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which gives rise to over-adsorption if the exchange rate is low, will be of interest in the future.

Registry No. Polystyrene, 9003-53-6.

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Polyureas Containing Diaza Crown Ether Units: Synthesis and Influence of Ring Size on the Glass Transitions and Secondary Relaxation Processes

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ABSTRACT: A series of polyureas have been prepared by linking together diaza crown ether units of sizes 12, 18, and 24 atoms by using diisocyanates of differing rigidity. Measurement of the glass transition temperature, T_g, showed that as the ring size increased from 12 to 24 atoms, T_g decreased in polymers with a common linking unit. When the ring size was held constant, T_g varied with the flexibility of the spacing unit. Several secondary relaxations were located. It was possible to identify intramolecular relaxation processes in the diaza crown ring that occurred at decreasing temperatures as the ring size increased in the order 200 K (12-crown) > 152 K (18-crown) > 148 K (24-crown) when methylenedi-*p*-phenylene diisocyanate was the linking unit. Tentative assignments for other relaxation processes were also made that involved rotation of the amide unit.

Introduction

Studies of the dynamic mechanical behavior of polymers containing large ring units, in excess of six atoms, have largely been confined to structures in which the ring is pendant to the main chain. Intramolecular relaxations in cycloalkyl rings attached to polyitaconate[1,2] and polymethacrylate[3] backbones have been studied in some detail from investigations of the glassy state in these systems. We have recently reported[4] the effect of incorporating cycloalkyl rings with sizes from 8 to 22 carbon atoms into linear polyurethane structures and have now extended this to aza crown ether rings, which might be expected to be inherently more flexible. In this paper an examination of the dynamic mechanical response of polyureas, containing in the main chain 12-, 18-, and 24-membered aza crown ether structures, is presented.

Experimental Section

Diaza crown ethers were synthesised by using a high-dilution technique and following the general procedures described by Lehn.[5] The major steps are outlined for the 12- and 24-membered rings, which had to be prepared, whereas the diaza-18-crown-6 ether (kryptofix 2,2) was available commerically and purchased from Merck.

Synthesis of 5,9-Dioxo-1,7-dioxa-4,10-diazacyclododecane. A solution of 3.24 g of 1,5-diamino-3-oxapentane in 32 cm^3 of anhydrous benzene and a solution of 2.68 g of diglycolic acid dichloride in 32 cm^3 of anhydrous benzene were added to 500 cm^3 of benzene over a 50-min period, under a nitrogen atmosphere, with vigorous stirring. After the residue was filtered and washed, the solutions were evaporated to dryness, leaving a solid that was recrystallized from a hot mixture of chloroform and heptane to give the required product: mp 172 °C; ^{1}H NMR (CDCl$_3$) 3.6 (m), 4.5 (s), and 7.65 (br) ppm.

Synthesis of 1,7-Dioxa-4,10-diazacyclododecane. A suspension of 5,9-dioxo-1,7-dioxa-4,10-diazacyclododecane (0.6 g) in hot anhydrous tetrahydrofuran (20 cm^3) was added to $LiAlH_4$ (0.6 g) in THF (15 cm^3) over a period of 1 h. The mixture was refluxed with stirring under nitrogen for 18 h and then cooled to room temperature. Excess $LiAlH_4$ was removed by adding a water/THF mixture (50/50) followed by sodium hydroxide and more water. The mixture was then filtered, and the solvent evaporated to leave a residue that was passed through a neutral column with benzene as eluant. Recrystallization from benzene gave the desired product: mp 83–84 °C; ^{1}H NMR (CDCl$_3$) 2.4 (s), 2.8 (t), and 3.66 (t) ppm; trivial name diaza-12-crown-4 ether.

