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Intramolecular Motion in Flexible Cycloalkyl Rings, Ranging from Cycloheptyl to Cyclododecyl, Contained in the Side Chains of Poly(dicycloalkyl itaconates)

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ABSTRACT: The dynamic mechanical behavior of a series of poly(itaconic acid diesters) containing pendant cycloalkyl rings has been investigated. Ring sizes vary from the cycloheptyl to the cyclododecyl. In these polymers, substantial damping, measured at 1 Hz, in the glassy state is observed in the temperature range 100–200 K, and the apparent activation energy for a number of these damping processes has been either measured experimentally or estimated. It has been found possible to attribute some or all of the observed damping in a particular polymer glass to intramolecular motion in the flexible cycloalkyl groups. By comparing the energy requirements of these molecular relaxations, measured from either NMR studies or strain energy calculations, with our experimental data, we have been able to propose which of the various molecular mechanisms are likely to occur in the glassy state for the several derivatives. While such relaxations can account for most of the damping peaks in the spectra, there are a few damping processes which remain unexplained by intramolecular motions in the ring, particularly in the dicyclononyl and dicyclododecyl derivatives.

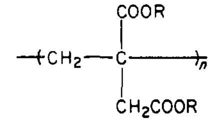
Introduction

It is now well established that the relaxation of small groups can occur in glassy polymers at temperatures well below the glass transition temperature. These are often detected by locating a loss process in a dynamic mechanical spectrum, and various suggestions have been made as to the molecular origin of these relaxations. To date the exact molecular mechanisms involved in these relaxations have been established in only a few systems with some degree of accuracy, and of these perhaps one of the best documented is the chair → chair′ transition of the cyclohexyl ring, identified by Heijboer[1] in poly(cyclohexyl methacrylate).

The molecular interpretation proposed by Heijboer has been confirmed by our own work[2] on a series of poly(dicyclohexyl itaconates) and by Seefried and Koleske,[3] who studied poly(vinylcyclohexane) and related structures. In all these investigations it was observed that polymer chains containing pendant cyclohexyl rings exhibited damping peaks in their dynamic thermomechanical spectra which were absent in the spectra of comparable structures containing rigid, pendant, phenyl rings. Furthermore, measurment of the apparent activation energy, ΔH^*, for this damping process yielded values in the range 48–65 kJ mol^{-1}, depending on chain structure, which compare well with the value of $\Delta H^* = 47$ kJ mol^{-1} reported by Anet and Bourn[4] for the ring inversion of the cyclohexane molecule.

There is further evidence to suggest that the type of intramolecular ring motion observed in pendant cyclohexyl rings is not confined to this group and that other cycloalkyl rings can also behave as flexible units.[5] The conformational changes which are possible in large isolated cycloalkyl rings have been studied by a number of workers[6] and it is of interest to investigate the behavior of polymers containing similar ring systems. It should also be particularly instructive to compare the energy requirements for an observed relaxation process in the polymer glass with that calculated for the possible and various ring inversions in the corresponding small molecules.

This consideration has been studied in some detail by using a series of diesters of poly(itaconic acid) substituted with cycloalkyl units ranging in size from 7 to 12 carbon atoms. The basic structural unit is



$$-\!\!\left(CH_2-\underset{CH_2COOR}{\overset{COOR}{\underset{|}{\overset{|}{C}}}}-\right)_n$$

where R is the cycloalkyl ring.

Experimental Section

Monomer Preparation. Dicycloalkyl esters of itaconic acid were prepared either by reacting the acid (1 mol) with the appropriate alcohol (3 mol) in the presence of an acid catalyst such as sulfuric acid/*p*-toluenesulfonic acid or by making use of the diacid chloride of itaconic acid in a toluene solution under a nitrogen atmosphere.[3] The dicycloheptyl diester was isolated by vacuum distillation of the reaction mixture after neutralization with aqueous sodium carbonate. In all other cases a silica gel column had to be used and the diester was separated with a chloroform eluent. The purified monomers were characterized by NMR and IR spectroscopy.

Polymerization. All monomers were polymerized *in bulk*, using a radical initiator [α,α'-azobis(isobutyronitrile)]. Reactions were carried out under vacuum at temperatures between 333 and 343 K for periods of 24–48 h. The product was dissolved in chloroform and isolated by precipitation with methanol. Purification was achieved by repeated dissolution and precipitation, followed by drying in vacuo. Each polymer was characterized by IR spectroscopy, and number-average molecular weights were obtained by osmometry.

