
<td>225</td>
<td>192</td>
</tr>
<tr>
<td>BI-2</td>
<td>TDI-DCP</td>
<td>210</td>
<td>210</td>
</tr>
<tr>
<td>BI-3</td>
<td>IPDI-DCP</td>
<td>240</td>
<td>230</td>
</tr>
<tr>
<td>BI-4</td>
<td>HMDI-DCP</td>
<td>262</td>
<td>254</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound no.</th>
<th>Blocked isocyanate adducts</th>
<th>Dissolution temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BI-1</td>
<td>MDI-DCP</td>
<td>98</td>
</tr>
<tr>
<td>BI-2</td>
<td>TDI-DCP</td>
<td>60</td>
</tr>
<tr>
<td>BI-3</td>
<td>IPDI-DCP</td>
<td>30</td>
</tr>
<tr>
<td>BI-4</td>
<td>HMDI-DCP</td>
<td>72</td>
</tr>
</tbody>
</table>
which is a novel binder used in solid rocket propellants. The reason for choosing HTPB is that it suffers from a short pot life in a system containing aromatic isocyanate due to the high reactivity of the primary hydroxyl groups of HTPB with the isocyanate groups. Therefore, the use of blocked isocyanates instead of isocyanate with HTPB increases pot life; a long pot life is crucial for a system to be suitable for practical applications. At elevated temperatures, the isocyanate functionality will be regenerated, and the cure reaction will occur. The cure reaction of 1,3-dichloro-2-propanol-blocked isocyanate with HTPB is given in Scheme 2. During the course of the reaction, the viscosity is increased, and then the free flow is arrested. The time at which the free flow is arrested is noted as the cure time. The time required to cure HTPB by blocked isocyanates is given in Table 2. In the present study, the cure reactions of 1,3-dichloro-2-propanol blocked-isocyanates derived from different diisocyanates were investigated. The cure times of 1,3-dichloro-2-propanol-blocked TDI and MDI adducts are lower compared to blocked isocyanates based on IPDI and HMDI due to low the deblocking temperature and high reactivity of TDI and MDI towards HTPB.

**Solubility analysis**

The solubility of blocked isocyanate is an important factor for uniform curing with the hydroxyl co-reactant. The solubilities of 1,3-dichloro-2-propanol-blocked isocyanate adducts and 1,3-dichloro-2-propanol-blocked polyisocyanates were determined separately in four different polyols, and the
results are given in Table 3. All blocked polyisocyanates and blocked diisocyanate adducts based on IPDI (BI-3) were found to be readily soluble at room temperature in all four polyols due to the presence of a large number of aliphatic groups in the blocked isocyanates. The blocked isocyanate adduct based on TDI (BI-2) showed better solubility than the adduct based on MDI (BI-1), which may be due to the dissociation rather than the solvation of the adduct by the polyol. Among the four different polyols, PPG-2000 showed the best solvating effect.

Conclusion

In the present study, a series of 1,3-dichloro-2-propanol-blocked isocyanates were prepared, and their deblocking temperatures, cure behavior of blocked isocyanates with HTPB and solubility behavior in polyols were investigated. Aromatic isocyanates were found to be more reactive than aliphatic ones in the reaction with the blocking group, but nevertheless the deblocking is faster. The deblocking temperatures of blocked isocyanates were determined by TGA, DSC and the CO$_2$ evaluation method. The results reveal that 1,3-dichloro-2-propanol is a potential blocking agent for isocyanates.

References