

SYNTHESIS OF SOME LOW GLASS TRANSITION TEMPERATURE POLYTETRAHYDROFURAN POLYMERS

G. P. RAJENDRAN, V. MAHADEVAN and M. SRINIVASAN*

Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

(Received 31 May 1988; in revised form 23 September 1988)

Abstract—Samples of hydroxy-terminated and amine-terminated (polytetrahydrofuran; PTHF) of various molecular weights were prepared by the polymerization of tetrahydrofuran with boron trifluoride etherate in three steps. These PTHFs were characterized by molecular weight, hydroxyl number, amine equivalent and i.r. They were then converted to isocyanate-terminate prepolymers and then cured with diols and diamines. The resulting polymers were characterized by i.r., viscosity and density measurements.

INTRODUCTION

Polyurethanes have extensive and wide applications in various fields. Property variation is possible by use of reactants of different structures in their preparation. They are usually formed through the polyaddition of diisocyanates to hydroxy-terminated polyethers or polyesters. Polyethers are usually favoured in urethane technology because of their lower viscosity as well as good flexibility even at low temperatures. While three principal types of polyethers, viz. polyoxyethylene glycols, polyoxypropylene glycols and polyoxytetramethylene glycols [also known as polytetrahydrofuran (PTHF) glycols] find extensive application, the tetrahydrofuran (THF) based polymers have shown themselves to be superior to the others [1-4]. It has been shown that the THF based polymers [5] had secondary transitions operative well below the glass transition temperature (T_g) and hence make them useful far below their observed T_g .

In our earlier paper [6], we reported the preparation and properties of some chain extended THF-based polyurethanes. We now report some novel segmented copolyurethanes. Two different THF-based polymers viz. tetrahydroxy-terminated PTHF (PTHF 1 and 2) and amine-terminated PTHF (PTHF 3) were prepared and independently reacted with excess toluene diisocyanate (TDI) to give isocyanate-terminated prepolymers which were then cured with diols and diamines (Schemes 1 and 2). The prepolymers were characterized by hydroxyl number, amine equivalent, molecular weight and i.r. spectra. Properties such as viscosity, thermal stability and T_g of these derived polyureaurethanes, polyurethaneureas and polyureas are reported.

EXPERIMENTAL PROCEDURES

Methods and materials

The viscosity-average molecular weights of the PTHFs were determined from the intrinsic viscosities measured in

benzene at 30°C using the reported Mark-Houwink constants [7]. The hydroxyl number and amine equivalents of the PTHFs were estimated by standard methods [8, 9]. The i.r. spectra of the polymers were recorded in a Perkin-Elmer 257 spectrometer (KBr pellets). Density measurements were done with a pycnometer using hexane as non-solvent at 30°. The intrinsic viscosity measurements were made in an Ubbelohde suspended level viscometer. The T_g s of the polymers were determined by the dilatometric technique [10]. The thermograms of the polymers were recorded in a Stanton Thermobalance at a constant heating rate of 8°/min in air.

