Detection of sub-glass transition events in amorphous polymers using differential scanning calorimetry:
3. Further observations on polymers containing pendant cycloalkyl rings

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Heat capacity (C_p) contributions have been calculated from the partition function which describes the conformational energies of cycloalkyl rings containing from 9 to 12 carbons. The magnitude of these contributions depends on the number of conformations available to the ring system, and is a maximum for cyclodecane. The heat capacity has been measured as a function of temperature for two dicycloalkyl itaconate polymers, one containing pendant cyclodecyl rings, and the other pendant cyclododecyl rings. In the case of the former polymer an inflection in the C_p–T curve is observed below the glass transition temperature. The experimental values associated with this inflection correlate with the calculated contribution from the conformational energies of the cyclodecyl rings, and this supports our assignment of the molecular origin of glassy state relaxations in such polymers. Any similar contributions to the glassy state heat capacities of the other polymers in the series are below the levels of detection of our present equipment.

Keywords Heat capacity measurement; differential scanning calorimetry; sub-glass transition; poly(dicycloalkyl itaconate); ring conformational changes

INTRODUCTION

In the first two papers in this series dealing with sub-glass transition events detected by differential scanning calorimetry (d.s.c.), we have reported that, for poly(di-n-alkyl itaconates) and for one example of a poly(dicycloalkyl itaconate), contributions to the glassy-state heat capacity (C_p), arising from limited molecular motions, may be detected using d.s.c.[1,2]. In the n-alkyl polymers substantial inflections in the C_p–T curves occur in the glassy state when the side chain contains more than six carbon atoms, and the molecular origins of these (referred to as T_g^L) are believed to involve independent relaxation of the side chains. A model for the relaxation has been proposed which provides a satisfactory quantitative explanation of the magnitude of the inflection (ΔC_p^L)[3]. T_g^L may also be detected using thermomechanical methods as a pronounced sub-ambient damping peak[2,4].

A corresponding series of dicycloalkyl itaconate polymers also shows identifiable glassy-state relaxations[5] which, for ring sizes of eight carbons and above, manifest themselves as large damping maxima in the 150–200K region of the 1 Hz spectrum, comparable in size to those of the glass transitions. The relaxation mechanism involves conformational interconversions of the pendant cycloalkyl rings over appropriate energy barriers. In the particular case of poly(dicyclooctyl itaconate), careful d.s.c. measurements reveal a small but distinct inflection in the C_p–T curve corresponding to the mechanically active transition[2]. A statistical thermodynamic analysis of the heat capacity contribution from the non-equienergetic cyclooctane conformers, treated as a series of energy levels, successfully predicts the magnitude of the observed inflection. As a further study it was decided to investigate other members of the cycloalkyl series in which the mechanically active relaxation processes might also be detectable by d.s.c.

EXPERIMENTAL

The preparation and characterization of the samples used have been described previously[5]. Heat capacity measurements were carried out as before[2] using a Perkin-Elmer DSC-2, but with the added convenience of a data capture system based on an Apple II microcomputer. A scan rate of 20K min^{-1} was employed over the temperature range 95–300K, the samples first having been cooled at 320K min^{-1} from above their glass transitions. Data were sampled at 1K intervals and stored for eventual processing.

RESULTS AND DISCUSSION

Heat capacity prediction for cycloalkyl rings

If the sets of stable cycloalkyl conformers are considered to represent corresponding sets of energy levels which the molecules can occupy, then the partition function Q is given by

$$Q = g_0 + g_1 e^{-\varepsilon_1/kT} + g_2 e^{-\varepsilon_2/kT} + \ldots + g_n e^{-\varepsilon_n/kT} \quad (1)$$

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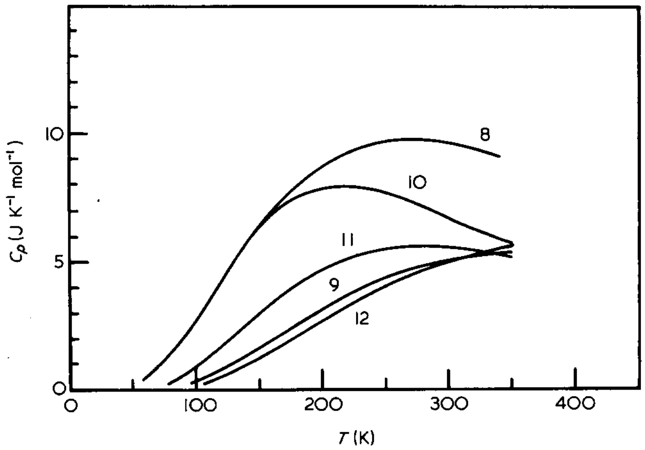

