Synthesis and some properties of polyurethanes incorporating cycloalkyl rings in the main chain

John M. G. Cowie* and Hak H. Wu
Department of Chemistry, University of Stirling, Stirling FK9 4LA, Scotland, UK
(Received 28 September 1987; accepted 12 October 1987)

A series of polyurethanes have been prepared in which cycloalkane diols, ranging in ring size from 8 to 22 atoms, have been linked by diisocyanates such as hexamethylene diisocyanate, diphenylmethane-4,4'-diisocyanate and tolylene-2,4-diisocyanate. Glass and sub-glass transitions have been identified by differential scanning calorimetry and torsional braid analysis. The glass transition temperatures varied with both the type of linking unit and the ring size and passed through a maximum when the ring size was between 12 and 14 atoms. Sub-glass transitions in the temperature range 210–220 K were assigned to intramolecular relaxations in the rings while those located around 275–285 K were thought to be due to rotation of the amide groups.

(Keywords: polyurethanes; cycloalkyl rings; glass transition; secondary relaxations)

INTRODUCTION

It is now well established that localized groups in a polymer molecule are capable of undergoing relaxation processes in the glassy state. These sub-glass transition motions can influence the properties of the polymer and it has been suggested that some may even affect the toughness of the material. One type of group incorporated into a polymer molecule which has been studied in some depth is the cycloalkyl ring, which when it has a size of six atoms or greater is capable of undergoing intramolecular relaxations through conformational changes in the ring. Detailed investigations, of polyitaconates[1,2] and polymethacrylates[3] containing cycloalkyl rings pendant to the main chain, have been made in which these relaxation processes were found to occur in the glassy state. The mechanisms involved in these relaxations were identified and it was also observed that they appear to be decoupled from the main polymer backbone and independent of its structure. Consequently, the damping processes, which were found using dynamic mechanical measurements, did not seem to affect the general properties of the polymer to any significant extent.

These large rings may have more influence on the bulk properties if they are incorporated into the polymer backbone chain, where they might act to absorb energy transmitted along the chain more effectively than when placed in a pendant position.

It was decided to explore the feasibility of preparing this type of structure and to examine first the effect of ring size on polymer behaviour.

EXPERIMENTAL

Cycloalkane diol synthesis

cis-Cyclooctane-1,5-diol was purchased from Aldrich and distilled prior to use. All the other cycloalkane diols were synthesized using procedures outlined in the literature.

Cyclodecane-1,6-diol[4] was prepared by dehydrating decahydro-2-naphthol with P_2O_5 and H_3PO_4 to form first 9,10-octalin. This was converted to 9,10-decalin diol using formic acid and hydrogen peroxide followed by conversion to the diketone which was reduced with $LiAlH_4$ to the diol.

Cyclododecane-1,7-diol[5] was obtained by allowing cyclododeca-1,5,9-triene to isomerize on a surface prepared from sodium coated on rigorously dried aluminium oxide, to form bicyclo[5.5.0]dodecadiene. The latter was then partially hydrogenated to yield bicyclo[5.5.0]dodecane, which was converted to the diketone by ozonolysis. Reduction of the diketone by $LiAlH_4$ in tetrahydrofuran (THF) gave the required diol.

Cyclohexadecane-1,9-diol[6] was synthesized, starting from nonanedioic acid, which was converted to the diacid chloride and dehydrogenated using triethylamine to yield the bifunctional ketone derivative. Using high dilution conditions the cyclic ketone can be formed which, on hydrolysis and decarboxylation, gave the cyclic diketone. Reduction of the ketone gives the required diol.

Cyclooctadecane-1,10-diol[7] was prepared via a Dieckmann cyclization of diethyl sebacate using potassium *t*-butoxide in xylene under high dilution conditions. Following hydrolysis and decarboxylation, effected by overnight refluxing in the presence of 3 M HCl, the cyclooctadecane-1,10-dione was obtained and reduced to the diol using $LiAlH_4$/THF.

Cyclodoeicosane-1,12-diol[7] was prepared using conditions described above and a Dieckmann cyclization.

Polymerization

A number of polyurethanes were prepared in which cycloalkane diols of various sizes were linked by reaction with diisocyanates. Those used were hexamethylene diisocyanate (HDI), diphenylmethane-4,4'-diisocyanate (MDI) and tolylene-2,4-diisocyanate (TDI).