Dynamic Mechanical Measurements. Two techniques were used to obtain the dynamic thermomechanical spectra of the samples: torsional braid analysis (TBA) and a Rheovibron viscoelastomer (RV). Both techniques have been described in detail elsewhere.[7] The TBA has a nominal frequency of 1 Hz while the

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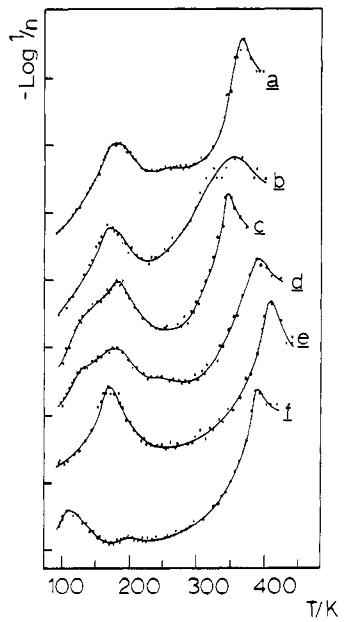

Figure 1. 1-Hz damping spectra of poly(dicycloalkyl itaconates): (a) dicyclododecyl; (b) dicycloundecyl; (c) dicyclodecyl; (d) dicyclononyl; (e) dicyclooctyl; (f) dicycloheptyl. Spectra are displaced vertically for clarity.

RV covers the range 3.5–110.0 Hz, thus allowing samples to be studied over a 2-decade range. Apparent activation energies, $\Delta H^{\ddagger}$, could be estimated by using an Arrhenius plot. For samples which were mechanically weak at room temperature glass fiber filter strips were used as inert supports for the polymer in the RV; the TBA samples are supported on a glass braid. It has been demonstrated that if there is no need for absolute measurements of the modulus or damping parameters, then these inert support systems give results which are equivalent to those obtained from unsupported polymers and the results can be used for comparison purposes and the location of relaxation processes.[8] The data displayed here are in the form of a characteristic mechanical damping index $1/n$, where n is the number of oscillations counted for a decay pattern between fixed boundary amplitudes.

Results and Discussion

The TBA damping spectra for the poly(dicycloalkyl itaconates) are shown as a function of ring size in Figure 1, where $-\log(1/n)$ is plotted as a function of temperature for each sample. The spectra are displaced vertically to allow easier comparison.

Two major features are evident in each spectrum. A large damping peak is located at temperatures above 300 K while smaller, but significant, damping features are seen between 100 and 200 K. The peak appearing at higher temperatures has been shown to be associated with the glass–rubber transition[9] and this has been confirmed by differential scanning calorimetry. As this aspect has been examined, we shall concentrate here on the sub-glass transition processes. It has been demonstrated that intramolecular ring motion can account for the sub-glass transition events observed in the damping spectra of poly(dicyclohexyl itaconates), and it is useful to pursue this idea and consider intramolecular motions as possible relaxation mechanisms in other derivatives containing flexible cycloalkyl groups.

The apparent activation energy ($\Delta H^{\ddagger}$) associated with such secondary relaxation processes in the glass can be estimated by making use of the relation

$$\nu = \nu_0 \exp(-\Delta H^{\ddagger}/RT_{\mathrm{m}}) \qquad (1)$$

which relates the frequency of the measurement (ν) to the temperature (T_{m}) at which the damping process appears.

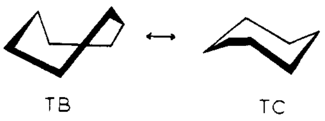

Figure 2. Proposed mechanism for the damping process in poly(dicycloheptyl itaconate) observed at 113 K (1 Hz): a twist-boat (TB) to twist-chair (TC) conversion.

