

Cyclohexanone Oxime-Blocked Polyisocyanates

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SYNOPSIS

Cyclohexanone oxime-blocked isophorone diisocyanate and cyclohexanone oxime-blocked toluene diisocyanate were synthesized and analyzed by infrared spectra, nuclear magnetic resonance spectra, elemental analysis, etc. Decomposition temperatures of the blocked isocyanates were determined by thermogravimetry. The solubilities of blocked isocyanates in various polyols were tested. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Blocked isocyanates are utilized mainly in coatings and propellant formulations. Peterson¹ described in 1949 the blocking agents used for blocked isocyanates. Many patents covered the use of oximes as blocking agents in a wide range of applications. All the patents are based on methyl ethyl ketoximes, acetoxime, cyclohexanone oxime, acetophenone oxime, etc. In 1972, Levine and Fech² investigated the kinetics and mechanism of the reaction of dibutylamine with carbamates derived from benzophenone oximes and phenyl isocyanate. In 1979, Guise, et al.³ determined the influence of blocking agents such as acetoxime and cyclohexanone oxime on the cure rate of toluene diisocyanate prepolymers. In 1982, Kordomenos et al.⁴ determined the decomposition temperature of methyl ethyl ketoxime-blocked isocyanurate of isophorone diisocyanate and toluene diisocyanate by thermogravimetry. But there is no reference in the literature for cyclohexanone oxime-blocked toluene diisocyanate and isophorone diisocyanate. This paper deals with the synthesis, characterization, thermal analysis, and solubility analysis of blocked isocyanates in various polyols.

EXPERIMENTAL

Materials

Cyclohexanone and hydroxylamine hydrochloride used were of analytical grade (AR/BDH). Solvents

were perfectly dried prior to use. Toluene diisocyanate (TDI) and isophorone diisocyanate (IPDI) were used as such.

Preparation of IPDI-Cyclohexanone Oxime Adduct

Cyclohexanone oxime was synthesized by the reported procedure.⁵ Six grams of cyclohexanone oxime was dissolved in 50 mL of anhydrous ether contained in a two-necked round-bottomed flask. The solution was stirred magnetically to dissolve the oxime completely. To this, 5 mL of IPDI was added dropwise by using an addition funnel. The solution was refluxed well for about 3–4 h. A white solid mass was formed. Then, 50 mL of anhydrous ether was added into the flask. The solid mass was filtered, washed with ether, and then dried. Melting point: 110–115°C.

ANAL: Calcd: C, 64.2%; H, 8.91%; N, 12.4%.
Found: C, 64.19%; H, 9.1%; N, 12.5%.

Preparation of TDI-Cyclohexanone Oxime Adduct

The TDI used was a mixture of isomers of 80% toluene 2,4-diisocyanate, and 20% toluene 2,6-diisocyanate. The same procedure reported before was performed for this adduct synthesis by taking 4 mL of TDI instead of IPDI. Melting point: 87–90°C.

ANAL: Calcd: C, 62.9%; H, 6.9%; N, 13.9%.
Found: C, 63.1%; H, 7.1%; N, 13.7%.