---

*To whom correspondence should be addressed

0032-3861/88/050934-04$03.00

It has been suggested by Lyman[8] that high molecular weight polyurethanes can be obtained in the absence of a catalyst if an aprotic solvent such as dimethylsulphoxide is used at reaction temperatures below 420 K. This approach was tested using cyclooctanediol and TDI but the product had a number-average molecular weight, M_n, of 4000 and an intrinsic viscosity of 0.097, measured in dimethylformamide at 323 K. Consequently two catalysts were used, stannous octoate and triethylenediamine. The former proved to be the better and at 2.8 % concentration produced polymer with an intrinsic viscosity of 0.157 compared with 0.144 for the triethylenediamine. Even better results were achieved by changing the solvent to chlorobenzene and using only 0.8 % stannous octoate. This yielded a polymer with an intrinsic viscosity of 0.345. Similar tests using MDI gave a product of $M_n = 12\,000$ (intrinsic viscosity 0.09) using stannous octoate in dimethyl sulphoxide, which could be increased to intrinsic viscosity 0.3 when the solvent was changed to chlorobenzene/stannous octoate.

Based on these observations all other polymers were prepared at temperatures between 370–380 K using chlorobenzene as solvent and stannous octoate (0.8 %) as catalyst.

Characterization

Viscosities were measured in a Cannon Ubbelohde viscometer using dimethylformamide as solvent at 323 K. Glass transition temperatures (T_g) were located using a Perkin–Elmer DSC2 differential scanning calorimeter interfaced with an Apple II microcomputer. The T_g was taken as the onset of the baseline shift which occurs during the transition. Dynamic mechanical measurements were made using a torsional braid analyser. Details of the method have been given elsewhere[9] and the data are displayed as $-\log(1/n)$ as a function of temperature, where n is the number of oscillations between two arbitrarily fixed boundaries on the decay curve. The parameter is proportional to the logarithmic decrement although the method is non-absolute. Spectra are displaced vertically for clarity in the figures.

RESULTS AND DISCUSSION

The synthesis of the larger cycloalkyl rings is quite difficult and only small quantities of ring sizes 12–22 were obtained. Enough of each was synthesized to allow an estimate of the effect of ring size and spacer stiffness on the T_g, but only in the case of the 8 and 10 membered rings was there sufficient polymer to measure the dynamic mechanical damping response.

Glass transitions

Table 1 Glass transition temperatures as a function of cycloalkyl ring size and type of diisocyanate linking unit

	T_g (d.s.c.) (K)		
Ring size	HDI	MDI	TDI
8	303	359	398
10	363	415	428
12	–	420	–
16	382	408	–
18	369	376	–
22	348	366	–
n-Butyl	–	–	346

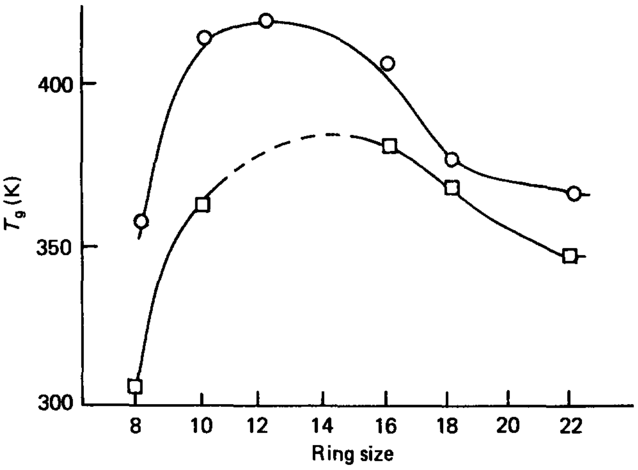


Figure 1 Variation of glass transition temperature, T_g, with the size of the cycloalkyl ring

Two sets of polyurethanes were prepared using HDI and MDI to link the cycloalkanediols into chains. The T_g of each is shown in *Table 1* and the trends in T_g as a function of ring size are more clearly seen in *Figure 1* for both series. The T_g is observed to increase from the cyclooctyl derivative and pass through a maximum value at ring sizes of between 12 and 14 atoms, before decreasing again as the rings become larger. This behaviour can be explained by assuming that any small change in the flexibility of the rings as they increase in size from 8 to 14 is submerged in the increase of the molar volume of the ring, which will sterically hinder rotation of the backbone chain making it inherently stiffer. The effect of this change in molar volume and shape can also be seen by comparing cyclooctyl rings linked by TDI with a polymer in which the ring is replaced by an n-butyl segment. The T_g of this butyl analogue (Bu-TDI), with one (CH_2) unit less than one side of the ring in the chain, is 52 K lower than the cyclooctyl (8-TDI) polymer. The increase in T_g is then due to the ring acting as a more rigid and much bulkier unit in the chain which impedes rotation of the adjacent segments and makes cooperative chain motion more difficult.