Figure 1 Heat capacity contribution vs temperature curves calculated from equation (3) for the stable conformers of cycloalkyl rings; number of carbons per ring indicated on the figure

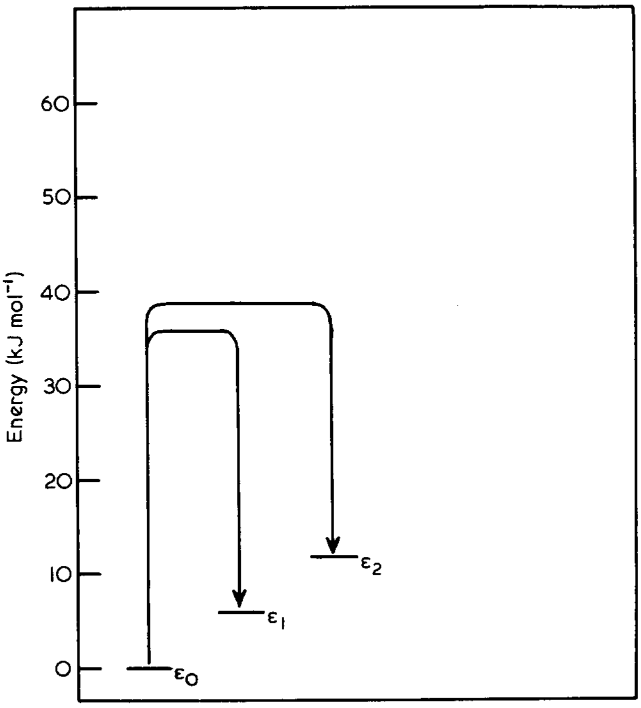

Figure 2 Cyclononane conformation energy diagram: conformers are ε_0=[333], ε_1=[234] and ε_2=[12222]; see *Figure 9* and *Table 3*

where the degeneracy of the ith energy level ε_i is g_i and k is the Boltzmann constant. The heat capacity C_v is given by

$$C_v = \frac{k}{T^2}\frac{\partial^2 \ln Q}{\partial(1/T)^2} \simeq C_p \qquad (2)$$

Neglecting the difference between C_p and C_v allows equation (2) to be recast as

$$C_p \simeq \frac{k}{T^2}\left[Q\left(\frac{\mathrm{d}^2Q}{\mathrm{d}T^2}\right) - \left(\frac{\mathrm{d}Q}{\mathrm{d}T}\right)^2 \Big/ Q^2\right] \qquad (3)$$

and substitution for Q enables C_p to be calculated as a function of T for any system of n energy levels.

Equation (3) was evaluated for cycloalkanes containing from nine to twelve carbon atoms and the results are shown in *Figure 1*, along with the previous result for cyclooctane[2]. The sets of ε_i values used were obtained from literature calculations on the stable conformations of large cycloalkane rings and these are shown schematically in *Figures 2–5*. The data on cycloundecane and cyclododecane are derived from iterative force field-type calculations[6,7], while those for cyclononane and cyclodecane are from Dale's semi-empirical prescriptions[8,9]. The notation used to describe the conformer is also that of Dale, and indicates the number of carbon atoms per 'side' of a plan view of any conformer.

The magnitude of any ring conformational contribution to the C_p of a system clearly depends on the

