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Dynamic Thermomechanical Behavior of Poly(dicycloalkyl itaconates) Containing Pendant Cyclopropyl, Cyclobutyl, and Cyclopentyl Groups

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ABSTRACT: Poly(itaconic acid diesters) have been prepared with cycloalkyl rings pendant to the main chain. Two distinct groups of dicyclopropyl, dicyclobutyl, and dicyclopentyl derivatives have been studied: (a) polymers with the rings attached directly to the oxycarbonyl units ($n = 0$) and (b) polymers with the rings spaced out by methylene units ($n = 1$ or 3) inserted between the ring and the oxycarbonyl unit. Two main sub-glass transition damping peaks have been detected in the dynamic thermomechanical spectra. These are designated T_β for peaks lying in the temperature range 200–220 K and T_γ for those lying below 150 K. It has been suggested that these cycloalkyl rings will behave as rigid units, and relaxation mechanisms involving movement of the ring as a rigid system have been proposed to account for the observed damping behavior.

Introduction

In previous papers[1,2] the damping characteristics of poly(itaconic acid diesters), with flexible cycloalkyl ring systems pendant to the main chain, were examined. Distinctive relaxation processes were detected in the glassy state of these polymers, which could be attributed to intramolecular motions in the cycloalkyl rings. Determination of the activation energies for these processes allowed us to propose, as the molecular mechanisms responsible for the observed damping behavior, various conformational changes in these flexible rings, which have been deduced from NMR studies and strain energy calculations.[3] For rings whose sizes vary from cyclohexyl to cyclododecyl, conformational changes involving only the ring are possible, and these intramolecular ring motions appear to act independently of movement in both the main chain and the unit to which they are directly attached.

It is of interest then to examine systems containing less flexible pendant rings where intramolecular motion is either unlikely or of a limited nature. Some work has been reported on a comparison of the behavior of rigid phenyl rings with flexible cyclohexyl rings in a glassy polymer matrix when these are either attached directly to the polymer chain, as in polystyrene and poly(vinylcyclohexane),[4] or attached to an oxycarbonyl unit, as in poly(methacrylic acid ester)[5] and poly(itaconic acid diester).[2]

Dynamic mechanical damping spectra have been reported for a number of cyclopentyl derivatives, poly(vinylcyclopentane),[4] poly(3-cyclopentyl-1-propene),[4] and poly(cyclopentyl methacrylate),[5] but the results differ sufficiently to merit the reexamination of the role of the cyclopentyl unit.

In this paper we present a study of a series of poly(itaconic acid diesters) which contain pendant cyclopropyl, cyclobutyl, and cyclopentyl rings. These either are connected to the chain directly via an oxycarbonyl unit or have methylene units inserted between this group and the ring to increase the flexibility of the side chain.

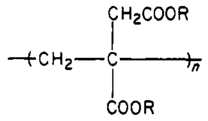
Experimental Section

Sample Preparation and Characterization. Dicycloalkyl itaconate monomers were prepared by standard methods described elsewhere.[6] Polymerizations were carried out in bulk, under vacuum, using α,α'-azobis(isobutyronitrile) as initiator, at temperatures of 333–343 K. Polymers were isolated and purified as before.[6] Number-average molecular weights were measured with a Knauer membrane osmometer, using toluene as solvent. Samples were also examined by both IR and NMR spectroscopy to ensure the structure and purity of the product.

Dynamic Mechanical Measurements. Damping spectra were obtained by using (i) torsional braid analysis (TBA), in which the nominal frequency was 1 Hz, and (ii) a Rheovibron (RV) viscoelastometer, which covers the frequencies 3.5–110 Hz. Both methods have been described fully in previous publications.[2,6] The polymers were examined as supported systems: in TBA this was a glass braid and in the RV it was a glass fiber filter strip. These methods have been shown to give reliable and reproducible results, and although the data produced are not absolute,[7] they can be used in a qualitative manner.

Results and Discussion

The basic repeat unit of each of the polymer samples is



$$-\!\left[CH_2-\overset{\displaystyle CH_2COOR}{\underset{\displaystyle COOR}{C}}\right]_n\!-$$

where R = $-(CH_2)_n-$(ring) and $n = 0$, 1, or 3. Damping spectra at ~1 Hz for poly(dicyclobutyl itaconate) and poly(dicyclopentyl itaconate) derivatives with $n = 0$ and the spectrum of the poly(dicyclohexyl itaconate) for comparison are shown in Figure 1. The spectra for the series with $n = 1$ are shown in Figure 2, together with those for both six- and eight-membered cycloalkyl rings, which help to highlight the distinct differences in the polymer response as the ring increases beyond a critical size and becomes more flexible.

