

## Thermoplastic urethane elastomers based on optically active poly(oxy-1,2-propylene)- $\alpha,\omega$ -diol

R. R. Aitken

Imperial Chemical Industries Limited, Organics Division, Hexagon House, Blackley, Manchester, M9 3DA, UK

It is now generally accepted that thermoplastic polyurethane elastomers which are derived from a polymeric diol, bis(4-isocyanatophenyl)methane (MDI) and 1,4-butanediol exist at equilibrium as two phase systems<sup>1</sup>. The continuous elastomeric soft phase consists of segments derived mainly from the polymeric diol in which are dispersed a proportion of the hard phase segments in the form of domains, these being derived from the MDI and butanediol.

The mechanical properties of such elastomers may be varied by varying the constitution of the polymeric diol<sup>2</sup>. At a given ratio of polymeric diol:MDI:butanediol and a given molecular weight for the polymeric diol, crystalline or partly crystalline polyesters as a general rule provide a higher level of mechanical properties in derived polyurethanes than crystalline or partly crystalline polyethers. This has been attributed to the stronger interchain forces between ester and urethane groups as opposed to those between ether and urethane groups<sup>2</sup>. An even lower level of mechanical properties has been reported for polyurethanes derived from the amorphous polyether, atactic poly(oxy-1,2-propylene)- $\alpha,\omega$ -diol (PPG) compared with the properties of a comparable polyurethane from poly(oxytetramethylene)- $\alpha,\omega$ -diol (PTHF) which is a crystalline polyether. The difference in this case has been attributed to the ability of the soft segment to crystallize in the derived polyurethane on the application of strain<sup>2</sup>.

The purpose of the present study was to test the hypothesis that the use of a crystalline PPG would result in polyurethanes having mechanical properties comparable with polyurethanes derived from PTHF.

### EXPERIMENTAL

(-)-(S)-Propylene oxide was made by the method of Golding *et al.*<sup>3</sup>. Atactic and optically active PPGs were made by reacting a solution of potassium hydroxide in propylene glycol with optically inactive and optically active propylene oxide respectively at elevated temperatures and pressures. Residual alkaline catalyst was removed by treatment with synthetic magnesium silicate.

Analysis of the polyethers so made, together with that of the PTHF ('Polymeg 2000' from Quaker Oats Ltd) is given in Table 1. Hydroxyl values were obtained by the acetylation method and were used to calculate the  $\bar{M}_n$  values cited. A du Pont Thermal Analyser was used to detect thermal transitions,  $T_g$  and  $T_m$ . The optical activity was

measured using a Perkin-Elmer 141 Polarimeter. A Bruker WH 90 NMR Spectrometer was used to measure <sup>13</sup>C n.m.r. spectra at 22.62 MHz.

Polyurethane elastomers were made from the polyethers by reaction at 80°C with an excess of MDI to give a prepolymer of isocyanate content 11.9% followed by reaction of the prepolymer with butanediol at 80°C. After completing reaction by heating at 110°C for 16 h the elastomers were granulated and injection moulded at 195°–205°C. The properties of the elastomers are given in Table 2.

Thermal transitions and optical activity were measured as described above. Stress/strain, hardness and tear strength properties were measured according to BS 903, Part 2; ASTM D790-71 and DIN 53507, respectively. A Perkin-Elmer 225 Spectrophotometer was used to record infra-red absorption spectra on films made by casting 10% solutions of the elastomer in dimethylformamide and allowing the solvent to evaporate.

### DISCUSSION

The lower melting point (35°C) of the optically active PPG used in this study, compared with that quoted by Shibatani *et al.*<sup>6</sup> for atactic PPG in a similar study, is probably attributable to the different methods of synthesis. Made by Shibatani's method the linkages in the PPG would be ex-

Table 1 Properties of polyethers

	PTHF	Atactic PPG	Optically active PPG
Hydroxyl value (mg KOH.g <sup>-1</sup> )	54.7	54.4	58.6
$\bar{M}_n$	2050	2060	1915
$T_g$ (°C)	-94	-76	-75
$T_m$ (°C)	38	—	35
Optical activity [ $\alpha$ ] <sub>D</sub> <sup>20</sup> (degrees)	—	0.000 <sup>a</sup>	-0.655 <sup>a</sup>
NHR resonances <sup>b</sup>			
75.70 ppm	—	Present	Present
75.60 ppm	—	Present	Absent
75.47 ppm	—	Present	Absent
73.72 ppm	—	Present	Present
73.52 ppm	—	Present	Absent

<sup>a</sup> 10% Solutions in dimethylformamide

<sup>b</sup> According to Oguni *et al.*<sup>5</sup> resonances at 75.70, 75.60 and 75.47 ppm from tetramethylsilane are methine resonances attributable to atactic, heterotactic and syndiotactic triads, those at 73.72 and 73.52 ppm to isotactic and syndiotactic diads arising from methylene groups