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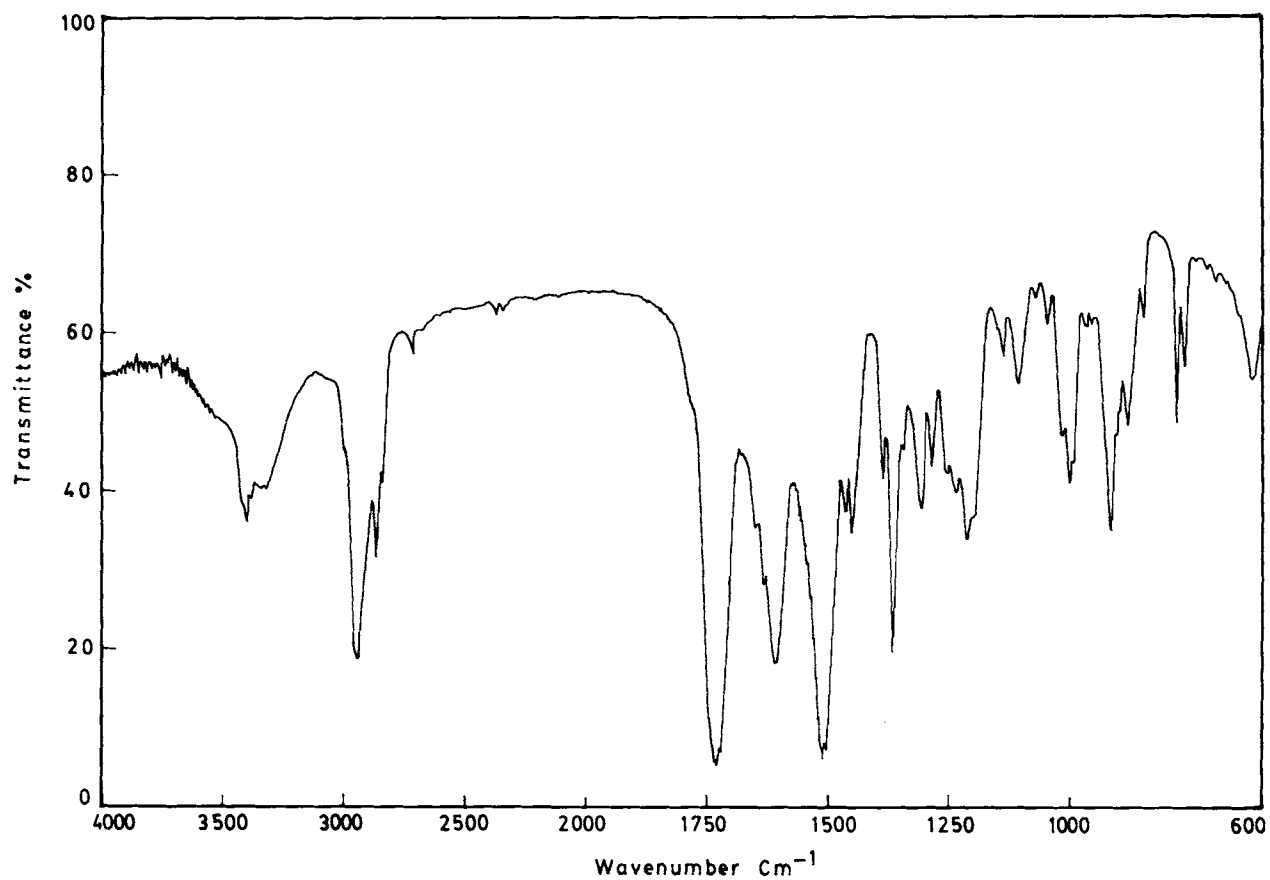


Figure 1 FTIR spectrum of cyclohexanone oxime-IPDI adduct.