Table I
Temperatures of Damping Maxima Measured at 1 Hz for Poly(itaconic acid diesters) Containing Pendant Cycloalkyl Rings

derivative	T_g/K	T_β/K	T_γ/K	$T_{\gamma'}$/K
dicycloheptyl	390	200	113	
dicyclooctyl	413		175	
dicyclononyl	390	250	180	128
dicyclodecyl	345		184	133
dicycloundecyl	350		170	
dicyclododecyl	366	260	179	

Heijboer[10] has demonstrated the validity of eq 1 for a number of secondary relaxation processes in the glassy state when the constant ν_0 lies in the range 10^{13}–10^{15} Hz. Implicit in the use of eq 1 is that $\Delta H^{\ddagger}$ is determined by the local barrier to rotation within the molecule and that both matrix effects and entropy contributions can largely be neglected. Bearing these assumptions in mind, one can estimate $\Delta H^{\ddagger}$ from eq 1 for a relaxation process in the polymer glass and compare this with values of $\Delta H^{\ddagger}$ calculated from strain energy considerations for a particular molecular mechanism or with an experimentally determined value. Each derivative will now be considered separately, and temperatures at which the various peak maxima occur, nominally at 1 Hz, are listed in Table I.

Poly(dicycloheptyl itaconate). Two low-temperature damping maxima can be seen in this spectrum, one at $T = 113$ K and a much smaller one at $T = 200$ K. The low-energy forms of a seven-membered cycloheptyl ring have been shown to be[11] a twist-chair (TC) and a twist-boat (TB), both of which can undergo pseudorotations involving very low energy barriers. In addition, conformational changes of the TC conformer to its mirror image and of TC to the TB form have been observed. The apparent activation energy for the former is ~23 kJ mol^{-1}, which would place the 1-Hz damping peak below 100 K and out of our experimental range,[6] but it has been calculated that the TC → TB conversion,[6,11-13] shown in Figure 2, has a $\Delta H^{\ddagger}$ of 34.3 kJ mol^{-1}. This, according to eq 1, would give rise to a damping process in the temperature range 117–136 K and 1 Hz, which compares favorably with the lower peak in the damping spectrum. It is postulated that this relaxation mechanism is responsible for the more prominent sub-glass transition process.

The less prominent peak, seen at 200 K, cannot be explained in this way, but similar peaks have been detected[5] in poly(cycloheptyl methacrylate). It has been suggested that this may be due to the presence of water in the sample, and while our polymers were rigorously dried before use, this possibility cannot be ruled out.

Poly(dicyclooctyl itaconate). The spectrum of the dicyclooctyl derivative is much simpler than that of the previous polymer, displaying only one broad damping peak centered on $T = 175$ K. From NMR studies[12,14] it has been shown that the two low-energy forms of cyclooctane are a boat–chair (BC) and a twist-boat–chair (TBC). Experimental determination of $\Delta H^{\ddagger}$ for this damping process gave a value of 45 ± 5 kJ mol^{-1}, and this would correspond to three possible conformational changes in the cyclooctyl ring. These are illustrated in Figure 3 and are (a) BC ↔ TB, with $\Delta H^{\ddagger} = 45.4$ kJ mol^{-1},[12] (b) BC ↔ BB, for which

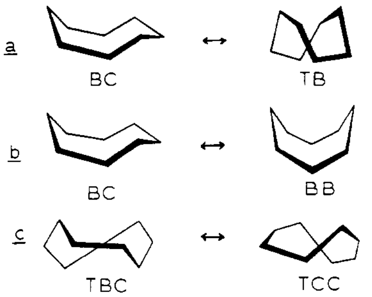

Figure 3. Three mechanisms to account for damping at 175 K (1 Hz) in poly(dicyclooctyl itaconate): (a) a boat–chair (BC) to a twist-boat (TB) conformational change, (b) a boat–chair (BC) to a boat–boat (BB) conversion, and (c) a twist-boat-chair (TBC) to a twist-chair–chair (TCC) conversion.

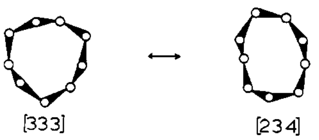

Figure 4. A [333] to [234] conformational change, suggested as the molecular mechanism for the relaxation in poly(dicyclononyl itaconate) at 128 K (1 Hz).

$\Delta H^{\ddagger} = 45.0$ kJ mol^{-1},[12] and (c) TBC ↔ TCC, which has $\Delta H^{\ddagger} = 43.3$ kJ mol^{-1}.[12] As the experimental damping peak is quite broad, it is reasonable to postulate that all three mechanisms will contribute. The energy requirements are also adequately described by eq 1.

