Eur. Polym. J. Vol. 23, No. 11, pp. 905–906, 1987
Printed in Great Britain. All rights reserved

0014-3057/87 $3.00 + 0.00

SYNTHESIS AND CHARACTERIZATION OF POLY(AMIDE–UREAS)

JAYALAKSHMI GOPAL and M. SRINIVASAN
Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

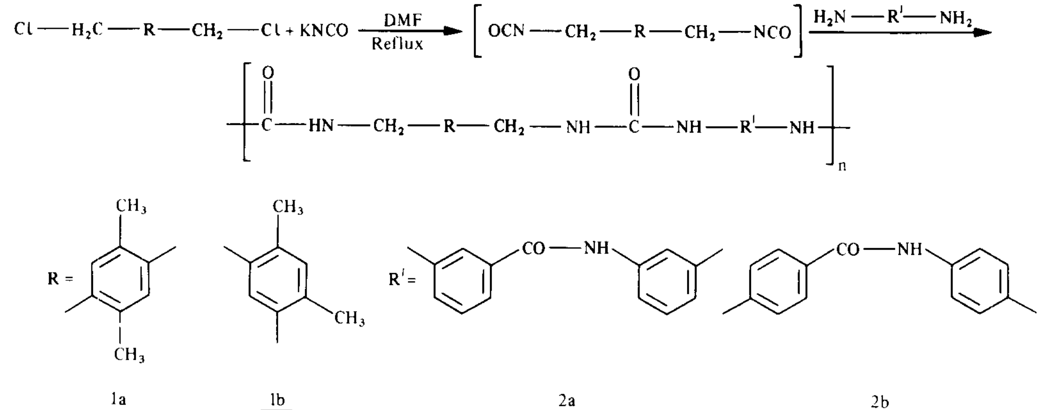
(*Received* 21 *November* 1986; *in revised form* 23 *February* 1987)

Abstract—Poly(amide–ureas) have been prepared by the action of di-isocyanates generated *in situ*, a technique so far not used for the preparation of poly(amide–ureas). The polymers were characterized by i.r., X-ray, thermal and viscosity measurements.

INTRODUCTION

Di-isocyanates essential for production of polyurethanes and polyureas can be obtained by a number of well established methods [1]. The di-isocyanates thus obtained generally undergo autopolymerization on standing and also decompose due to environmental moisture. However, a few attempts have been made to generate di-isocyanates *in situ*, bringing about polymerization simultaneously. Alkyl halides undergo ready substitution with alkali cyanates at elevated temperature to give alkyl isocyanates. Using this approach, a number of symmetrical di-isocyanates have been prepared from the corresponding alkyldihalides [2–5]. Synthesis of polyurethanes from *trans*-1,4-dichloro-2-butene, sodium cyanate and ethylene glycol has been achieved by this approach [6]; a few polyurethanes incorporating acetylenic bonds have also been prepared [7].

However there has been no report on the preparation of poly(amide–ureas) from di-isocyanates generated *in situ*. This, as well as the fact that benzylic(allylic) halogen is more easily replaceable by isocyanate than in alkyl chlorides, prompted us to undertake the work now presented.



Polymer	R	R'
PDA-PDlCl	1a	2b
MDA-PDlCl	1b	2b
MDA-MDlCl	1b	2a
PDA-MDlCl	1a	2a

EXPERIMENTAL

The i.r. spectra were taken in a PE-257 instrument. The intrinsic viscosity measurements were made in a Ubbelohde suspended level viscometer. The thermo-gravimetric analyses were done with Stanton Redcroft simultaneous thermal analyser in N_2 at a heating rate of 10°/min. DMF was refluxed over phosphorus pentoxide and distilled under reduced pressure.

1,4-Bis(chloromethyl)-2,5-dimethylbenzene (1a) and 1,5-bis(chloromethyl)-2,4-dimethyl benzene (1b) were prepared by the chloromethylation of *p*-xylene and *m*-xylene respectively [8].

4,4′-Diaminobenzanilide (2b) and 3,3′-diaminobenzanilide (2a) were prepared by the reduction of the respective dinitro compounds using Raney nickel and hydrazine hydrate [9].