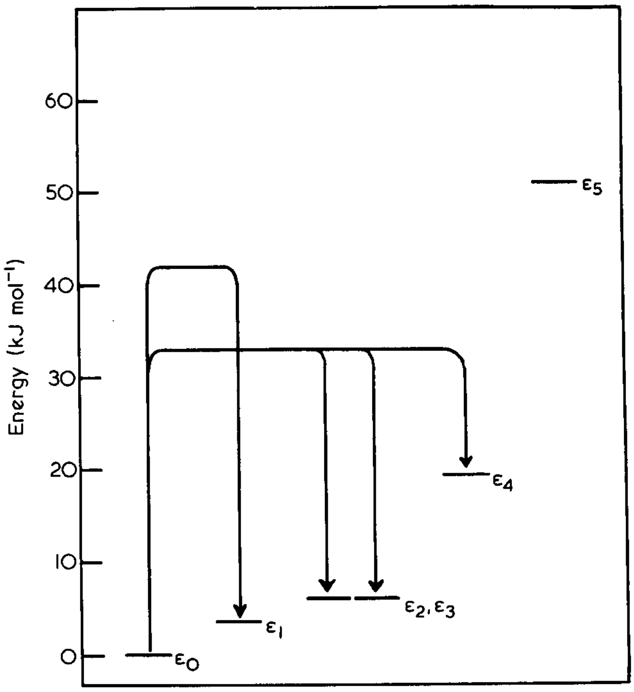

Figure 3 Cyclodecane conformation energy diagram: conformers are ε_0=[2323], ε_1=[1414], ε_2=[2233], ε_3=[1333] and ε_4=[1324]; see *Figure 9* and *Table 3*

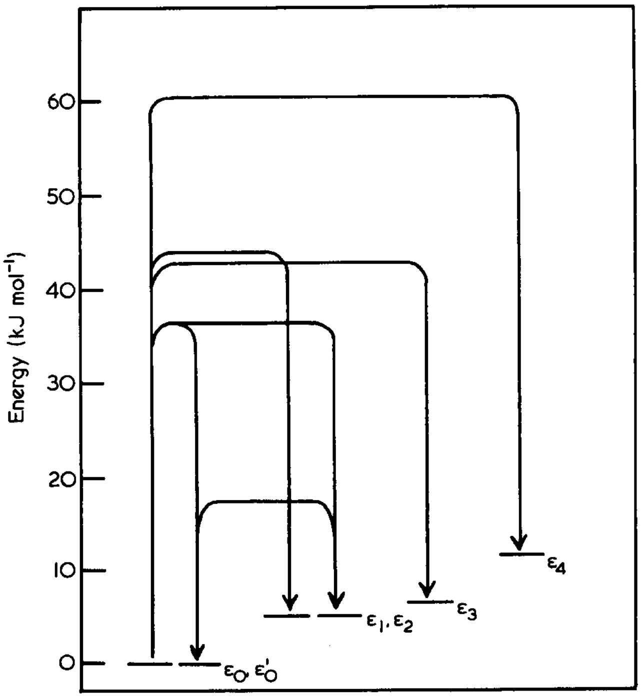

Figure 4 Cycloundecane conformation energy diagram: conformers are ε_0=[12323], ε_0'=[335], ε_1=[12314], ε_2=[344], ε_3=[13223] and ε_4=[245]; see *Figure 9* and *Table 3*

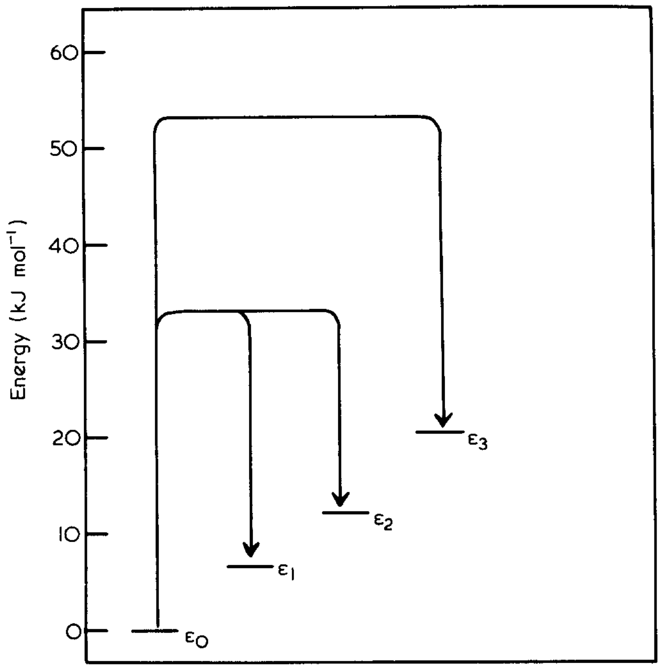

Figure 5 Cyclododecane conformation energy diagram: conformers are ε_0 = [3333], ε_1 = [2334], ε_2 = [2343] and ε_3 = [2424]; see *Figure 9* and *Table 3*

