

## Synthesis and characterization of some polyurethanes and polyurethane-ureas

A.A. KHALIL and S.K. BADR

Chemistry Department, Faculty of Science, Benha University, Benha (Egypt)

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### ABSTRACT

Polyurethanes and polyurethane-ureas were prepared by the reaction of diethylene glycol and polyethylene glycol with excess of aromatic and aliphatic diisocyanate to yield isocyanate terminated prepolymers which were subsequently reacted with diols and diamines. These polymers were characterized by IR, <sup>1</sup>HNMR spectra, viscosity measurements and thermogravimetric analysis.

**Key words:** Polyurethanes, polyurethane-ureas and glycols.

### INTRODUCTION

Polyurethanes form a class of industrially useful materials because of their excellent properties. The polyurethanes are used in a wide variety of applications but relatively few isocyanates are employed commercially in their manufacture. Polyurethanes are prepared by the polyaddition reactions of diisocyanates and diols<sup>1</sup>. In the chemistry of an isocyanate, an aromatic isocyanates is understood to have higher reactivity than an aliphatic isocyanate toward a nucleophile<sup>2</sup>. The most important are the toluene diisocyanate (TDI), although other types are now being developed and adopted industrially. The initial studies on polyurethane synthesis were based on simple diisocyanates and diols but the main important of the reaction is now concerning with the use of intermediates which are often themselves polymeric in character (polyester, polyethers) and carry terminal groups (usually-OH or NCO) capable of further reaction and thus of increasing the molecular size, often during the actual fabrication processing, by either chain extension, branching or crosslinking. One such method preparing a polyurethane derivatives is first to prepare an isocyanate terminated prepolymer which is often reacted with diols<sup>3-5</sup>, diamines<sup>6,7</sup> and water<sup>7,8</sup>. Hydroxy terminated

polyesters are the starting materials for many of the urethane polymers. The polyesters were prepared by melt condensation of glycols and dibasic acids of both aliphatic and aromatic types or a mixture of both<sup>5-10</sup>.

In the present work, some polyurethanes and polyurethaneureas were prepared by the reaction of isocyanate terminated prepolymers with diols and diamines, respectively.

### EXPERIMENTAL

#### Material

Toluene-2,4-diisocyanate, triethylamine and hexamethylene diamine were pure grade products of BDH Co. (England) and were used directly. Glycols (diethylene, 1,4-butane, 1,6-hexane and polyethylene glycol) were obtained from E. Merck, Darmstadt. 2,6-Diaminopyridine was obtained from Aldrich Co. All solvents used were of A.R. or equivalent grade.

#### Preparation of polyurethanes and polyurethane-ureas

To a solution containing 0.1 equivalents of diethylene glucol or polyethylene glycol (PEG) (M.wt. 400) in 50 ml dimethylformamide (DMF) and some

drops of triethylamine as catalyst, 0.3 equivalents of toluene diisocyanate (TDI) or methylene diisocyanate (MDI) in 20 ml DMF were added at room temperature in  $N_2$  atmosphere. The reaction mixture was heated to  $80^\circ C$  with stirring for 1h, followed by addition of (0.2) equivalents of diol or diamine in the cases of polyurethanes and polyurethane-ureas, respectively. Reaction was done at  $120^\circ C$  for 3h. The same reaction conditions were adopted for all polymerization to ensure the same amount of chain extension. The viscous solution was precipitated with water, filtered, washed with water, methanol and dried in a vacuum desiccator. The yield of polymers was 75-85%.

#### Characterization of polymers

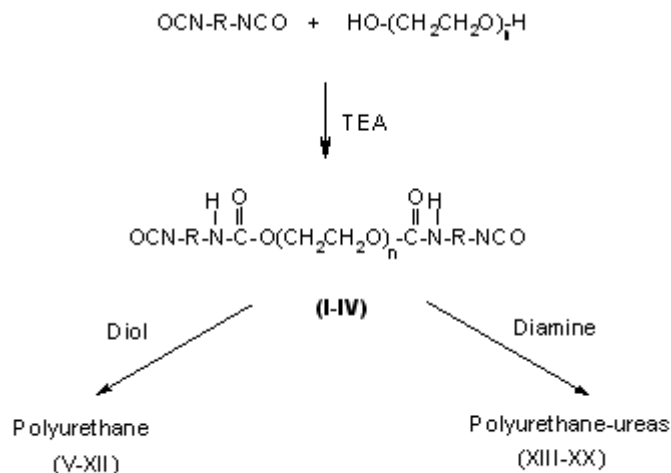
Viscosity measurements were carried out with an Ostwald viscometer using 1% solution in DMF. Densities were measured, by means of a pycnometer using hexane at  $30^\circ C$ . The infrared spectra were recorded on Perkin-Elmer 683 spectrophotometer. Polymer samples were examined as KBr discs.