Synthesis of 1,7,10,13,19,22-Hexaoxa-4,16-diazacyclotetracosane. A high-dilution technique was used to prepare first the precursor 5,15-dioxo-1,7,10,13,19,22-hexaoxa-4,16-diazacyclotetracosane. Benzene solutions of 1,11-diamino-3,6,9-trioxaundecane (8 g/300 cm^3) and tetraglycolyl chloride (5.4 g/300 cm^3) were added, with vigorous stirring, over a period of 20 h to anhydrous benzene (800 cm^3) under a nitrogen atmosphere. A viscous oil was isolated from this reaction, and this was reduced

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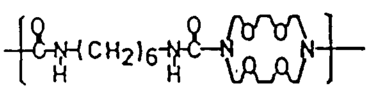
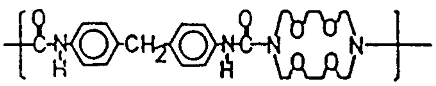
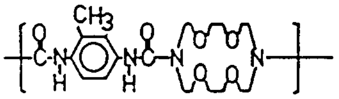
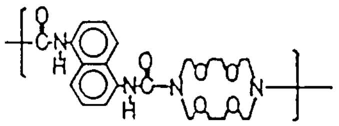
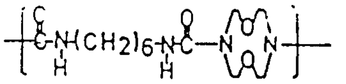
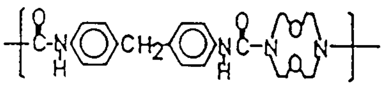
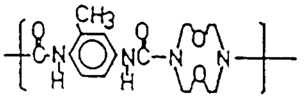
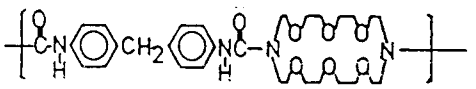
Table I
Glass and Subglass Transition Temperatures Measured by DSC and TBA, Respectively, for a Series of Polyureas Incorporating Diaza Crown Ether Rings

		DSC		TBA	
polymer structure	notation	T_g, K	T_β, K	T_γ, K	T_δ, K
	HDI-AZA-18C	303		216	160
	MDI-AZA-18C	387	280	212	152
	TDI-AZA-18C	392	260	216	160
	NDI-AZA-18C	413	288	216	164
	HDI-AZA-12C	315		208	136
	MDI-AZA-12C	455		200	
	TDI-AZA-12C	470		200	
	MDI-AZA-24C	380	284	200	148

by using $LiAlH_4$ in THF solution at 70 °C for 24 h. The product was analyzed: ^1H NMR ($CDCl_3$) 3.5–3.9 (br) and 4.0–4.3 (br) ppm. This was consistent with the desired product; trivial name diaza-24-crown-8 ether.

Polymerization. Polymers were prepared by linking the diaza crown ethers together by using diisocyanates. Four were used to give a range of rigidity in the linking unit; these were hexamethylene diisocyanate (HDI), methylenedi-*p*-diphenylene diisocyanate (MDI), 2,4-tolylene diisocyanate (TDI), and 1,5-naphthalenediyl diisocyanate (NDI). The diisocyanates were purified by vacuum sublimation before use. In each case stannous octoate was added as catalyst at a concentration of 0.8% on the basis of the amount of the ring present in the reaction. The solvent was chlorobenzene, and the polymerization reaction was carried out at 100 °C for 24 h.[4]

Torsional Braid Analysis. The dynamic mechanical behavior of the samples was investigated by using a torsional braid analyzer (TBA) that has a nominal frequency of 1 Hz. A glass fiber braid was impregnated with the polymer sample by immersion in a 10% solution of the polymer under study. This composite was then thoroughly dried with the braid held under slight tension and then loaded into the instrument. The method of measurement has been described in detail elsewhere.[6] The data are displayed as $-\log(1/n)$ against temperature, where n is the number of oscillations occurring between two fixed boundary amplitudes in the decay wave. While the method is nonabsolute, $\log(1/n)$ is proportional to the logarithmic decrement and gives good comparative studies of the damping behavior.

Glass Transition Temperatures (T_g). A Perkin-Elmer DSC2 differential scanning calorimeter was used to measure T_g, which was taken as the onset of the base-line shift, at a scanning rate of 20 K/min.