The temperatures corresponding to the various damping maxima are recorded in Table I. The largest damping peaks, lying mainly above 300 K, represent the glass–rubber transitions in these amorphous polymers and this has been confirmed by differential scanning calorimetry.[8] A number of less prominent damping maxima or shoulders have been detected in the glassy state and are identified as T_β or T_γ in order of decreasing temperature. Here we have used the convention that the T_γ nomenclature is confined to processes lying below 150 K.

It has been demonstrated by Heijboer[9] that the apparent activation energy ΔH^* for a localized molecular motion occurring in the glassy state can be estimated from the relation

$$\nu = \nu_0 \exp(-\Delta H^*/RT_m) \qquad (1)$$

where ν is the frequency of the measurement, ν_0 is normally assumed to have a constant value in the range 10^{13}–10^{15} Hz, T_m is the temperature of the relaxation process, and R is the gas constant. The applicability of eq 1, when ν_0 is taken to be 10^{15} Hz, has been demonstrated[2] for poly(dicyclohexyl itaconates), where experimentally determined values of $\Delta H^* = 50$–65 kJ mol^{-1}, relating to the chair–chair

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Table I
Temperatures for Glass and Sub-Glass Transitions Detected by Dynamic Mechanical Measurements at 1 Hz for Poly(dicycloalkyl itaconates)

derivative	$10^{-4}M_n$	T_g/K	T_β/K	$T_{\beta'}{}^a$/K	T_γ/K	Bondi ring volumes/ (cm^3 mol^{-1})
$n = 0$						
dicyclobutyl	2.12	366	200			36.3
dicyclopentyl	10.10	395	221		128	46.5
bis(2-methylcyclopentyl)	2.97	377	210		135	58.0
dicyclohexyl	6.80	431	(260)	186		56.8
$n = 1$						
dicyclopropyl	5.32	329	(220)		108	26.1
dicyclobutyl	8.17	335	(210)		113	36.3
dicyclopentyl	10.70	338	(220)		118	46.5
dicyclohexyl	50.0	361	(220)	186	105	56.8
$n = 3$						
dicyclopentyl	5.20	270	(200)		116	46.5

[a] $T_{\beta'}$ represents intramolecular ring motions present only in flexible rings.

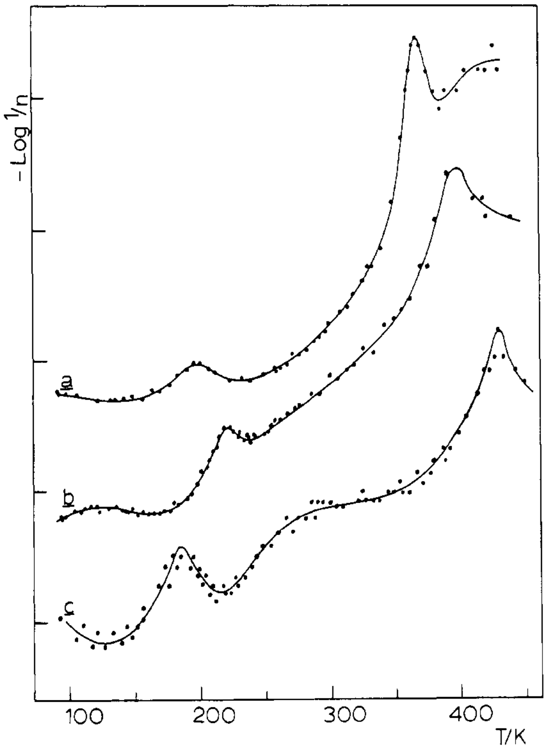

Figure 1. Damping spectra for derivatives with $n = 0$: (a) poly(dicyclobutyl itaconate); (b) poly(dicyclopentyl itaconate); (c) poly(dicyclohexyl itaconate).

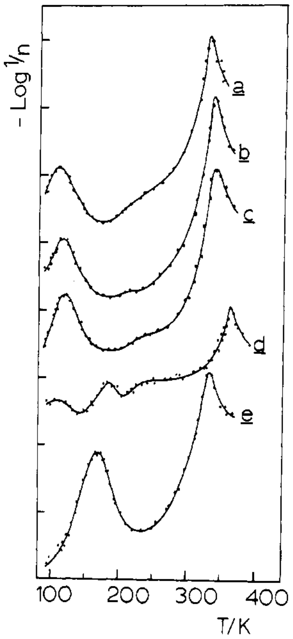

Figure 2. Damping spectra for derivatives with $n = 1$: (a) dicyclopropyl; (b) dicyclobutyl; (c) dicyclopentyl; (d) dicyclohexyl; (e) dicyclooctyl.

transition in the cyclohexyl ring, compared reasonably well with $\Delta H^* = 54$ kJ mol^{-1} derived from eq 1. Approximate values of ΔH^* for a sub-glass transition relaxation process can then be estimated from eq 1 and used as a guide to the possible molecular mechanism.