The  $^1H$  NMR spectra (in  $d_6$ -dimethylsulfoxide and using TMS as zero reference) were obtained with a Varian EM-390 spectrometer.

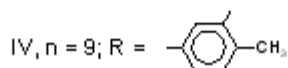
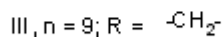
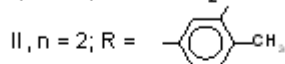
DTA was performed at a heating rate of  $10^\circ /min$  using a Shimadzu X-D30 thermal analyzer. TG Thermogram were obtained at a heating rate of  $10^\circ /min$  using a DT-30B thermal analyzer.

### RESULTS AND DISCUSSION

In the present work, the reaction of diethylene glycol and polyethylene glycol (PEG-400) with toluene diisocyanate (TDI) and methylene diisocyanate (MDI) were carried out in DMF using TEA as catalyst to give isocyanate terminated prepolymers. Polyurethanes and polyurethane-ureas were prepared by the reaction of isocyanate terminated prepolymers (I-IV) with diol and diamine, respectively, according to the following scheme:

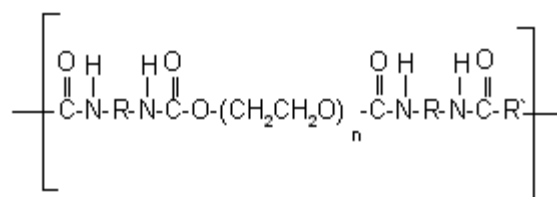


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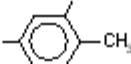
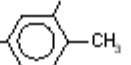
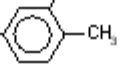
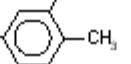
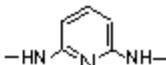
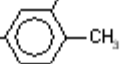
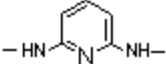
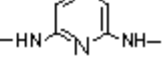
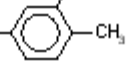
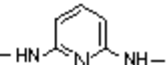
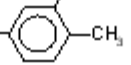
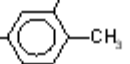


The structures of the prepared polyurethanes and polyurethane-ureas can be illustrated as follows:

The structures of the prepared polyurethanes and polyurethane-ureas were established by studying their IR and <sup>1</sup>H NMR spectra. The infrared spectrum of polyurethane (VIII)



Where:

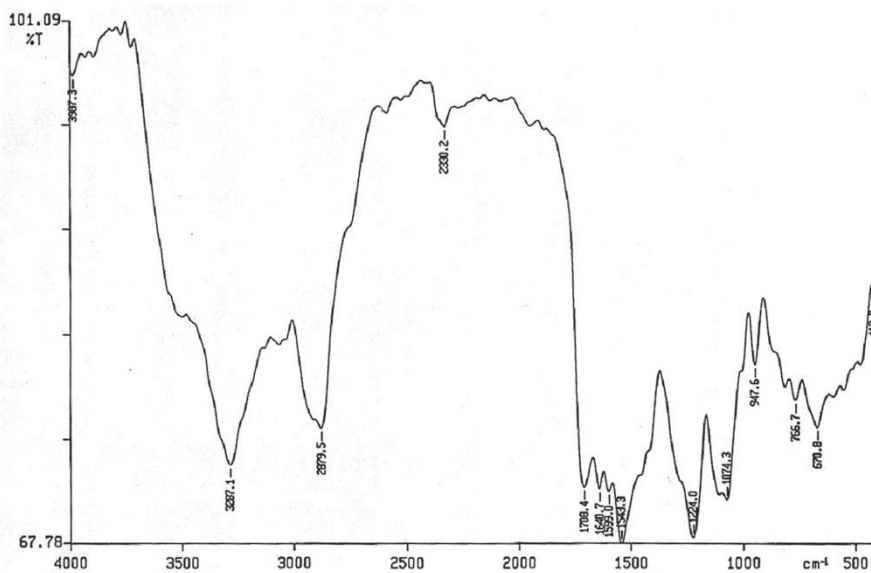
	n	R	R'
V	2	-CH <sub>2</sub> -	-O-(CH <sub>2</sub> ) <sub>4</sub> -O
VI	2		-O-(CH <sub>2</sub> ) <sub>4</sub> -O
VII	9	-CH <sub>2</sub> -	-O-(CH <sub>2</sub> ) <sub>4</sub> -O
VIII	9		-O-(CH <sub>2</sub> ) <sub>4</sub> -O
IX	2	-CH <sub>2</sub> -	-O-(CH <sub>2</sub> ) <sub>6</sub> -O
X	2		-O-(CH <sub>2</sub> ) <sub>6</sub> -O
XI	9	-CH <sub>2</sub> -	-O-(CH <sub>2</sub> ) <sub>6</sub> -O
XII	9		-O-(CH <sub>2</sub> ) <sub>6</sub> -O
XIII	2	-CH <sub>2</sub> -	
XIV	2		
XV	9	-CH <sub>2</sub> -	
XVI	9		
XVII	2	-CH <sub>2</sub> -	-HN-(CH <sub>2</sub> ) <sub>6</sub> -NH-
XVIII	2		-HN-(CH <sub>2</sub> ) <sub>6</sub> -NH-
XIX	9	-CH <sub>2</sub> -	-HN-(CH <sub>2</sub> ) <sub>6</sub> -NH-
XX	9		-HN-(CH <sub>2</sub> ) <sub>6</sub> -NH-