Results and Discussion

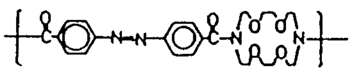
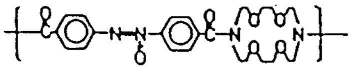
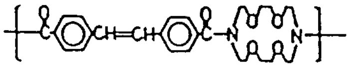
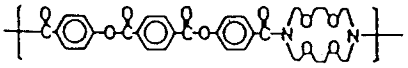
The glass and subglass transitions were located in the polyureas by using both DSC and TBA. The effect of ring size and the rigidity of the interring linking unit on T_g can be assessed from the data that are listed in Table I.

Glass Transition Temperatures. As expected, the T_g for each series of polyureas with a fixed ring size increases with increasing rigidity of the linking diisocyanate unit in the order HDI < MDI < TDI < NDI, with T_g for the very flexible HDI polymers being about 110 K lower than the most rigid NDI polymer in the diaza-18-crown-6 series. From examination of the DSC scans there is no evidence of crystallinity in these polymers, although there are hydrogen bonding sites that might be expected to encourage some molecular ordering in the polymer matrix. The flexibility of the ring in each case appears to be sufficient to maintain disorder in the system and to produce an essentially amorphous material.

Hydrogen bonding in these polymers may actually hinder chain rotation and raise T_g, however, and a comparison with a comparable series of polyamides illustrates this effect. These polyamides were synthesized with different linking units as shown in Table II, and it can be seen that the T_g values are generally lower when the hydrogen atom is no longer attached to the nitrogen atom so that hydrogen bonding is now nonexistent in these structures. This series is included here purely for comparison of T_g values; the polymers were found to display some liquid crystalline characteristics and are discussed more fully in another publication.[7]

The effect of ring flexibility can be gauged by comparing the samples in which the three sizes of ring are linked by a common unit MDI. This shows that T_g is highest for the 12-membered ring and decreases as the ring size increases. However, the difference in T_g between the diaza-18- and diaza-24-crown rings is only 7 K, indicating that the influence of ring flexibility becomes less pronounced once the ring size exceeds about 20 atoms. The behavior is similar to that observed in a series of polyurethanes containing cycloalkyl rings ranging in size from 8 to 22 carbon

Table II
Glass and Subglass Transitions in Polymers Containing Diaza-18-crown-6 Linked by Various Mesogenic Units

polymer structure	notation	T_g,[a] K	T_β, K
	AZO-AZA-18C	355	156
	AZOXY-AZA-18C	349	164
	STIL-AZA-18C	386	156
	TA-AZA-18C	317	140

[a] DSC.

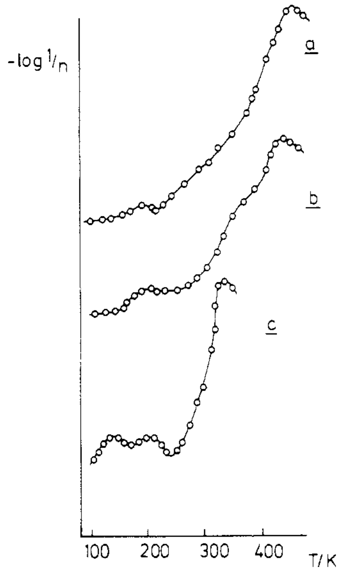


Figure 1. Temperature dependence of the damping index for (a) TDI-AZA-12C, (b) MDI-AZA-12C, and (c) HDI-AZA-12C.

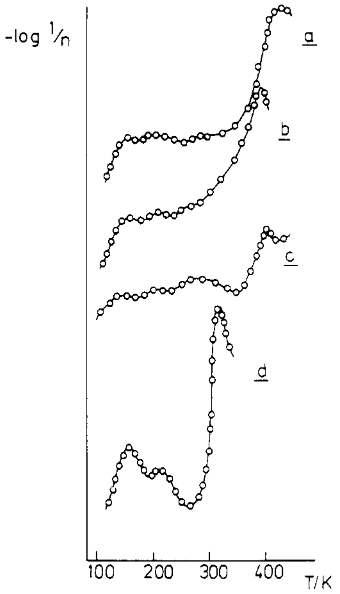


Figure 2. Temperature dependence of the damping index for (a) NDI-AZA-18C, (b) TDI-AZA-18C, (c) MDI-AZA-18C, and (d) HDI-AZA-18C.