Poly(dicyclononyl itaconate). The damping behavior of this polymer is more complex than those for the smaller ring derivatives. The major peak, lying between 100 and 200 K, appears to be composed of at least two overlapping loss peaks, with maxima at 180 and 128 K. There is also the suggestion of a small damping maximum around 250 K. Studies on cyclononane have shown[15,16] that there is one low-energy stable conformation, designated [333]. Here we will resort to an accepted numbering system[6] to describe the conformations. These designations refer to the number of bonds on each side of the "wedge" diagram, which is the most convenient method of representing these large ring systems.

The [333] conformer can undergo a transition to a higher energy [234] conformer,[15] which constitutes an intermediate state in the conformational change eventually ending in the mirror image [333]′. The $\Delta H^{\ddagger}$ for the transition [333] → [234], shown in Figure 4, is calculated from strain energy considerations[15,16] to be of the order 32–36 kJ mol^{-1}. This would result in a peak lying between 110–140 K and would match the low-temperature shoulder of the sub-glass transition damping process in the cyclononyl derivative, but not the upper portion.

Other low-energy conformers do exist but strain energy calculations indicate that the $\Delta H^{\ddagger}$ values for conformational changes involving these are usually less than 35 kJ mol^{-1}. Consequently it seems unlikely that the unaccounted damping at 180 and 250 K in the dicyclononyl derivative is a consequence of intramolecular ring motion.

Poly(dicyclodecyl itaconate). There are distinct similarities between the damping spectra of the dicyclononyl and the dicyclodecyl derivatives. A broad loss peak in the dicyclodecyl derivative covers the 100–200 K range, which again seems to be a composite of at least two distinguishable damping processes. The shoulder at the lower temperature is not as well resolved but the maxima are located at similar temperatures of 133 and 184 K. It was found possible to estimate experimentally the $\Delta H^{\ddagger}$ for the process centered on 184 K (1 Hz) and a value of 56 ± 5 kJ mol^{-1} was obtained. This is an acceptable value when compared with that obtained from eq 1, but this equation had to be used to estimate a $\Delta H^{\ddagger}$ of 33–38 kJ mol^{-1} for the lower damping process, which proved difficult to measure experimentally because resolution was lost at higher frequencies.

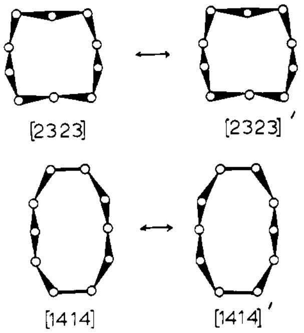

Figure 5. Conformational changes [2323] and [1414] to their respective mirror images. These are the suggested damping mechanisms in poly(dicyclodecyl itaconate) at 133 K (1 Hz).

The stable low-energy conformers of cyclodecane[17] are a [2323] rectangular, diamond lattice structure and a [1414] conformer. The strain energy calculation for the transitions [2323] ↔ [2323]′ and [1414] ↔ [1414]′ yield $\Delta H^{\ddagger}$ of 33.2 and 38.6 kJ mol^{-1}, respectively.[15] Both are illustrated in Figure 5 and could be responsible for the damping observed in the temperature region 115–156 K, but again not the damping process apparent at higher temperatures. There are no obvious intramolecular ring relaxations which would account for the loss process at 184 K.

Poly(dicycloundecyl itaconate). Only one broad damping peak is detected in the low-temperature region of the spectrum for this polymer, followed by a steady and somewhat extended damping increase as the temperature moves toward that of the glass transition. This behavior suggests that there may be some process lying just below T_g which cannot be resolved by TBA.

The main sub-glass transition process has a maximum at $T = 170$ K and the approximate $\Delta H^{\ddagger}$ is estimated to be 42–49 kJ mol^{-1}. A number of conformational changes would correspond to this value. There are several stable low-energy forms proposed[18] for cycloundecane. The two lowest are the [335] and the [12323] conformers followed by the [1334] and [13223] structures, which have slightly higher energies. Both [1334] and [335] conformers can transform into their mirror images but the energy barriers are too low to be observed with our experimental techniques. An alternative sequence of transformations for this ring system involves the following steps:[18] a [335] → [12323] transition, requiring a $\Delta H^{\ddagger}$ of 33.6 kJ mol^{-1}, followed by either [12323] → [13223], for which $\Delta H^{\ddagger} = 43$ kJ mol^{-1}, or [12323] → [12314], a higher energy crown form. The strain energy calculations do not give very accurate values for the last step but the $\Delta H^{\ddagger}$ is in excess of 45 kJ mol^{-1}. Any of these mechanisms could result in damping peaks in the temperature range 120 to >180 K and this encompasses the broad peak located experimentally. The conformational changes are illustrated in Figure 6.