Derivatives with $n = 0$. Two clearly distinguishable relaxation processes can be identified in the damping spectra of polyitaconates with pendant cyclopentyl units when $n = 0$ (see Figure 1) and $n = 1$ (see Figure 2). These differ significantly in intensity, depending on the value of "n".

If we examine the process occurring at the higher temperature first, T_β, then it can be seen that the temperature range covered is centered on 220 K for most samples, but the relaxation is most prominent when the ring is attached directly to the oxycarbonyl unit. When the ring is spaced out from the chain by insertion of a methylene unit, the intensity of the T_β peak is greatly reduced. The reverse is true for the T_γ-damping process.

Likely molecular mechanisms can now be considered. One possibility is that intramolecular ring motion takes place, similar to that shown to be present in poly(cyclohexyl methacrylate)[5] or poly(dicyclohexyl itaconate).[2] By comparing the relative positions of the dicyclopentyl and dicyclohexyl derivatives with $n = 0$, one can see that the T_β process in the former occurs at a higher temperature than in the latter, where it is associated with the chair–chair transition. Thus on the basis of eq 1 the T_β process in the cyclopentyl derivative should have a higher value of ΔH^*. It proved difficult to measure ΔH^* for T_β in the dicyclopentyl derivative experimentally, but it can be estimated as being about 64 kJ mol^{-1}. The T_β process in the dicyclobutyl derivative also appears at a higher temperature than the chair–chair transition.

Conformational changes in the cyclopentyl ring can normally be achieved by simple pseudorotations involving very low energy barriers.[10] The most stable conformation is postulated to be the "envelope" form shown in Figure 3A, and one could expect that the conformational change shown would take place, passing through a planar form as

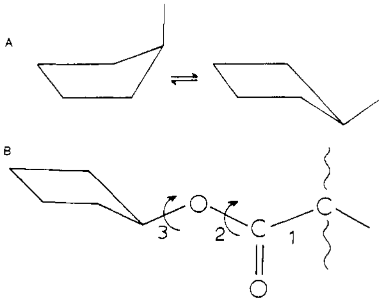

Figure 3. (A) Envelope inversion for cyclopentane. (B) Suggested bond rotations in poly(dicyclopentyl itaconate).

an intermediate. The barrier to the planarity has been measured by Raman spectroscopy[11] to be ~21.8 kJ mol^{-1}, whereas ab initio calculations[12-14] suggest that it should lie in the range 16.8–34.7 kJ mol^{-1}. Both are much larger than the simple pseudorotation barriers and one might ask why the envelope → envelope′ change would be selected when low-energy pseudorotation is available to the molecule. In addition, these activation energies suggest (on the basis of eq 1) that the T_m for the process might be observed around 60–120 K, which could correspond to T_γ but not T_β. This we consider an unlikely mechanism for either relaxation, and so credible alternatives must be sought.

Loss peaks have been observed[4] in the dynamic mechanical spectra of poly(vinylcyclopentane) and poly(3-cyclopentyl-1-propene) at T_m's of 130 and 120 K, respectively, corresponding to the T_γ peaks observed in the itaconates, and damping processes corresponding to the T_β relaxations are noticeably absent. Also the T_γ peak is strengthened when the cyclopentyl ring is moved further away from the main chain and the oxycarbonyl unit by insertion of methylene units.

Consideration of these features leads us to propose two possible relaxation mechanisms which do not involve intramolecular ring motion: (i) a hindered torsional oscillation of the cyclopentyl ring about the oxygen–ring bond number 3 in Figure 3B and (ii) a similar hindered rotation about the carbonyl–oxygen bond (bond number 2 in Figure 3B).

In process i complete rotation of the ring is sterically hindered by either the oxycarbonyl unit or the main chain. However, we have carried out elementary strain energy calculations assuming a rigid skeleton for the polymer unit and have considered[15] torsional interactions and van der Waals interactions for rotation about bond 3. The apparent activation energy for the barrier to complete rotation is extremely high but there is a much smaller barrier to overcome if movement is restricted to an oscillation over 120°. The actual barrier we calculated is only ~12 kJ mol^{-1}, but there is a large uncertainty concerning the potential associated with the oxygen lone pairs and this value of ΔH^* could be higher if the positioning of the lone pairs was changed.