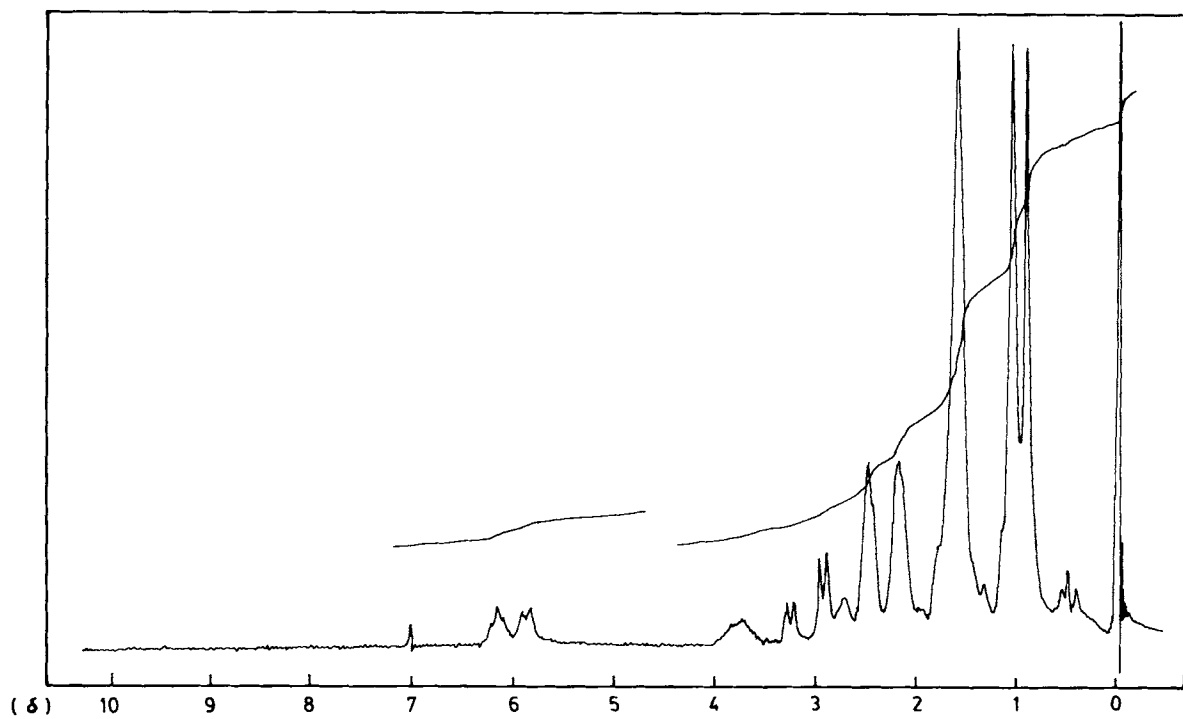


Figure 2 ^1H -NMR spectrum of cyclohexanone oxime-IPDI adduct.

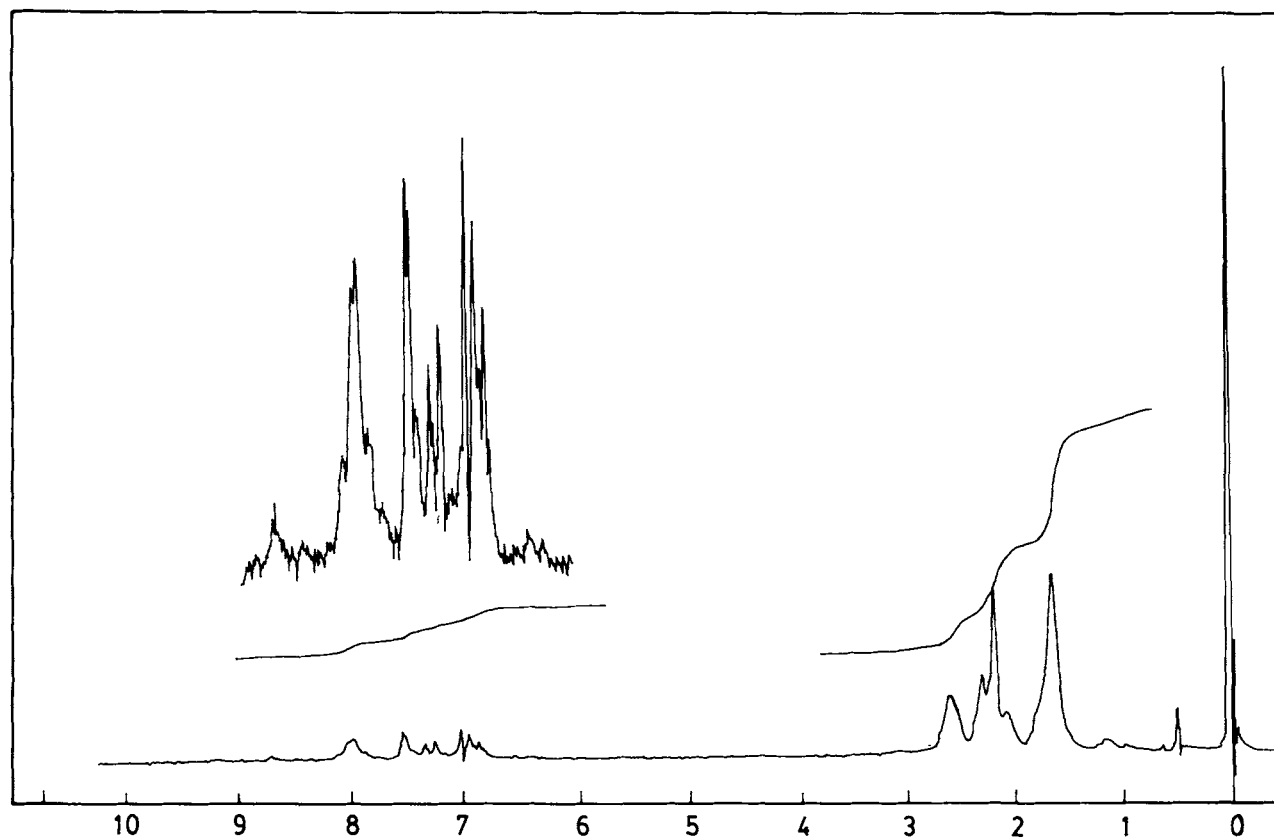


Figure 3 ^1H -NMR spectrum of cyclohexanone oxime-TDI adduct.