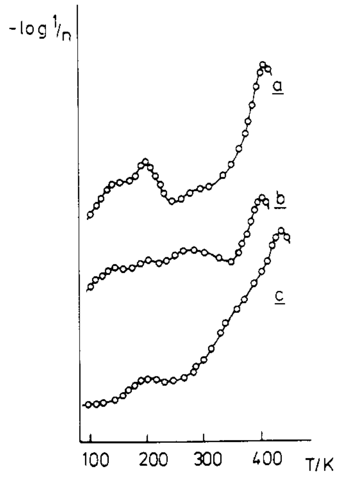


Figure 3. Comparison of damping response of (a) MDI-AZA-24C with corresponding samples with the same linking unit but smaller rings, (b) MDI-AZA-18C, and (c) MDI-AZA-12C.

atoms.[4] It was found that T_g increased up to a ring size of 12–14 carbon atoms and then decreased as the ring expanded to 22 atoms, and again the change in T_g became smaller when the ring size exceeded 18 atoms.

Secondary Relaxation Processes. The damping spectra for the polyureas with differing ring sizes are shown in Figures 1–3, with the spectra displaced vertically for convenience. Up to three damping peaks can be located below the T_g, and these are clearly seen in the most complete series prepared from the diaza-18-crown-6 unit. The relaxations have been designated β, γ, δ in order of decreasing temperature, and the corresponding temperatures of the damping maxima are recorded in Table I as T_β, T_γ, and T_δ. This terminology is not meant to imply that the molecular mechanisms for the relaxations classified in this way are the same in different polymers, as will become clear in the analysis to follow.

δ-Relaxation (136–164 K). The damping maxima observed in the temperature region 130–170 K may have different molecular origins depending on the structure of the polymer. In the diaza-12-crown series there is evidence of a damping peak at 136 K only in the HDI-AZA-12C polymer, whereas nothing can be detected in this region for the other two samples. Examination of the structures shows that the HDI-AZA-12C sample has a sequence of six methylene units in the main chain. It has been suggested that in polyethylene and related structures, limited bond reorientation can take place in a six-carbon sequence. More intensively studied have been relaxations in polymers with alkane side chains which show mechanical damping maxima at ~120 K (1 Hz) when there are sequences of C–C–C–C– or O–C–C–C or greater in the side chain, and the temperature of the damping maximum is also found to remain unchanged with the length of this side chain once it reaches or exceeds four atoms.[8] One of the earlier

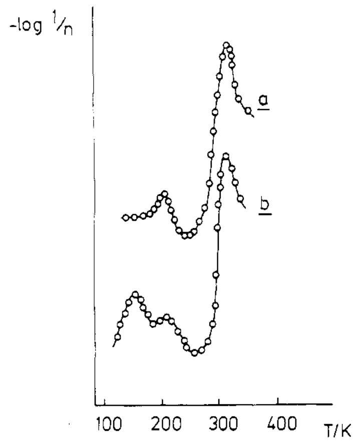


Figure 4. Damping characteristics for sample HDI-AZA-18C (a) with added KSCN and (b) without the salt.

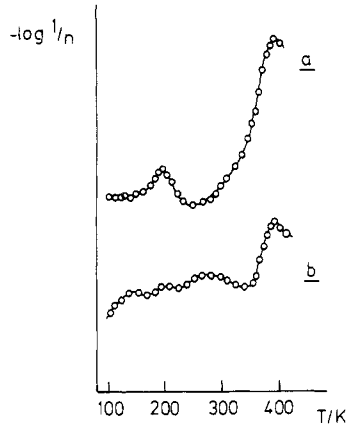


Figure 5. Damping characteristics for sample MDI-AZA-18C (a) with added KSCN and (b) without the salt.