Similar calculations for a rotation about bond 2 result in a comparable situation. The barrier to complete rotation is very large, but a limited 120° oscillation over an energy barrier of ~50 kJ mol^{-1} was found to be possible. Again, the contribution from the lone pairs was the most uncertain factor but if the relative magnitudes of ΔH^* for these two molecular relaxation processes are considered, then one can tentatively suggest the followng assignments. The T_γ process in the dicyclopentyl derivative is located at 128 K, and while this suggests a process involving a ΔH^* of approximately ~30 kJ mol^{-1}, which is over twice our calculated value, the uncertainty in the calculation could easily account for this discrepancy. The mechanism of this relaxation is then suggested to be an oscillation of the pendant unit around bond 3, the oxygen–ring bond.

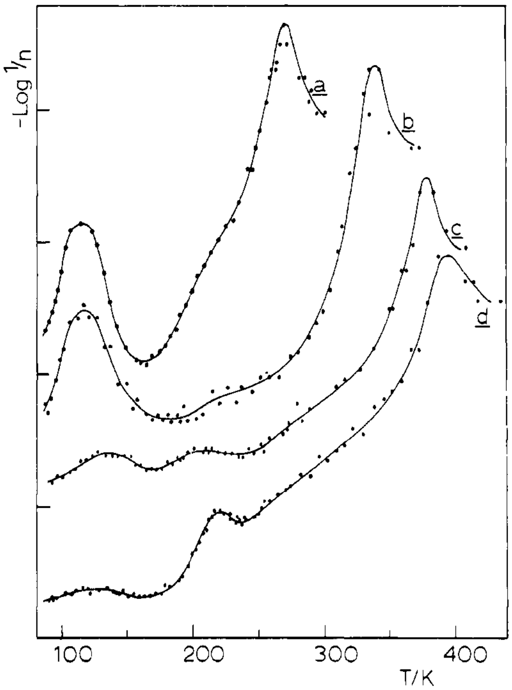

Figure 4. Damping spectra for various dicyclopentyl derivatives: (a) $n = 3$, (b) $n = 1$, (c) $n = 0$, bis(2-methylcyclopentyl) derivative, and (d) $n = 0$.

Estimation of ΔH^* from eq 1 for the T_β process, located at 221 K, is ~56 kJ mol^{-1}. Here the expected ΔH^* and that obtained from our strain energy calculations are much closer, and although this could be fortuitous in the light of uncertainties concerning the oxygen lone pairs, it does appear to be of the correct magnitude. This leads us to propose that the mechanism for the T_β process is a restricted oscillation about the carbonyl–oxygen bond 2 of the pendant unit.

It must be stressed that in all cases we are assuming that the barriers to rotation are intramolecular and that there is sufficient free volume for the pendant unit to move without having to consider matrix effects. Steric restrictions refer to those encountered from near-neighbor interactions from the segment of polymer chain to which the ring is attached.

These molecular interpretations appear to satisfy most of our observations. The poly(dicyclobutyl itaconate) with $n = 0$ exhibits a damping peak at $T_\beta = 200$ K but no T_γ peak within our temperature range, as it is likely that the T_γ process in this polymer appears at temperatures <100 K. The cyclobutyl ring will also behave as a rigid unit with no intramolecular relaxation processes of any importance and if process ii is assigned to the T_β peak, one would expect it to occur at a lower temperature, as the ring is smaller and the steric restrictions will be less than for the cyclopentyl ring. This appears to be the case, as the damping maximum is located about 20 K lower than for the cyclopentyl derivative. The methyl-substituted cyclopentyl ester shows similar features to the unsubstituted ring system; see c in Figure 4. The T_β peak now has a reduced intensity, reflecting the increased steric hindrance caused by the methyl group on the ring, and the T_γ peak is moved to a slightly higher temperature. This latter peak is more prominent and it may include a contribution from methyl group roation, which for a CH_3 unit attached to secondary carbon would be active mechanically at temperatures of 100–130 K.[16]

Derivatives with $n \geq 1$. Significant changes in the damping spectra are obtained when the ring is spaced out from the oxycarbonyl unit by insertion of a methylene unit between the ring and the oxygen atom of the ester group. These are clearly seen in Figures 2 and 4, where pronounced damping peaks appear in the temperature range 100–150 K. Experimental estimations of the activation energy for this T_γ process from our mechanical and dielectric measurements indicate ΔH^* to be about 30 ± 5 kJ mol^{-1}, which is close to the values of 25–30 kJ mol^{-1} estimated from eq 1.