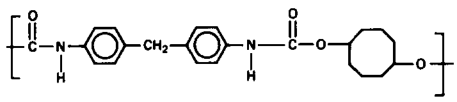
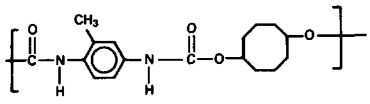
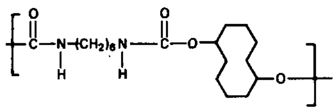
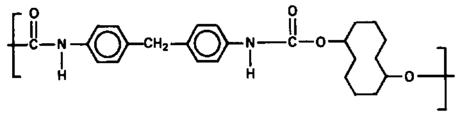
Eventually, as the ring size continues to increase it will act more like a flexible linear spacer in the chain which partially offsets the increase in molar volume. The T_g is then seen to decrease and approach a plateau value around the 22 atom ring size. Thus, small rings tend to act like large double bonds restricting chain motion thereby requiring that the ring moves as a complete bulky unit. As the ring size increases beyond 14 atoms it becomes floppier and the effect of its large molar volume is moderated because the ring can flex more easily hence the increase in T_g is less.

The effect of the rigidity of the linking unit can be seen by comparing the T_g values for two ring sizes and three diisocyanates, HDI, MDI and TDI. These are listed in *Table 1* and show, as expected, that T_g increases as the linking unit becomes more rigid, i.e. HDI < MDI < TDI.

Secondary relaxations

The dynamic mechanical damping spectra for the cyclooctyl and cyclodecyl polyurethanes are shown in *Figures 2* and *3*, respectively. Three secondary damping maxima can be located, only one of which is common to all the polymers. The temperatures at which these

Table 2 Glass and sub-glass transition temperatures for some polyurethanes with eight and ten membered cycloalkyl rings

Structure	Notation	Transition temperatures (K)			
		T_g	T_β	T_γ	T_δ
	8 MDI	359	277	211	–
	8 TDI	398	276	211	–
	10 HDI	363	–	219	163
	10 MDI	415	285	220	–

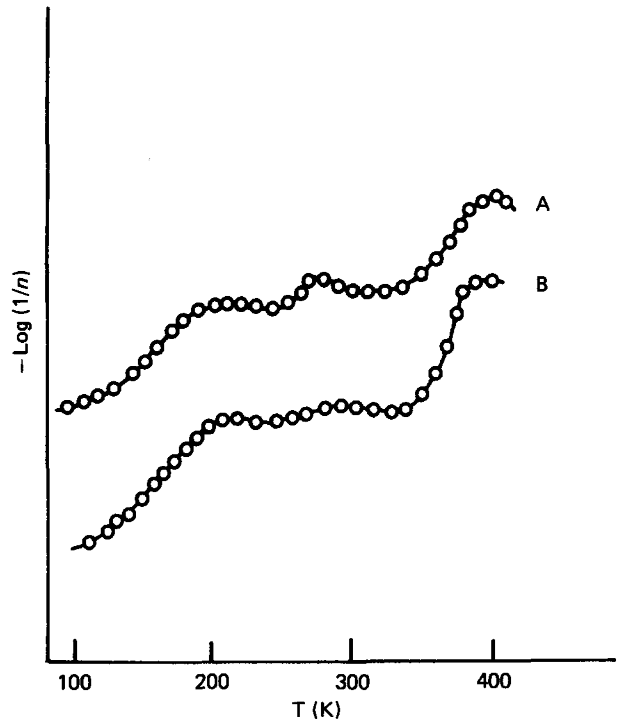


Figure 2 Temperature dependence of the mechanical damping index for samples: A, 8-TDI; B, 8-MDI