Analytical Techniques

FTIR spectra of the blocked isocyanates were recorded on a Perkin-Elmer Model 1760 Fourier transform IR spectrophotometer (FTIR). ^1H -NMR spectra were recorded on a EM 390 90 MHz NMR spectrometer in CDCl_3 solution. Tetramethylsilane was used as an internal standard. Decomposition temperatures of blocked isocyanates were determined by using a Perkin-Elmer thermogravimetric analyzer in nitrogen atmosphere at a heating rate of $20^\circ\text{C}/\text{min}$. Elemental analyses were done by using

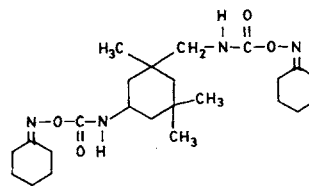
a Heraeus CHN-O-Rapid analyzer. The solubilities of blocked isocyanates in various polyols were tested by a reported procedure.⁶ The polyols chosen were polyethylene glycol (average molecular weight 400), polypropylene glycol (average molecular weight 1000), and hydroxyl-terminated polybutadiene (average molecular weight 2500). A dilute dispersion of the adduct in the polyol was heated on a hot stage at a heating rate of 3°C per min and that temperature was recorded at which the solution was complete.

Table I Solubility of Blocked Isocyanate in Various Polyols

Adduct	Polyethylene Glycol ($T^\circ\text{C}$)	Polypropylene Glycol ($T^\circ\text{C}$)	Hydroxyl-Terminated Polybutadiene ($T^\circ\text{C}$)
IPDI-cyclohexanone oxime	82	125	130
TDI-cyclohexanone oxime	45	100	105

RESULTS AND DISCUSSION

The FTIR spectrum of the IPDI-cyclohexanone oxime adduct is given in Figure 1. The characteristic bands appeared in the spectrum at 3400 cm^{-1} due to the N—H stretching vibration; at 2935 cm^{-1} , to the C—H stretching vibration; at 1734 cm^{-1} , to the C=O stretching vibration; and at 1510 cm^{-1} , to the NHCOO linkage. The same characteristic bands appeared in the region $3271, 2910, 1716,$ and 1460 cm^{-1} in the FTIR spectrum of the TDI-cyclohexanone oxime adduct. Absence of a band at 2270 cm^{-1} indicates the complete reaction of the isocyanate groups. $^1\text{H}^1$ -NMR spectra of the blocked isocyanates are given in Figures 2 and 3. FTIR spectra, $^1\text{H}^1$ -NMR spectra, and elemental analysis support the structure of the blocked isocyanate. The structure and chemical shift of the blocked isocyanates are given below:

1. isophorone diisocyanate-cyclohexanone oxime adduct

0.9	3H	CH ₃
1.1	6H	2CH ₃
1.5	12H	methylene groups (Oxime part)
2.1	4H	allylic —CH ₂ —
2.4	4H	allylic —CH ₂ —
2.8	2H	—CH ₂ — (isophorone part)
2.9	4H	2CH ₂ — (isophorone part)
3.2	2H	—N—CH ₂ —
3.8	1H	—C—H (isophorone part)
5.9	1H	NH
6.2	1H	NH