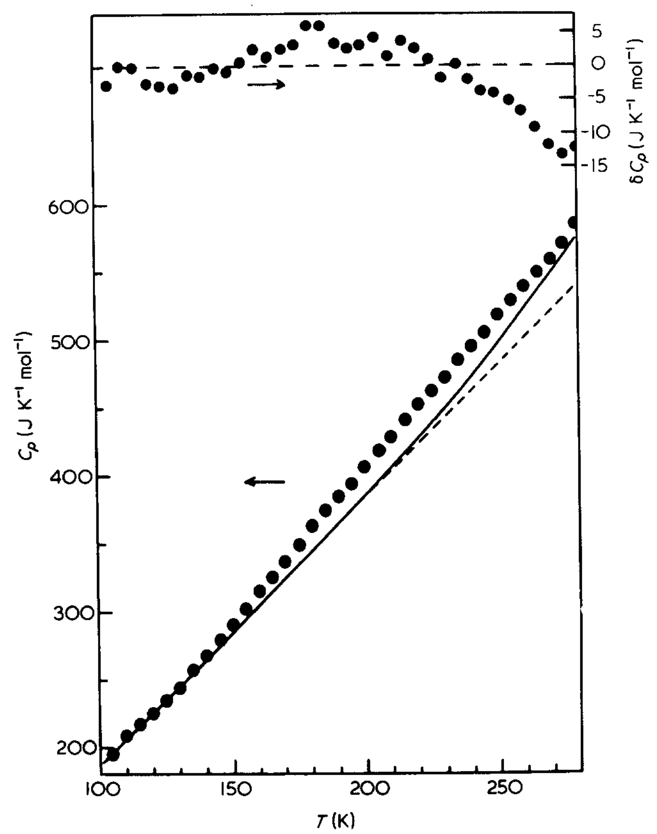

Figure 6 Experimental values of the heat capacity of poly(dicyclodecyl itaconate) as a function of temperature and the corresponding differences $\delta C_p = C_p$(experimental) – C_p(quadratic), where C_p(quadratic) is calculated from equation (5). The full curve represents the heat capacity calculated from equations (6) and (7) and fitted to the experimental data below 140K. The broken line is a linear extrapolation of the data below 140K

number of energy levels available, and the temperature at which a contribution reaches its maximum value depends on the absolute values of the energy levels. The relatively large contribution from the cyclooctane ring results from six low-lying conformers, all with energies below ~12 kJ mol^{-1}, and only for poly(dicyclodecyl itaconate) do the calculations predict a ring-derived contribution to C_p of comparable magnitude.

The average value of C_p in the glassy state at 200K is[1,2] about 1 J K^{-1} g^{-1} and if the calculated contributions (at 200K), shown in *Figure 1*, are expressed as percentages of this value they are 4.8, 1.6, 3.7, 2.0 and 1.1% respectively for the dicycloalkyl polymer series octyl to dodecyl. Since the reproducibility of our d.s.c. measurements in this temperature region[2] is of the order of ±1%, only the contribution in poly(dicyclodecyl itaconate) might reasonably be expected to be detectable using the present instrumentation. Measurements on this polymer, and on poly(dicyclododecyl itaconate) as a comparison, were carried out and the results are described in the following section.

Heat capacities of poly(dicyclodecyl itaconate) and poly(dicyclododecyl itaconate)

Figures 6 and *7* show the heat capacities as functions of temperature at 5K intervals in the sub-ambient region. Careful inspection of the data reveals that the two curves are somewhat different. Between 100 and ~170K both curves are slightly concave upwards but, although that for poly(dicyclododecyl itaconate) continues this trend, that of poly(dicyclodecyl itaconate) is either predominantly linear or concave downwards thereafter. The differences between the two curves may be quantified by the results of a least-squares fitting exercise to the data. The C_p–T