Poly(dicyclododecyl itaconate). The damping spectrum of the dicyclododecyl derivative exhibits two sub-glass transition peaks. A small peak is located at ~260 K while a large, broad peak is found centered on $T = 179$ K.

The most stable form of cyclododecane is the square crown [3333].[19] This can be transformed to a [2334]

Table II
Intramolecular Ring Motions Associated with Damping Processes in the Temperature Range 100-200 K in Poly(dicycloalkyl itaconates)

ring	damping T_{max}/K	$\Delta H^{\ddagger}$(calcd)^a/ (kJ mol^{-1})	$\Delta H^{\ddagger}$(exptl)/ (kJ mol^{-1})	conversions
cyclohexyl	180	45.0	50-65	C → C′
cycloheptyl	113	34.3		TC → TB
cyclooctyl	175	45.0		BC → BB
		45.4	46 ± 5	BC → TB
		43.3		TCC → TBC
cyclononyl	128	36.1		[333] → [1233] → [234]
	180	45-50		
cyclodecyl	133	33.2		[2323] → [2323]′
		38.6		[1414] → [1414]′
	184	46-53	56 ± 5	
cycloundecyl	170	33.6		[335] → [12323]
		43.0		[12323] → [13223]
		>45		[12323] → [12314]
cyclododecyl	179	57.0		[3333] → [2334]
				[2334] → [2424]

^{a} Obtained from strain energy calculations; for references, see text.

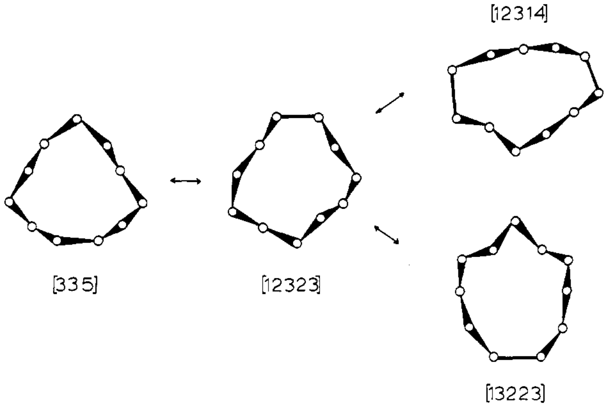

Figure 6. Molecular relaxation processes in poly(dicycloundecyl itaconate) responsible for damping at 170 K (1 Hz).

conformer by surmounting a barrier of 33.2 kJ mol^{-1}, and the conformational change can be continued to the diamond lattice conformer [2424] over a barrier of 53.3 kJ mol^{-1}; see Figure 7. Strain energy calculations by Dale[15] put the activation energy for the first transformation much higher, at $\Delta H^{\ddagger}$ = 57.1 kJ mol^{-1}, so there is some dispute as to the precise energetic requirements of this conformational change. Both of these intramolecular transformations would give rise to loss peaks in the 115–215 K range, in good agreement with experiments, and it is proposed that these are contributory relaxations and acceptable mechanisms for the sub-glass transition damping at 176 K. At the moment the origin of the minor peak is in some doubt.

Conclusions

Much of the damping observed in glassy poly(itaconic acid diesters) containing pendant cycloalkyl groups can be attributed to intramolecular motion in the ring systems. These are summarized in Table II. Some damping peaks do remain unaccounted for and cannot be explained, at present, on the basis of such relaxation processes. Most notable are the dicyclononyl and dicyclodecyl derivatives, which display composite damping peaks in the 100–200 K temperature region of the 1-Hz spectrum.

These interpretations are based on the assumption that there is no matrix effect contributing to the activation energy barriers involved in the ring motion and with these large ring systems this simplification may not be wholly justifiable. Work is in progress to attempt to resolve this problem.

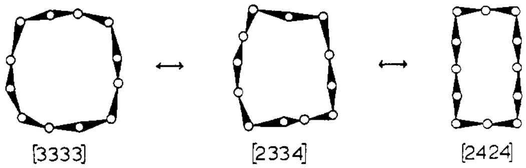

Figure 7. Two conformational changes suggested as possible relaxation processes in poly(dicyclododecyl itaconate) detected at 179 K (1 Hz).

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