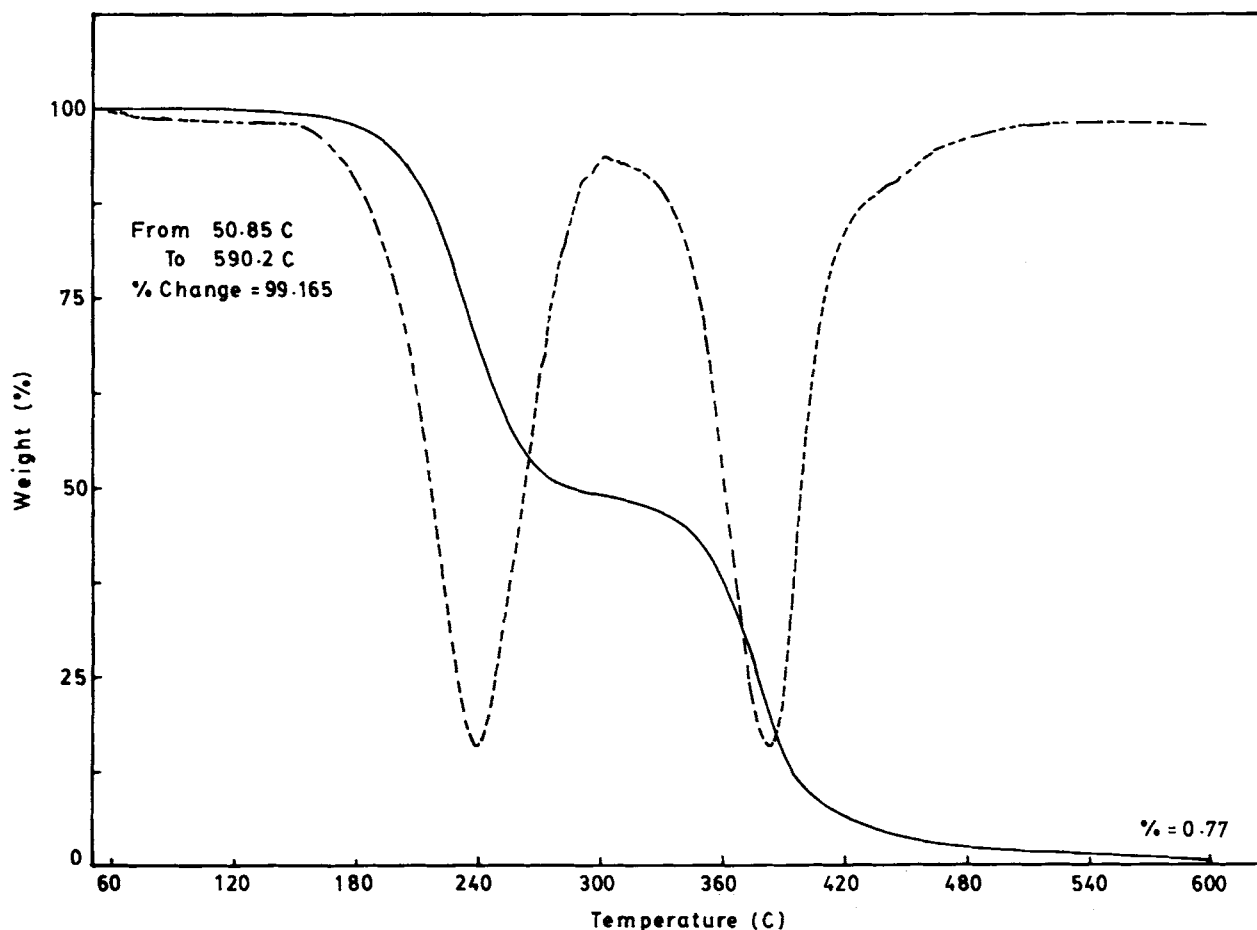


Figure 4 TGA of cyclohexanone oxime-IPDI adduct.