(Fig.1) showed characteristic absorption bands around  $3280\text{ cm}^{-1}$  ( $\nu_{\text{NH}}$ ) and an intense absorption band around  $1080\text{ cm}^{-1}$  ( $\nu_{\text{C-O}}$ ). The carbonyl absorption showed two peaks around  $1710\text{ cm}^{-1}$  and  $1640\text{ cm}^{-1}$  for the ester and urethane carbonyls, respectively. The  $^1\text{H}$  NMR spectra of the

polyurethane displayed bands at  $\delta 6.8-8.9$  due to protons of phenyl and NH groups,  $\delta 4.2$  due to protons of  $\text{CH}_2\text{-O-CO-}$  group;  $\delta 3.7$  due to protons of  $-\text{CH}_2\text{-O-CH}_2-$  group;  $\delta 2.1$  due to protons of methyl group of TDI. Fig. 2 illustrates the  $^1\text{H}$  NMR spectrum of polyurethane (VI) as example.

**Table 1: Physical properties of polyurethanes (V-XII) and polyurethane-ureas (XIII-XX)**

Polymer	Yield (%)	$\eta$ (dl/g)	Density (g/cm <sup>3</sup> )	Decomposition temperature
V	81	0.273	1.73	-
VI	79	0.312	1.02	-
VII	83	0.296	1.62	-
VIII	84	0.305	1.85	310
IX	89	0.227	1.13	-
X	83	0.308	2.25	-
XI	80	0.335	1.89	265
XII	84	0.209	1.97	-
XIII	85	0.212	1.83	320
XIV	79	0.287	1.56	330
XV	75	0.311	1.32	-
XVI	77	0.301	1.51	-
XVII	75	0.321	1.44	-
XVIII	76	0.302	1.91	-
XIX	82	0.286	1.68	-
XX	77	0.351	1.76	-



**Fig. 1: IR spectrum of polyurethane (VIII)**



The intrinsic viscosities ( $\eta$ ) of the polymers ranged from 0.20-0.35 dl/g when measured in DMF at 30 °C. The densities of the polymers were in the range 1.7-2.2g / cm<sup>3</sup>. The values of yields, intrinsic viscosities, densities and some decomposition temperature are gives in Table 1. Thermal analysis

of some polyurethane showed that the polymers were stable up to 265-330 °C. Figure 3 show the TG and DTA curves of polymer (VIII) as example. These high thermal stability values obtained for the prepared polyurethanes are in agreement with those reported by Rajendran *et al*.

## REFERENCES

1. A. Nishio, A. Mochizuki, J. Sugiyama, Ktakeuchi, M.Asai, K.Yonetake and M.Ueda, *J.polym. Sci., part A polymer chemistry*, **39**: 416 (2001).
2. Sato, M., *J. Am.Chem.. Soc.*, **82**: 3893 (1960).
3. K.A.Pigott, B.F.Frye, K.R. Allen, S.Steningizer, W.C.Darr, J.H. Saunders and E.E. Hardy. *J.Chem.. Eng. Data* **5**: 391 (1960).
4. J. L. Boivin. *Can. J. Chem.*. **36**: 1405 (1958).
5. A.F. Shaaban, M.A.El-Safty, H.Y.Moustafa and N.N.Messiha, *Die Angewandte Makromol. Chem.*. **161**: 123 (1988).
6. E.Muller, O.Bayer, S.Peterson, H. Piepenbrink, W.Schmidt and E.Weinbreuner: *Angew. Chem.*, **64**: 523 (1952).
7. A.F.Shaaban, A.A.Hamed and I.A.G.El-Karim *J. Appl. Polym. Sci.*, **29**: 3855 (1984).
8. O. Bayer, E. Müller, S. Peterson, H. Piepenbrink and E.Windemuth, *Angew. Chem.*, **62**: 27 (1950).
9. G.P.Rajendran, V.Mahadevan, M.Srinivasan: *Eur. Polym. J.* **18**, 953 (1982).
10. M.A.Radwan, *Pigment&Resin Technology*, **28**: 2,70 (1999).