Table 2 Properties of polyetherurethanes

	PTHF	Atactic PPG	Optically active PPG
Appearance	Transparent	Turbid	Turbid
Optical activity [ $\alpha$ ] <sub>D</sub> <sup>20</sup> (degrees)	—	-0.002 <sup>a</sup>	-0.451 <sup>a</sup>
$T_g$ (°C)	-78	-53	-50
Main endotherm (°C)	193	198	196
Hardness (° Shore A)	94	94	94
Stress at rupture (MN.m <sup>-2</sup> )	38.7	26.5	34.2
Stress at 100% strain (MN.m <sup>-2</sup> )	13.8	13.8	16.0
Stress at 300% strain (MN.m <sup>-2</sup> )	23.2	20.4	23.9
Strain at rupture (%)	484	428	418
Tear strength (KN.m <sup>-1</sup> )	54	46	52
Infra-red analysis <sup>b</sup>			
Absorption at 3500 cm <sup>-1</sup>	Absent	Absent	Absent
Absorption at 3320 cm <sup>-1</sup>	Present	Present	Present
Ratio of peak heights at 1705 cm <sup>-1</sup> and 1730 cm <sup>-1</sup>	2.0	1.78	1.76

<sup>a</sup> 10% Solutions in dimethylformamide

<sup>b</sup> Absorptions at 3500, 3320, 1705 and 1730 cm<sup>-1</sup> are attributed to free NH, bonded NH, bonded carbonyl and free carbonyl, respectively

pected to be virtually 100% atactic and head-to-tail whereas in the optically active PPG of the present study some head-to-head linkages would be expected to be present<sup>7</sup>.

The  $T_g$  processes noted in all three elastomers at temperatures somewhat higher than the  $T_g$  processes in the corresponding polyethers together with the high-temperature endothermic processes is strong evidence for the typical two-phase structure of block copolyurethanes. Whilst there is no evidence from thermal analysis of crystallinity attributable to the polyether block in any of the polyurethanes the optical activity and therefore the ability to crystallise is shown to be retained in the polyurethane derived from the optically active PPG.

There is no clue from infra-red analysis as to why the optically active PPG should provide polyetherurethanes of improved mechanical properties over those derived from atactic PPG. However, the higher proportion of hydrogen-

bonded carbonyl in the PTHF-derived analogue may be indicative of a more perfect structure in this elastomer and hence provide at least part of the explanation of its improved mechanical properties. The likelihood of a more perfect structure in this elastomer is supported by the smaller change in  $T_g$  which occurs on conversion of the polyether to a polyurethane (16°C vs. about 25°C for both PPG types).

No direct evidence is available that strain-induced crystallization is the reason for the improved mechanical properties of the optically active PPG-derived elastomer. However, this seems a likely explanation and is in accord with the conclusions of Shibutani *et al.* from a study of comparable polyetherurethaneureas<sup>6</sup>.

#### ACKNOWLEDGEMENTS

The author wishes to acknowledge the assistance in this study of Dr R. Pierce (optically active propylene oxide preparation), Dr J. Hughes (optically active propylene oxide polymerization), Mr J. Hynds (preparation of elastomers), Dr A. M. Chippendale (n.m.r. interpretation), Mr E. Mather (optical activity measurements), Dr G. M. F. Jeffs and Dr A. Cunningham (thermal analysis) and Mr G. Dent (i.r. measurements).

#### REFERENCES

- 1 Wilkes, G. L. and Wildnauer, R. J. *Appl. Phys.* 1975, **46**, 4148
- 2 Allport, D. C. and Janes, W. H. 'Block Copolymers', Applied Science Publishers Ltd, London, 1973, pp 445-455
- 3 Golding, B. T., Hall, D. R. and Sakrikar, S. J. *Chem. Soc. (Perkin I)*, 1973, p 1214
- 4 Sorenson, W. R. and Campbell, T. W. 'Preparative Methods of Polymer Chemistry', Interscience, New York, 1968, p 155
- 5 Oguni, N., Lee, K. and Tani, H. *Macromolecules* 1972, **5**, 819
- 6 Shibutani, K., Lyman, D. J., Shieh, D. F. and Knutson, K. *J. Polym. Sci. (Polymer Chem. Edn)* 1977, **15**, 1655
- 7 St. Pierre, L. E., Polyethers Part I Polyalkylene Oxides and Other Polyethers (Gaylord N. G. Editor), Interscience, 1963, pp 135-8

## Electrical conductivity of polyvinylcarbazole—tetracyanoquinodimethane complexes

A. Kuczkowski, Z. Dreger, T. Stupkowski and B. Jachym  
Institute of Physics, Technical University of Gdańsk, Poland  
(Received 9 February 1979)

#### INTRODUCTION

Poly(vinyl carbazole) (PVK) and its charge transfer complexes have recently been investigated owing to possibilities of application of those materials in electrophotography. In comparison with other poly(vinyl carbazole) complexes, the complex with tetracyanoquinodimethane (TCNQ) has been described in only a few studies relating mainly to its spectral properties<sup>1-3</sup>. The electrical properties of the complex were described only by Taniguchi and coworkers<sup>1</sup>. By sedimen-

tation in chloroform, they obtained a series of complexes with the TCNQ:PVK molar ratio in the range 1:51 to 1:37, with a corresponding conductivity range 10<sup>-16</sup> to 10<sup>-14</sup> Ω<sup>-1</sup> cm<sup>-1</sup>.

In this paper, results of investigations on electrical conductivity are presented for poly(vinyl carbazole) — tetracyanoquinodimethane (PVK-TCNQ) complexes of TCNQ:PVK molar ratio\* from 1:111 to 1:2.2.

\* The term 'molar ratio' represents here the ratio of a number of TCNQ molecules to a number of monomer units