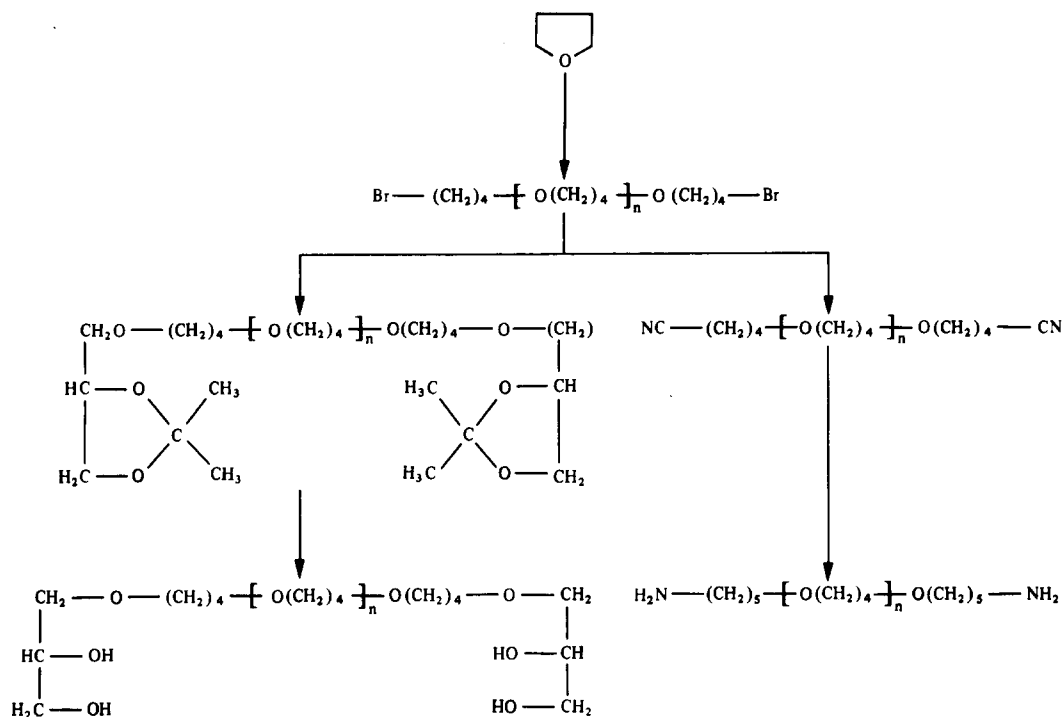
Boron trifluoride-etherate (Fluka AG) and TDI (80/20 mixture of 2,4- and 2,6-isomers, Riedel) were distilled before use. The THF, dioxane, isopropanol, triethylamine, ethylene glycol (EG) and diethylene glycol (DEG) (AR samples) were purified by literature methods [11]. Hexamethylenediamine (HMDA, BDH) and bis(4-amino,3-chlorophenyl)methane (MOCA, prepared from *o*-chloroaniline [12]) were freshly recrystallized and used as curing agents in the urea and urea-urethane preparation. Commercially available samples of polyoxyethylene glycol, with \bar{M}_w 6500, 1500 and 650 (PEG, Fluka AG) were used as such. Their hydroxyl numbers were estimated before use; PEG 6500 (Exp. (OH) 16.8, cal. 17.3) PEG 1500 (72.7 and 74.8) and PEG 650 (168.1 and 172.6). They were employed in the NCO-terminated prepolymer curing to obtain urethanes and urethane-ureas.

Tetrahydroxyl terminated PTHF [6]