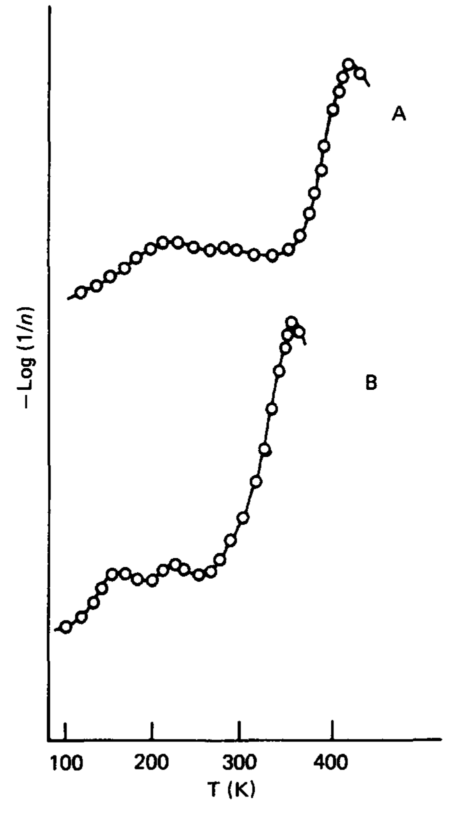


Figure 3 Temperature dependence of the mechanical damping index for samples: A, 10-MDI; B, 10-HDI

maxima appear are summarized in *Table 2*, and are designated T_β, T_γ and T_δ in order of decreasing temperature. These secondary relaxations do not appear to be affected by the nature of the diisocyanate linking unit when this is MDI or TDI and probably originate in the ring and connecting bonds which are common to the polymers. The 10 HDI polymer shows a δ peak which does result from the linking unit.

Cyclooctyl polymers. In previous work[1,2] it was observed that polyitaconates with pendant cyclooctyl rings displayed prominent damping peaks with maxima around 175 K (1 Hz). This was identified with intramolecular conformational changes in the cyclooctyl ring and the energies required to effect these changes matched the temperature in the 1 Hz spectrum at which the corresponding damping processes appeared. In the systems under consideration here the cyclooctyl ring is now joined at two points to the main chain rather than pendant, and consequently it would be expected that this would affect the ability of the ring to undergo some of these possible conformational changes. The temperature at which the relevant damping process appears should then be slightly higher and the most appropriate is the one appearing at 211 K, which would also reflect the correct

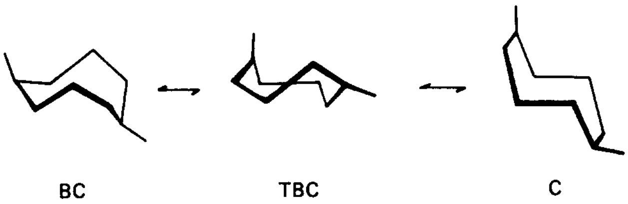


Figure 4 Conformational transformation from boat–chair (BC) through the twist–boat–chair (TBC) to the chair (C) form with minimal movement of stem bonds

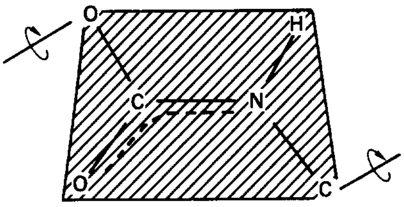


Figure 5 Schematic diagram of delocalized amide unit with suggested rigid plane of rotation

order of magnitude for the expected activation energy of $\sim 50\,\mathrm{kJ\,mol^{-1}}$ (ref. 10).

The lowest energy conformation for the cyclooctyl ring is the boat–chair–chair (BCC) form which can interconvert into nine other conformations with activation energy barriers of between 39 and 59 kJ mol^{-1} (ref. 10). The most probable transformations in the present systems will be those which can be effected without substantial perturbation of the bonds linking the ring to the chain, so that ring motion is then accomplished without having to move the adjacent chain segments to any significant extent. Assuming that the low energy BCC form is present in the chain the transformation which best satisfies the criteria of correct activation energy and the minimum stem bond displacement is movement through the twist–boat–chair (TBC) to the chair (C) form, as illustrated in *Figure 4*.