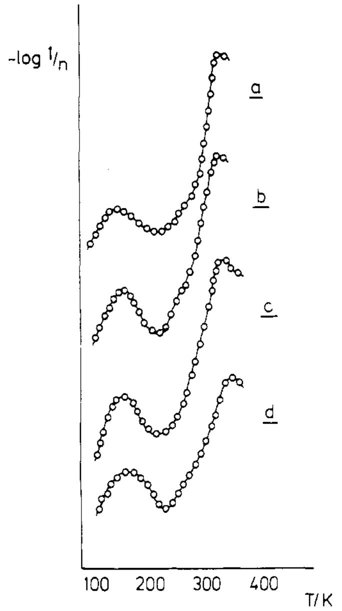


Figure 6. Damping index presented as a function of temperature for samples (a) TA-AZA-18C, (b) STIL-AZA-18C, (c) AZO-AZA-18C, and (d) AZOXY-AZA-18C.

molecular mechanisms proposed as an explanation for this type of relaxation was the Schatski "crankshaft", which involved rotation of a six-atom unit with bonds 1 and 7 collinear. This latter requirement is rather restrictive, and other more feasible mechanisms have since been proposed. These include the Boyer[9] and Boyd–Breitling[10] "flip-flop" model and a gauche bond migration mechanism[11] (ttg$^-$ → g$^-$tt), all of which are more probable from the point of view of both the volume requirements of the molecular rearrangements involved and the activation energies needed for each process. It is likely that relaxations involving these latter mechanisms would be appropriate for the process detected in HDI-AZA-12C, associated with the methylene sequences spacing the rings.

Damping maxima in the 148–164 K range were also detected in the diaza-18-crown-6 and diaza-24-crown-6 polymers, where only in one case, the HDI-AZA-18C, could one say that the relaxation mechanism described above would be an appropriate explanation. In previous studies[1,2] of the dynamic mechanical response of polymers with pendant cycloalkyl rings ranging in size from 7 to 12 carbon atoms, damping maxima were located at temperatures between 113 and 184 K, which were identified as being caused by intramolecular motions within the ring systems. These involved molecular rearrangements of the rings as they adopted different conformations under the application of a stress. Such conformational changes are also possible in the crown ether ring systems, but first a more positive identification of the damping due to the ring may be possible. Addition of an alkali-metal salt to a crown ether usually results in coordination of the cation by the ether oxygens. If a cation of a size comparable to that of the cavity in the crown ether is used, coordination will stiffen the ring and so restrict intramolecular motion. This could suppress the damping arising from these ring conformational changes.

Potassium thiocyanate was added to samples HDI-AZA-18C and MDI-AZA-18C in quantities sufficient to ensure interaction of K$^+$ with the majority of rings present in the polymer. The damping spectra obtained are shown in Figures 4 and 5. In HDI-AZA-18C there is suppression of the peak at 160 K, whereas that at 216 K remained unaffected. In sample MDI-AZA-18C, the peaks at 152 and 280 K were suppressed, while the peak at 212 K was again unchanged.

This would lead to an interpretation of the damping maxima in the 148–164 K range as being caused by intramolecular motion in the diaza crown ether unit for both diaza-18- and diaza-24-crown rings. This conclusion is supported further by inspection of the damping behavior of the polyamide series described in Table II, as seen from Figure 6. Only two major damping features are seen in this polyamide group, one due to the T_g at the higher temperatures and one feature in each polymer centred in the range 140–164 K. This must come from the one structural feature common to these four polymers, namely, the diaza-18-crown-6 ring.

