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A. Sultan Nasar^a; Ganga Radhakrishnan^a; H. Kothandaraman^b

^a Polymer Division, Central Leather Research Institute Adyar, Madras, India ^b Department of Polymer Science, University of Madras, Madras, India

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ELECTRON IMPACT MASS SPECTRA OF PHENOL BLOCKED ISOCYANATES

A. Sultan Nasar and Ganga Radhakrishnan *

Polymer Division
Central Leather Research Institute
Adyar, Madras-600 020, India

H. Kothandaraman

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

ABSTRACT

The electron impact mass spectra of a series of substituted phenol blocked toluene diisocyanate crosslinkers were analyzed and a suitable dissociative pathway proposed.

INTRODUCTION

The extreme reactivity of isocyanates with hydroxy compounds make them attractive crosslinking agents for different polyurethanes in the form of fibers, soft and hard elastomers, coatings, adhesives, binders and highly crosslinked plastics. In some of these applications, it is necessary to delay the desired isocyanatehydroxyl reaction until the final stages of fabrication. In order to achieve this objective, blocked isocyanates are used to generate the isocyanate functionality at the proper stage. The dissociation or deblocking temperature of the blocked isocyanate is one of the limiting factors in industrial applications. The thermal dissociation temperature of urethanes in very general terms varies in the following order [1].

Alkyl - NHCOO - Alkyl	- 250°C
Aryl - NHCOO - Alkyl	- 200°C
Alkyl - NHCOO - Aryl	- 180°C
Aryl - NHCOO - Aryl	- 120°C

Phenols are very popular blocking agents, particularly for aromatic isocyanates, since the resulting urethane linkage is unstable at elevated temperatures. Moreover, the adduct does not give any byproducts except phenol and isocyanate during the dissociation reaction.

Few reviews [2, 3] have been published in which hundreds of patents are covered dealing with applications of blocked polyisocyanates. The phenol blocked isocyanates play a main role in the preparation of many types of urethane coatings, tire-cord adhesive systems, plastic bonded propellants, textiles, vulcanized rubbers, crosslinking of elastomeric solid rocket propellant binders and herbicidal applications. Recently, the use of blocked diisocyanates to prepare rigid rod-like polyimides [4], hyper branched polymers [5] and epoxy resin [6, 7] has been reported. Blocked polyisocyanates are preferred for many technical and economical reasons. They are essentially non sensitive to moisture. The storage stability of blocked polyisocyanate based systems is generally high [8].

A number of authors have studied the thermal dissociation of phenol blocked isocyanates using IR spectrophotometer [9-12], differential scanning calorimeter [13, 15], thermogravimetric analysis combined with pyrolysis gas chromatograph [16] and titrimetric methods [17]. Here, we report the mass spectral studies of a series of blocked toluene diisocyanates with a view to understand the dissociative pathway of blocked isocyanates.

EXPERIMENTAL

The preparative methods for phenol blocked toluene diisocyanates (TDI) have been described in our previous publications [12, 18]. The adducts were reprecipitated in toluene and analyzed for mass spectra. The mass spectra were recorded using Finnigan Mat 8230 mass spectrometer operating at 70eV with emission current 0.5mA.

RESULTS AND DISCUSSION

The common fragments found by electron impact method are listed in Table 1. The molecular ion (M^+) peaks are very insignificant and in some cases are