With the insertion of a methylene unit in the side chain a more facile relaxation process is now possible, namely, rotation about the ring–methylene carbon bond. Our strain energy calculations[15] for this rotation show a threefold potential, with apparent activation energy barriers of 18–20 kJ mol^{-1}. Changing the size of the ring did not affect the calculation to any significant extent and these calculated energy barriers would correspond to a relaxation appearing at about 100 K (1 Hz). This is slightly lower than observed experimentally for the T_γ process but is of the correct order of magnitude. The calculations can also be regarded with greater confidence, as the interactions involving the lone pairs are of lesser importance, being further removed from the rotating unit than those considered for the rings attached directly to the oxycarbonyl group. Again the calculated value of ΔH^* is probably low, as only the nearest-neighbor steric restrictions were taken into account, but the value is sufficiently close to the experimental and expected values for us to assign as the most likely mechanism for the T_γ process a rotation of the ring about the ring–methylene bond in dicyclopropyl, dicyclobutyl, and dicyclopentyl itaconates with $n = 1$. It is also a satisfactory mechanism for the T_γ process in the dicyclopentyl derivative with $n = 3$. The T_γ values increase generally with increasing ring size, corresponding to the greater steric restriction encountered during rotation, but this is a relatively small change, suggesting that any matrix effect is relatively minor in this context. The polymer with $n = 3$ has a T_γ value which is the same as that for $n = 1$ derivative, suggesting that the extra methylene units which space the ring further from the chain do not alter the energy barrier of the relaxation process significantly.

As there is now an –(O–C–C–C)– unit in the pendant group, relaxation of this unit[17] may occur. Shimizu et al.[17] have proposed that rotation about the central carbon–carbon bond in this unit would result in a relaxation at 120 K (1 Hz) and this may contribute to the T_γ relaxation in the derivative with $n = 3$.

With increase of the ring size to cyclohexyl there is a decrease in the T_γ peak intensity and it disappears completely when the dicyclooctyl derivative is examined. The cyclooctyl ring is probably too large to rotate as a rigid unit at this temperature, and as it is also capable of undergoing intramolecular relaxations, it is these which contribute to the large damping peak appearing at higher temperatures. While the cyclohexyl ring is flexible, it does seem capable of undergoing rotation as a rigid unit, similar to the cyclopropyl, cyclobutyl, and cyclopentyl units to a limited extent. The Bondi volume[18] for cyclohexane is 56.8 cm^3 mol^{-1}, which is about 10 cm^3 mol^{-1} larger than for cyclopentane, and this must represent the limiting volume for a group to rotate freely in this temperature range, in the available free volume.

Again in these arguments we are ignoring possible matrix effects and assuming that there are holes large enough to allow the ring systems to move without encountering restrictions other than intramolecular barriers. This seems justified for rings up to C$_6$ but our results suggest there may be insufficient free volume in the glass at these temperatures to allow the cyclooctyl ring to relax in this fashion. There is no relaxation in the 130 K region for this derivative, but it can undergo more facile intramolecular ring motions and these are manifest in the damping observed at 175 K.

The T_β peak in this ($n = 1$) series is now of very low intensity and of minor importance. The rotation about the methylene carbon–oxygen bond is again impeded by the carbonyl group and process ii would involve even greater steric restrictions than before. This could account for the loss of intensity and submergence of this peak into the general background damping.

Conclusions

The ring systems cyclopropyl, cyclobutyl, and cyclopentyl attached to the poly(itaconic acid) chain as pendant groups act as rigid units when contributing to relaxational processes in the glassy state. The sub-glass transition damping response of these poly(dicycloalkyl itaconates) can be interpreted on the basis of either limited or relatively unimpeded rotation of the ring system, depending on the number n of methylene spacing units in the side chain.

When $n \geq 1$, the main damping features look very similar for derivatives with ring sizes 3, 4, and 5. The major sub-glass transition process is that associated with T_γ and is attributed to rotation of the ring as a rigid unit about the bond joining the ring to the methylene carbon. This process has an apparent activation energy of about 30 kJ mol^{-1}, estimated from the frequency dependence of the damping spectra.

When $n = 0$, and the ring is attached to the main chain directly through the oxycarbonyl unit, then two relaxation mechanisms are proposed. For the major damping occurring around 200–220 K (T_β), a hindered rotation of the ring system about the carbonyl to oxygen bond is proposed, while for the T_γ damping a hindered torsional oscillation of the ring about the bond linking the ring to the oxygen atom is thought to be a likely mechanism.

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