In the polymers containing the diaza-12-crown-4 rings there is no damping peak below 200 K for MDI-AZA-12C or TDI-AZA-12C, and so ring motion is assigned to the damping peaks at 200–208 K. This suggests that in line with the T_g trends, the motion in the ring is energetically more demanding as the ring size decreases and the ease of ring relaxation follows the sequence, represented by the polymer series having MDI as the linking unit, as $\sim$200 K (12-crown) > 152 K (18-crown) > 148 K (24-crown). This trend is mirrored in the T_g values for these polymers.

Some conformational interchange sequences have been proposed by Dale[12] for both 12- and 18-crown ether structures. The suggested conformation for a 12-crown ether is a [3333] structure, which can undergo a full site exchange in a four-step cycle. The activation energy for this is estimated to be about 30 kJ mol^{-1} for the free molecule, but one would expect this to be somewhat higher when the ring is anchored at two points in a polymer chain.

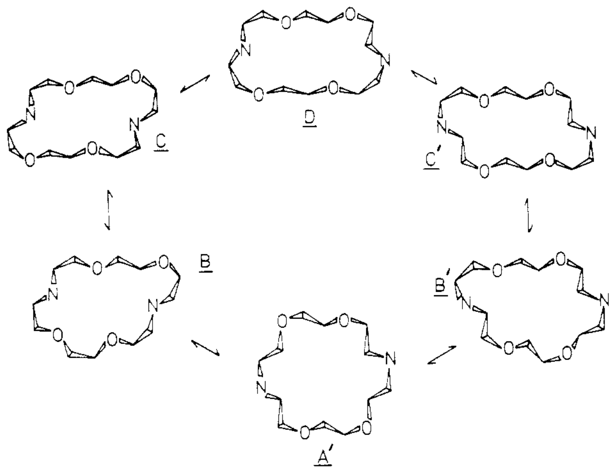


Figure 7. Proposed conformational change sequence for an 18-crown-6 ether through C → D → C′ → B′ → A′ → B → C.

The estimated activation energy for the 12-crown-6 relaxation in these polyureas is ~50 kJ mol^{-1}.

Dale[12] has also proposed the six-step total interconversion cycle for an 18-crown-6-ether, which is shown in Figure 7. Conformation C has been identified as that assumed in the noncomplexed hexaoxa ring in the crystalline state,[13] whereas conformation A is the one adopted when the ring is complexed with a potassium ion. The proposed interchange cycle is C → D → C′ → B′ → A′ → B → C, but no estimates of the activation energy are available for this system. Our own estimates of the energies involved in the diaza-18- and diaza-24-crown ether ring relaxations are ~38–40 and ~37 kJ mol^{-1}, respectively, based on our previous investigations.[1,2]

γ-Relaxation (200–216 K). In the diaza-12-crown-4 series the relaxation observed in this temperature regime is identified as a process associated with the intramolecular motions in the ring. This is not the case for larger rings where this damping peak in the diaza-18-crown-6 ring series remained unaffected by doping with a potassium salt.

There is no comparable damping maximum in this region for the polyamide series, and if the structural differences are examined, then the NH group in the polyureas is the one most likely to be involved in this relaxation process. A dielectric loss peak in the range 190–210 K (1 Hz) has been located in nylon 6,6 and nylon 6,10 by Curtis,[14] who has suggested that water becomes attached to the amide link and that the water–polymer complex then relaxes in this temperature range. Although the samples were dried carefully before use, it would be difficult to eliminate water entirely, and this type of mechanism may be responsible for the damping observed in the polymers. An alternative suggestion by Woodward et al.[15] to explain a damping peak at 210 K (1 Hz) in nylon 6,12 did not involve water, but considered that motion in the non-hydrogen-bonded NH was a likely mechanism. Thus the γ-relaxation could be associated with motion of the NH group possibly involving some bound water.