POLYMERIZATIONS

A typical polymerization procedure is as follows. To a solution of (1a) (1.01 g, 5 mmol) in DMF (25 ml) was added KCNO (0.9 g, 11 mmol); it was heated under N_2 at 95–100°C for 2 hr. A freshly crystallized sample of diamine (2a) (1.35 g, 5 mmol) was added and refluxing was continued for a further 6 hr. The reaction mixture was poured into ice-cold water, filtered and washed with acetone to remove all

Table 1. Physical properties of poly(amide–ureas)

Polymer	Yield (%)	Density* (gm/cm^3)	η† (dl/g)	$\overset{O}{\overset{\parallel}{-C-NH-}}$	$>$NH
PDA–PDICl	75	1.581	0.252	1620	3320
PDA–MDICl	62	1.623	1.168	1630	3320
MDA–PDICl	71	1.562	0.363	1620	3300
MDA–MDICl	62	1.316	1.662	1620	3300

*Measures in a small pycnometer at 30°C.
†Measures in DMF containing 5% $LiNO_3$ (C = 0.5 g/dl).

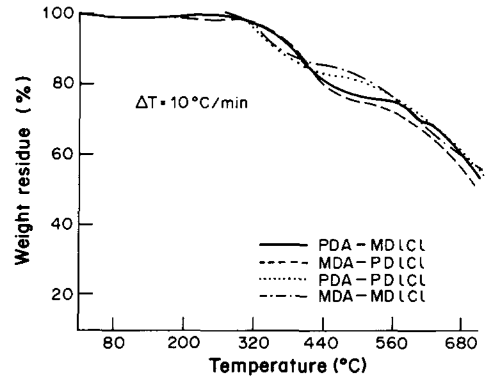


Fig. 1. TG curves of poly(amide-ureas) in N_2.

unreacted monomers and then dried at 80°C for 6 hr. Yield 1.65 g (75%).

RESULTS AND DISCUSSION

The polymerization was carried out by refluxing 1 mol of the dichloride, 2 mol of potassium cyanate, followed by addition of 1 mol of the diamino benzanilide in DMF. At this temperature, the chloride of the chloromethyl group is replaced by the isocyanate group which immediately reacts with the diamine giving the corresponding poly(amide–urea). The polymers were characterized by i.r. and viscosity measurements. The values of density, viscosity and yield are given in Table 1.

The i.r. spectra of the polymers showed absorption at 1650 cm^{-1} due to $>$C=O of the urea and amide groups. The $>$NH absorption occurs at 3300–3400 cm^{-1}. The X-ray diffraction pattern showed the polymers to be amorphous and the polymers were only partially soluble in DMF, DMAc, DMSO and HMPT.

The thermal degradation studies were carried out by TG. The TG curves are depicted in Fig. 1. The temperature at which 10% weight loss occurred was taken as a criterion for thermal stability. The temperatures for various percentage weight losses are given in Table 2. The polymers were thermally stable up to 340–380°C. The thermal stabilities of these poly(amide–ureas) compare well with those of the poly(amide–ureas) prepared by conventional method [10].

Table 2. Thermal properties of poly(amide–ureas)

Polymer	Temperature (°C) for various % weight losses 10	20	30	40
PDA–PDICl	340	500	585	655
PDA–MDICl	378	443	600	670
MDA–PDICl	380	432	578	650
MDA–MDICl	350	500	608	680

Acknowledgement—One of the authors (J.G.) thanks the Department of Atomic Energy, India, for financial assistance.

REFERENCES

1. H. G. J. Overmars. In *Encyclopaedia of Polymer Science and Technology* (Edited by H. F. Mark, N. G. Gaylord and N. M. Bikales), Vol. 11. p. 465. Interscience, New York (1969).
2. C. H. Himel and L. M. Richards. U.S. 2, 866, 801 (1958); Ethyl Corporation. *Chem. Abstr.* **53,** 9145i (1958).
3. B. Graham. U.S. 2, 866, 802 (1958); Ethyl Corporation. *Chem. Abstr.* **53,** 9146d (1958).
4. K. Fukui and H. Kitano. Japan, 36, 4372 (1962); *Chem. Abstr.* **57,** 12514f (1962).
5. K. F. Zenner, G. Oertel and H. Holtschmidt. Gen. 1, 205, 087 (1965); Bayer AG. *Chem. Abstr.* **64,** 19413g (1966).
6. S. Ozaki. *J. Polym. Sci.* **B5,** 1053 (1967).
7. B. Durairaj and K. Venkatrao. *Makromolek. Chem.* (*Rapid Commun.*) **1,** 473 (1980).
8. N. A. Peppas, G. Valkanes and E. T. D. Kotsida. *J. Polym. Sci., Polym. Chem. Edn* **14,** 1241 (1976).
9. K. Murata, K. Harada and H. Kuwata. *Hiroshima Daigaku Kenkyu Hokaku* **5,** 311 (1956); **51,** 10909i (1957).
10. Jayalakshmi Gopal and M. Srinivasan. *J. Polym. Sci. Polym. Chem. Edn* 2719 (1985).