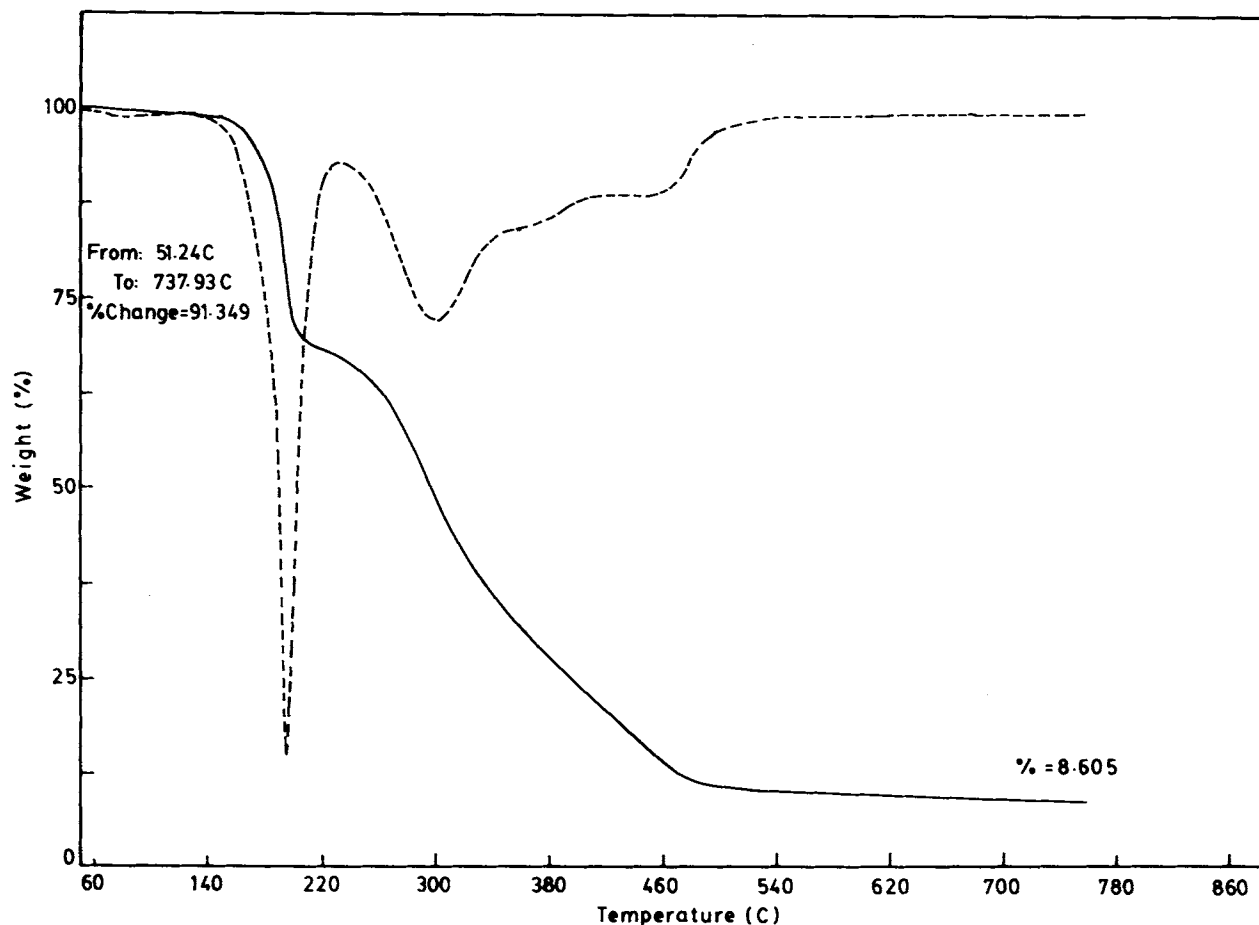
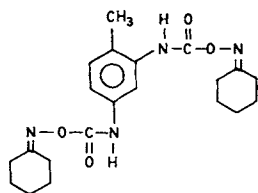


Figure 5 TGA of cyclohexanone oxime-TDI adduct.

2. Toluene diisocyanate-Cyclohexanone oxime adduct.



1-5	12H -CH ₂ - (Oxime part)
2-2	8H allylic -CH ₂ -
2-5	3H H ₃ C - Aromatic
6-8-7-5	3H Aromatic-H
8-0	1H NH
8-8	1H NH

The TG and DTG curves of the blocked isocyanates are given in Figures 4 and 5. Thermograms showed that the decomposition temperatures of TDI-cyclohexanone oxime adduct and IPDI-cyclo-

hexanone oxime adduct were found to be 199 and 238°C, respectively. Kordomenos et al.⁴ reported the decomposition temperatures of TDI-isocyanurate-methyl ethyl ketoxime adduct and the IPDI-isocyanurate-methyl ethyl ketoxime adduct as 133 and 157°C, respectively. These experimental results showed that the TDI adduct decomposes at a lower temperature than does the IPDI adduct. This is due to the reduction in negative charge density through the resonance structure of the aromatic ring, which lowers the decomposition temperature of the blocked isocyanate.

Solubility analyses of blocked isocyanates in various polyols are given in Table I. The TDI-cyclohexanone oxime adduct is highly soluble in polyethylene glycol at relatively lower temperatures than in other polyols. This is due to the presence of strongly nucleophilic oxygen atoms contained in more ether linkages and hydroxyl groups and also to the greater solvating power of the low molecular

weight polyethylene glycol than that of the other polyol.

CONCLUSION

Cyclohexanone oxime-blocked polyisocyanates were prepared by the reaction of 1 : 2 equivalent ratio of polyisocyanate (IPDI, TDI) and cyclohexanone oxime. Aromatic polyisocyanate-blocked cyclohexanone oxime decomposed at lower temperature than did the alicyclic one. Blocked isocyanates are highly soluble in polyethylene glycol at low temperatures.

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