β-Relaxation (260–290 K). This relaxation is not clearly resolved in the 12-crown series nor in sample HDI-AZA-18C, where the glass transition occurs at a lower temperature and may overlap the damping process. In the 18-crown series the damping peak is suppressed by the addition of a potassium salt, and so this molecular relaxation may be coupled with the ring and is apparently impeded as the ring becomes more rigid. It is difficult to determine unequivocally what the molecular mechanism for this event might be, but if it is to be coupled with ring motion then rotation of the complete NHCO unit should be considered. This unit can be regarded as a relatively rigid planar structure because of the possibility of resonance stabilization, and in proteins rotation of these complete "amide planes" about the bond joining the α-carbon atom has been proposed when describing the formation of secondary structures. Extending the concept to these polymers, the rigid amide unit usually lies between a phenyl ring and the flexible diaza crown ether unit (except for the HDI-linked polymers, where this damping peak is unresolved). If the crown ether structure was made more rigid, by coordination with the cations from the salt, then the rotation of the "amide plane" would become more difficult as it would by lying between two essentially inflexible units. Interaction of the amide with the salt cannot be ruled out, and again this would impede rotation although this effect might be much weaker than the coordination of the cation with the ring.

Further indirect evidence to support the idea of motion of the NHCO group being responsible for this relaxation comes from inspection of the damping spectra in Figure 6. Here there is no sign of a damping maximum in this temperature range, and as polymers lack the NHCO structure, this indicates the possibility that this unit is involved.

These assignments for the β- and γ-relaxations are, however, rather tentative and would require further confirmation.

Conclusions

It is possible to prepare polyureas containing large diaza crown ether rings that can act as flexible units in the chain. The T_g of these polymers is a function of both the rigidity of the diisocyanate linking unit and the size of the ring. In particular it was found that T_g decreased as the ring size increased from 12 to 24. This indicates that ring flexibility increases the bigger the ring and becomes more dominant than the large molar volume of the ring in determining the overall rigidity of the chain or the ease with which cooperative motion can take place. Several subglass transitions were observed and identified as being caused by conformational changes in the rings and relaxations involving the amide group.

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Registry No. (HDI)(AZA-18C) (copolymer), 75969-48-1; (HDI)(AZA-18C) (SRU), 75981-20-3; (MDI)(AZA-18C) (copolymer), 41385-70-0; (MDI)(AZA-18C) (SRU), 41310-08-1; (TDI)(AZA-18C) (copolymer), 41385-66-4; (TDI)(AAZ-18C) (SRU), 114299-53-5; (NDI)(AZA-18C) (copolymer), 114274-66-7; (NDI)(AZA-18C) (SRU), 114274-65-6; (HDI)(AZA-12C) (copolymer), 114274-67-8; (HDI)(AZA-12C) (SRU), 114274-64-5; (MDI)(AZA-12C) (copolymer), 114274-68-9; (MDI)(AZA-12C) (SRU), 114274-63-4; (TDI)(AZA-12C) (copolymer), 114274-69-0; (TDI)(AZA-12C) (SRU), 114299-52-4; (MDI)(AZA-24C) (copolymer), 114274-70-3; (MDI)(AZA-24C) (SRU), 114274-62-3; KSCN, 333-20-0; diaza-24-crown-8 ether, 31255-17-1; 1,5-diamino-3-oxapentane, 2752-17-2; diglycodic acid dichloride, 21062-20-4; 5,9-dioxo-1,7-dioxa-4,10-diazacyclodecane, 31249-98-6; diaza-12-crown-4 ether, 294-92-8.

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Mechanical and Dielectric Relaxations in Cycloaliphatic Polyester Networks