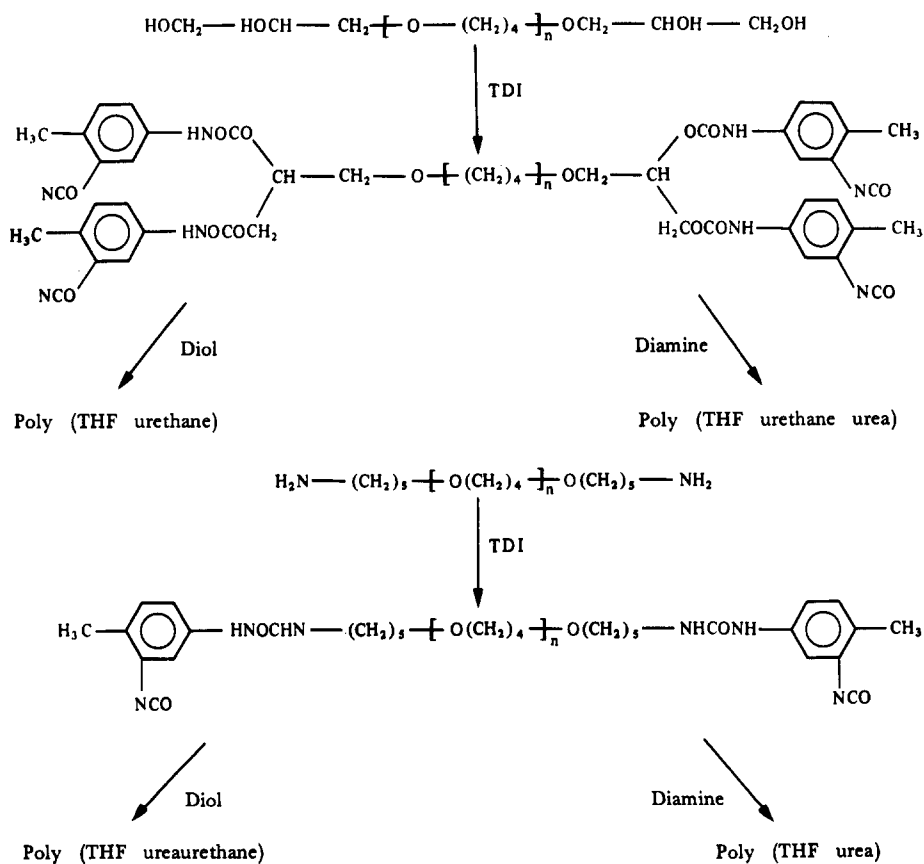
Dry THF (20 ml) was polymerized at -15° in a sealed tube with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (3 ml). After 2 hr the polymerization was terminated with HBr (3 ml 48%) and excess water was added to precipitate the polymer which was filtered, washed well with water and dried in vacuum. Bromine estimation indicated the bromine content to be 1.91 equivalents mol^{-1} . This bromine-containing PTHF was treated with monosodium acetone ketal of glycerol in dioxan at 80° for 10 hr. Washing the resulting polymer at 5-10° with 2% HCl for 2 hr led to the hydrolysis of the ketal and formation of PTHF-1 as a white powder. It was washed well with methanol to remove soluble low molecular weight intermediates. \bar{M}_w 10,200 \pm 100 i.r.(CHCl_3) 3240-3380 cm^{-1} (OH).

PTHF-2 of \bar{M}_w 3500 \pm 50 was prepared similarly from bromo-PTHF by terminating the polymerization of THF (20 ml) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (5.5 ml) after 1.5 hr with HBr (5 ml, 48%) Table 1.

*To whom all correspondence should be addressed.



Scheme 1



Scheme 2

Table I

PTHF, \bar{M}_w	Hydroxyl No.	
	Experimental	Calculated
10,200	21.3	21.9
3500	61.8	63.2

Amine-terminated PTHF-3

Bromine-terminated high molecular weight PTHF obtained earlier was converted to cyano-terminated PTHF with aqueous KCN (15 g, 50 ml water) in isopropanol as reaction medium at 80°. Hydrogenation of cyano PTHF in a autoclave with H_2 (20 atm) at 60° in isopropanol (200 ml) employing Raney Ni catalyst gave amine-terminated PTHF. i.r. ($CHCl_3$) $3380-40\text{ cm}^{-1}$ (NH_2 ; \bar{M}_w $10,200 \pm 100$ and amine equivalent: 1.87 group/mol.

Polymerization

PTHF-1. To a solution of TDI (5 mmol) in dry DMF (20 ml) warmed to 60°, a solution of PTHF-1 (1 mmol) and triethylamine (catalyst) (4.5 ml) in dry DMF (20 ml) was added during 10 min under N_2 and stirred for 1 hr. Then one of the curing agents (PEG, \bar{M}_w 6500, 1500 or 650 was added and the reaction mixture stirred at 60° for 3 hr. The solution was then poured into water, the precipitated polymer was filtered, washed with water and then hot acetone, and dried in vacuum. The use of PEG gave poly THF (urethane) in 65–70% yield.

The same reaction was repeated, but curing with amines (HMDA and MOCA) led to poly(THF-urethane-urea) in 70–74% yield.