TABLE I. Mass Spectral Data (70eV) of Phenol Block TDI Adducts

Adduct	Mol.wt.	Fragments found (Assignment)											
		m/z	I ^a	m/z	I ^a	m/z	I ^a	m/z	I ^a	m/z	I ^a	m/z	I ^a
Phenol - TDI	362.37	362 (M ⁺)	0.6	93(C ₆ H ₅ O Phenol-H) ^b	2	94 (C ₆ H ₅ O Phenol) ^c	100	268 (M ⁺ -c)	7	174(C ₉ H ₉ N ₂ O ₂ M ⁺ -2c)	44		
o-Cresol - TDI	390.43	390 (M ⁺)	0.9	107(C ₇ H ₇ O o-Cresol-H) ^b	24	108(C ₇ H ₇ O o-Cresol) ^c	100	282 (M ⁺ -c)	6	174(C ₉ H ₉ N ₂ O ₂ M ⁺ -2c)	10		
m-Cresol - TDI	390.43	390 (M ⁺)	0.2	107(C ₇ H ₇ O m-Cresol-H) ^b	35	108(C ₇ H ₇ O m-Cresol) ^c	100	282 (M ⁺ -c)	8	174(C ₉ H ₉ N ₂ O ₂ M ⁺ -2c)	12		
p-Cresol - TDI	390.43	390 (M ⁺)	0.05	107(C ₇ H ₇ O p-Cresol-H) ^b	38	108(C ₇ H ₇ O p-Cresol) ^c	100	282 (M ⁺ -c)	6	174(C ₉ H ₉ N ₂ O ₂ M ⁺ -2c)	10		
o-Methoxyphenol - TDI	422.43	422 (M ⁺)	0.1	123(C ₇ H ₇ O ₂ o-methoxy-phenol-H) ^b	5	124(C ₇ H ₇ O ₂ o-methoxy-phenol) ^c	100	298 (M ⁺ -c)	1	174(C ₉ H ₉ N ₂ O ₂ M ⁺ -2c)	13		
2,6-Dimethyl Phenol - TDI	418.47	418 (M ⁺)	0.3	121(C ₈ H ₉ O 2,6-Dimethyl-phenol-H) ^b	13	122(C ₈ H ₉ O 2,6-Dimethyl-Phenol) ^c	100	296 (M ⁺ -c)	4	174(C ₉ H ₉ N ₂ O ₂ M ⁺ -2c)	7		
o-Chlorophenol - TDI	431.27	431 (M ⁺)	0.6	127(C ₆ H ₄ ClO o-Chloro-phenol-H) ^b	6	128(C ₆ H ₄ ClO o-Chloro-phenol) ^c	100	302 (M ⁺ -c)	6	174(C ₉ H ₉ N ₂ O ₂ M ⁺ -2c)	74		
p-Chlorophenol - TDI	431.27	431 (M ⁺)	Nil	127(C ₆ H ₄ ClO p-Chloro-phenol-H) ^b	3	128(C ₆ H ₄ ClO p-Chloro-phenol) ^c	100	302 (M ⁺ -c)	3	174(C ₉ H ₉ N ₂ O ₂ M ⁺ -2c)	48		
2,4-Di-tert-butyl phenol - TDI	586.79	586 (M ⁺)	0.05	205(C ₁₁ H ₂₁ O 2,4-di-tert-butylphenol-H) ^b	1	206(C ₁₁ H ₂₁ O 2,4-di-tert-butylphenol) ^c	60	380 (M ⁺ -c)	3	174(C ₉ H ₉ N ₂ O ₂ M ⁺ -2c)	13		

(a) - I represents relative intensity; (b) - Phenolate ion; (c) - Phenol.