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ABSTRACT: Dielectric and mechanical loss tangent measurements performed on networks prepared from the cis (PCCS), trans (PTCS), and cis/trans (50/50, PCC) isomers of poly(oxymethylene-1,4-cyclohexylenemethyleneoxysebacoyl) present a well-defined α absorption associated with the glass–rubber transition, whose location and strength depends on the presence of crystallites on the samples. The α mechanical absorption at 1 Hz corresponding to amorphous PCCS and PCC networks is centered at −26 °C in both cases; however, the maximum of the peak is shifted to −17 °C for PTCS networks quenched from the melt. Only a weak dielectric α process is detected at low frequencies in the latter networks due to the presence of crystallites that presumably preclude the possibility that amorphous-phase dipoles can relax over all directions. Two subglass mechanical relaxations labeled β and γ and located at −60 and −140 °C (at 1 Hz), respectively, appear in both PCCS and PCC networks, whereas the relaxation spectra of PTCS networks present at 0.1 Hz a broad subglass β absorption that can be resolved in two overlapping peaks centered at −80 (β_1) and −105 °C (β_2). The fact that the mechanical relaxation spectra of PCCS and PCC are similar suggests that the β relaxation in PTCS must be associated with molecular motion modes involving more than two structural units. However, the dielectric loss tangent versus temperature plot of PCC presents in the subglass region all the absorptions corresponding to the parent homopolymers. The critical interpretation of the dielectric relaxation behavior of the networks indicates that subglass dielectric absorptions are probably caused by conformational changes that take place in the glycol residue, whereas the mechanical responses may be caused by molecular motions in which conformational changes take part that involve skeletal bonds beyond those of the glycol residue.

Introduction

In recent years attention has been paid to the studies of relaxation phenomena in aliphatic polyesters after a long period of relative neglect.[1–8] These systems show a well-developed glass–rubber transition that in some cases, owing to the relative low melting point of some members of the family, tend to interfere with the observation of crystalline α_c processes; consequently, the notation β is used to denote this transition. Below the β peak another prominent absorption appears, labeled γ, that can extend over an interval of temperature of ca. 100 °C, and its behavior is similar to the γ processes in polyethylene. Most of the investigations in these polymers were undertaken with the aim of elucidating the nature of the molecular motions that occurring either in the amorphous or in the crystalline phases give rise to the mechanical and dielectric relaxations observed in polymers in general.[6]

An important family of polyesters, from a basic point of view, is the one formed by polymers obtained by condensation of aliphatic diacids and glycols containing a cyclohexane residue in their structure.[9,10] The mechanical and dielectric properties should be strongly dependent on both the conformations of the cyclohexane ring and the relative positions of the carbon atoms in the cyclohexane in which the substitution of the hydrogen atoms is performed. Although three conformations (chair, boat, and skew) are possible for cyclohexane, it seems that this ring in the cycloaliphatic polyesters is in the chair form.[9,10] In the case of 1,4-disubstituted cyclohexanes, the equatorially substituted chair forms give rise to the trans isomers, whereas cis isomers are obtained if the substitution is equatorial/axial.

This work describes the results obtained from isocronal experiments performed on model networks prepared from the cis, trans, and copolymers cis/trans isomers of poly(oxymethylene-1,4-cyclohexylenemethyleneoxysebacoyl) (PCS) chains. Attempts have also been made to establish the molecular interpretation of the relaxations observed.

Experimental Section

Synthesis of the Polyesters. Hydroxyl-terminated chains of poly(oxymethylene-1,4-*trans*-cyclohexylenemethyleneoxysebacoyl) (PTCS), poly(oxymethylene-1,4-*cis*-cyclohexylenemethyleneoxysebacoyl) (PCCS), and the copolymer (50/50) of poly(oxymethylene-1,4-*cis*/*trans*-cyclohexylenemethyleneoxysebacoyl) (PCC) were obtained by condensation of sebacic acid with the corresponding isomers of 1,4-cyclohexanedimethanol. The polymerization was carried out in xylene solutions by using the procedure described elsewhere.[9] The glycol trans isomer had previously been isolated from the commercial mixtures of cis and trans (30/70) isomers by recrystallization from ethyl acetate. In the same way, 1,4-*cis*-cyclohexanedimethanol had been obtained by acetylation of commercial 1,4-cyclohexanedimethanol with acetic anhydride by using the method given in ref 9. The all-planar conformations of the repeating units of PTCS and PCCS are shown in Figure 1.

Preparation of the Networks. PTCS, PCCS, and PCC chains of number-average molecular weights 6000, 7200, and 6800, re-

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