PTHF-2. The reaction was performed as for PTHF-1 using PTHF-2 (1 mmol) to obtain the poly(THF-urethane) and poly(THF-urethane (urea)s in 75% yield.

PTHF-3. The amine-terminated PTHF-3 (2 mmol) was subjected to prepolymer-urea formation with excess TDI (5 mmol) and the resulting-NCO terminated prepolymer was cured with diols to give poly (THF-ureaurethane)s and with amines to give poly(THF-urea)s. The yields were in the range 65–85%.

RESULTS AND DISCUSSION

The i.r. spectra of the polymers showed characteristic absorption around $3280-40\text{ cm}^{-1}$ (NH) and an intense absorption around 1100 cm^{-1} ($-C-O-C-$). The diol-cured poly (THF-urethane)s had single carbonyl absorption around 1650 cm^{-1} . In the diamine cured polymers, due to the overlap of urea and urethane absorption, a broad band was seen in the region $1700-1640\text{ cm}^{-1}$.

The intrinsic viscosities were in the range 0.40–0.22 dl/g. The molecular weights of the poly-

mers were calculated from the intrinsic viscosities using Mark-Houwink constants $K = 2.27 \times 10^{-3}$ and $\alpha = 0.412$. These constants were computed from the viscosity values of PTHFs having different molecular weight, using DMF and benzene as solvents at 30°. The T_g s of the polymers were measured by dilatometry; they were in the range -40 to -70° . While T_g depended very much upon the nature of the starting prepolymer, the nature of the cure agent also influenced it. Increase in length of flexible ether links both in prepolymer and curing diols lower the T_g and all diol-cured polymers had lower T_g than amine-cured derivatives. That flexible groups had significant influence is also clear from the lower T_g s of HMDA derivatives compared to the aromatic MCCA derivatives.

Thermogravimetric analysis of the polymers showed that they had decomposition temperature (2% of weight loss was taken as the criterion for decomposition temperature) around 250–300°.

Acknowledgement—The authors thank ISRO, Govt of India for financial support, IIT Madras for facilities and RSIC, IIT Madras for spectral data.

REFERENCES

1. T. J. Dearlove, G. A. Campbell and R. P. Atkins. *J. appl. Polym. Sci.* **22**, 927 (1978).
2. T. J. Dearlove and G. A. Campbell. *J. appl. Polym. Sci.* **21**, 1499 (1977).
3. *Polymers in Space Research* (Edited by C. L. Segel, M. Shen and F. N. Kelley), pp. 331–345. Marcel Dekker, New York (1970).
4. J. Delmonte. *Adhesives Age* **18**(12), 29 (1975).
5. V. S. Lebdev, A. V. Simedrido and R. P. Shulgu. *Plast Massey (VSSR)* **1**, 6 (1987).
6. G. P. Rajendran, V. Mahadevan and M. Srinivasan. *Polym. J.* **13**, 99 (1981).
7. M. Kurata, M. Utiyama and K. Kamada. *Makromolek. Chem.* **88**, 281 (1965).
8. *Analytical Chemistry of Polyurethanes*, Vol. 14, Part III (Edited by D. J. David and H. B. Staley), p. 289. Wiley Interscience, New York (1969).
9. S. Siggia, J. G. Hanna and R. Culno. *Analyt. Chem.* **33**, 900 (1961). R. R. Koch. *J. Paint Technol.* **42** (543), 243 (1970).
10. J. D. Ferry and G. S. Parks. *J. chem. Phys.* **4**, 70 (1936). T. J. Gedemer. *Plast. Engng* **31**(2), 28 (1975).
11. A. I. Vogel. *Text Book of Practical Organic Chemistry*. Longman, Green, London (1978).
12. J. H. Billman, G. D. Thomas, M. Hedrick, G. Schrottenboer, D. K. Barries, J. Nemco, P. Trix and E. Cleveland. *J. org. Chem.* **11**, 773 (1946).