Cyclodecyl polymers. In the polyitaconates with pendant cyclodecyl rings the damping maximum associated with the intramolecular ring motion was located 10 K higher than in the cyclooctyl series[1]. In the polyurethanes the damping event at 220 K is common to both the HDI and MDI linked materials. This is assigned to cyclodecyl ring relaxation. The stable low energy conformers of the cyclodecyl unit are the distorted rectangular diamond lattice forms in which conformational interchanges are possible. However, it is difficult to be more precise about the nature of the process other than to say that these are feasible mechanisms.

β-relaxation. A second feature common to the more rigid polyurethanes, irrespective of ring size, is the damping peak lying in the range 275–285 K. A possible molecular mechanism for this relaxation could involve rotation of the amide (NH–CO) group as a complete unit. It has been postulated that this group can exist as a semi-rigid planar unit because of electron delocalization which imparts a resonance stabilization energy of ~ 85 kJ mol^{-1} to the unit. Thus it would be easier to rotate the whole group about the adjoining bonds, as shown in *Figure 5*, rather than move the (NH) and (CO) relative to one another. This assumes the absence of substantial hydrogen bonding which would make this motion more difficult.

γ-relaxation. In sample 10HDI a damping peak is resolved at 163 K which can be attributed to limited reorientation of the methylene sequence in the main chain. This type of relaxation has been identified in polyethylene and in polymers with pendant alkyl side-chains where the carbon sequence is 4 atoms[11]. Several mechanisms have been proposed for this relaxation including the Boyer crankshaft[12], which in its unstrained form is a $tg^+t \rightarrow tg^-t$ transformation, the Boyd–Brietling 'flip-flop' mechanism[13] involving a $tg^+tg^-tt \rightarrow ttg^+tg^-t$ movement, and a *gauche* bond transition $ttg^- \rightarrow g^-tt$ proposed by Cowie[14]. Each meets the appropriate energy and volume requirements for a relaxation process active in this temperature range and are all probable mechanisms.

CONCLUSIONS

It is possible to synthesize polyurethanes which incorporate cycloalkyl rings, of sizes ranging from 8 to 22 carbons atoms, into the main chain. The T_g values of these polymers are a function of both ring size and rigidity of the linking unit. A maximum in T_g is observed in polymers containing rings of 12 or 14 atoms and T_g decreases for both larger and smaller rings. Dynamic mechanical measurements indicate that there are several sub-glass transition relaxation processes. It is proposed that those in the temperature range 210–220 K are caused by conformational changes in the rings themselves whereas the damping processes around 275–285 K result from rotation of the amide link.

ACKNOWLEDGEMENTS

The authors wish to thank SERC for financial support which enabled them to undertake this project.

REFERENCES

1 Cowie, J. M. G. and McEwen, I. J. *Macromolecules* 1981, **14**, 1374
2 Cowie, J. M. G. and McEwen, I. J. *Macromolecules* 1981, **14**, 1378
3 Heijboer, J. and Pineri, M. in 'Non-metallics Materials and Composites at Low Temperatures', (Eds. G. Hartwig and D. Evans), Plenum Publ. Corp., New York, 1982, p. 89
4 Koli, A. K. *J. Indian Chem. Soc.* 1974, **L1**, 1012
5 Alvick, T. and Dale, J. *Acta Chem. Scand., Short Commun.* 1971, **25**, 1153
6 Blomquist, A. T., Prager, J. and Wolinsky, J. *J. Am. Chem. Soc.* 1955, **77**, 1804
7 Leonard, N. J. and Schimelpfenig, C. W. *J. Am. Chem. Soc.* 1958, **23**, 1708
8 Lyman, D. J. *Rev. Macromol. Chem.* 1966, **1**, 191
9 Cowie, J. M. G., Henshall, S. A. E., McEwen, I. J. and Velickovic, J. *Polymer* 1977, **18**, 612
10 Anet, F. A. L. and Krane, J. *Tetrahedron Lett.* 1973, **50**, 5029
11 Shimizu, K., Yano, O. and Wada, Y. *J. Polym. Sci., Polym. Phys. Edn.* 1975, **13**, 1959
12 Boyer, R. F. *Rubber Chem. Technol.* 1963, **36**, 1303
13 Boyd, R. J. and Breitling, S. M. *Macromolecules* 1974, **7**, 855
14 Cowie, J. M. G. *J. Macromol. Sci., Phys. (B)* 1980, **18**, 569