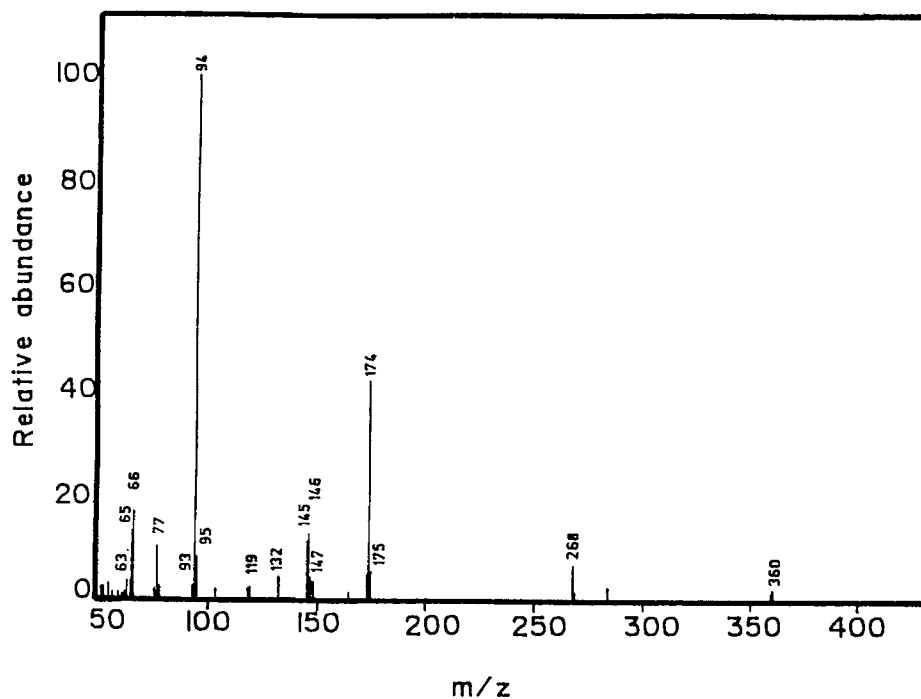
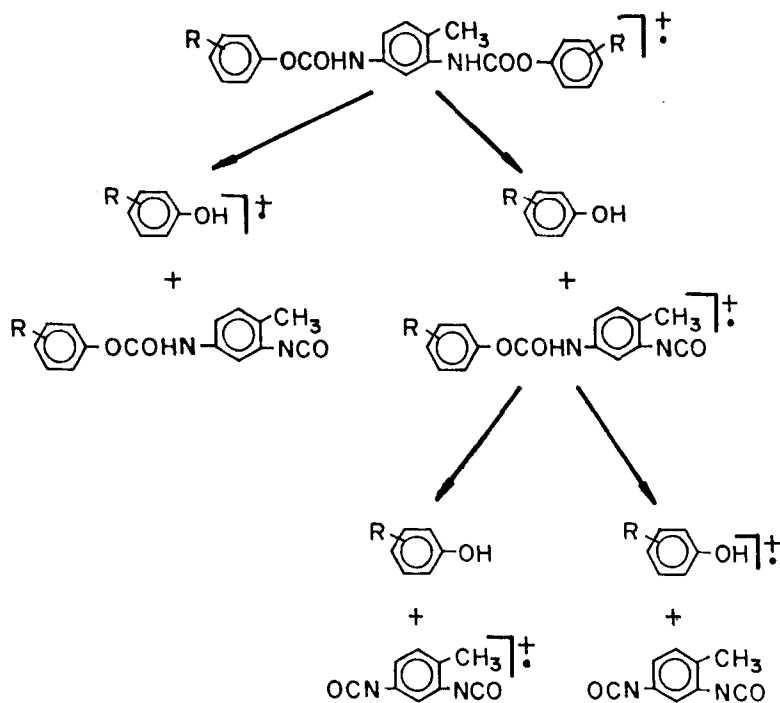


Figure 1. EI mass spectrum of phenol block TDI adduct.

not seen. This is due to the scission of -NH-CO-O- linkage in the adduct. As already mentioned, the urethane linkage formed from the aromatic reactants is labile because the urethane carbonyl carbon and oxygen of blocking agent possess partial positive charges. This identical charges will reduce the charge difference and weaken the bond. Since two molecules of the blocking agent could be generated by one molecule of the adduct dissociated, the base peak corresponds to the phenols except that of the adduct prepared with 2,6-di-*tert*.butylphenol (Figure 1, Table 1).

The lower intensity of di-*tert*.butylphenol in contrast to other phenols may be due to the breaking of *tert*.butyl group. The influence of branching on the breaking of skeleton of organic molecules is reported [19]. The fragmentation pattern of blocked isocyanate includes phenolate ion, phenol and TDI. Since the possibility of simultaneous expulsion of both phenolic groups is less, the peak due to M^+ -phenol also appears in the spectra. The higher intensity of M^+ -phenol compared to molecular ion indicates that the two urethane linkages dissociate at a different extent under identical conditions. The urethane linkage closer to methyl group will dissociate



Scheme 1.

initially, since the methyl substituent has influence on the deprotonation of urethane NH group. Mukaiyama and Iwanami [20] have reported that the ortho substituents in the isocyanate moiety accelerate the dissociation and facilitate the deprotonation of the urethane linkage. The fragmentation process involves instantaneous production of phenol and $(\text{R})\text{PhOCONHPh}(\text{CH}_3)\text{N}(\text{CO})$. Simultaneously, dissociation of $(\text{R})\text{PhOCONHPh}(\text{CH}_3)\text{NCO}$ occurs leading to phenol and TDI ($\text{OCNPh}(\text{CH}_3)\text{NCO}$, $m/z = 174$). This can be further supported by the peak observed at $m/z = 175$ which is due to expulsion of the phenolate ion from $(\text{R})\text{PhOCONHPh}(\text{CH}_3)\text{NCO}$. So, the prominent peaks commonly found in the phenol blocked TDI adducts can be better understood by the following scheme (Scheme 1).

This type of fragmentation pattern will be useful to understand the dissociative path way of blocked polyisocyanates employed in heat-curable systems like powder coatings.

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