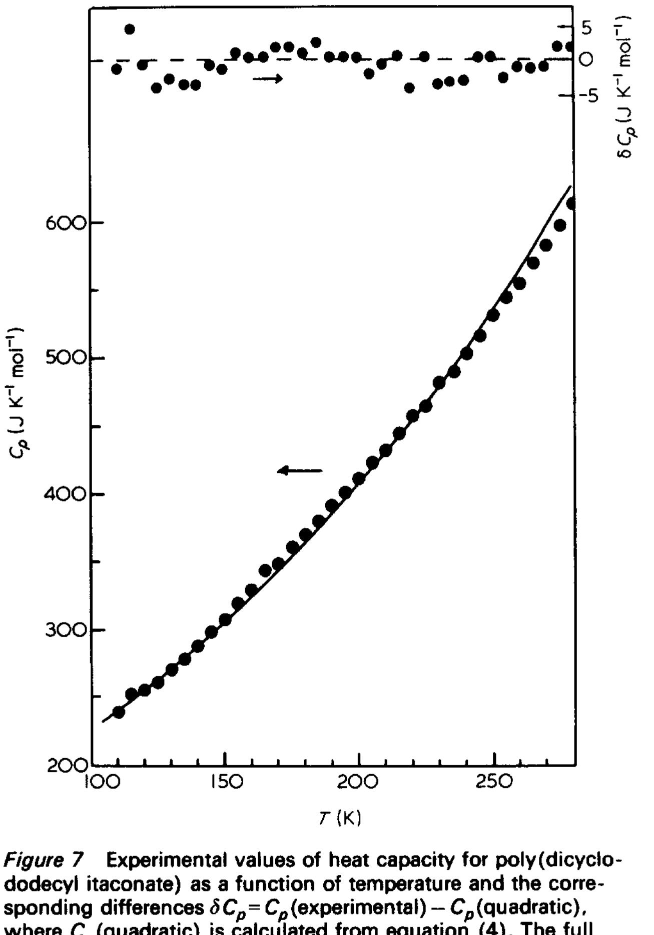

Figure 7 Experimental values of heat capacity for poly(dicyclododecyl itaconate) as a function of temperature and the corresponding differences $\delta C_p = C_p$(experimental) – C_p(quadratic), where C_p(quadratic) is calculated from equation (4). The full curve represents the heat capacity calculated from equations (6) and (7) and fitted to the experimental data

behaviour of poly(dicyclododecyl itaconate) is adequately described by the quadratic equation

$$C_p(\mathrm{J\,K^{-1}\,mol^{-1}}) = 103.3 + 0.8635T + 3.429 \times 10^{-3}T^2 \tag{4}$$

with a correlation coefficient of 0.9998 and standard deviation of 2.58. Such a fit implies that substantial inflections, or deviations from a smoothly changing C_p curve, are absent. The corresponding quadratic for poly(dicyclodecyl itaconate) is

$$C_p(\mathrm{J\,K^{-1}\,mol^{-1}}) = 0.1414 + 1.719T + 1.459 \times 10^{-3}T^2 \tag{5}$$

where the correlation coefficient is only 0.996 and the standard deviation is much higher at 11.93. Shown at the tops of *Figures 6* and *7* are the differences $\delta C_p = C_p$ (experimental) $- C_p$(quadratic), where it is quite obvious that the quadratic equation (5) is indeed a poor representation of the C_p–T data for the polymer containing the ten-membered rings and that in this case substantial deviation from monotonic behaviour is present. The curve is better described as possessing a shallow inflection around 150K, which is thought to arise from a heat capacity contribution due to the pendant rings, by analogy with the previously published data[2] on poly(dicyclooctyl itaconate).

The problem of quantifying the ΔC_p at such a shallow inflection has been noted already[2] and the expedient of a linear extrapolation of the data below 140K is again used. However, an alternative strategy can also be adopted. It has been shown[3] that the glassy-state heat capacity of poly(di-n-alkyl itaconates) may be satisfactorily represented by the heat capacity of poly(dimethyl itaconate) plus a contribution per added CH_2 group calculated from

$$C_p(\mathrm{J\,K^{-1}\,mol^{-1}}) = \sum_i k\left(\frac{\theta_i}{T}\right)^2 \frac{e^{\theta_i/T}}{(e^{\theta_i/T}-1)^2} \tag{6}$$

where the frequencies $v_i = k\theta_i/h$ are those of the normal modes of each added CH_2 unit and h is Plank's constant. In the case of the cycloalkyl analogues a similar additive procedure is also possible using the heat capacity of poly(dimethyl itaconate) (equation (2) of ref. 3) less twice the heat capacity of the ester methyl group of poly(methyl methacrylate)[10]. Equation (7) represents the C_p–T curve for the itaconate polymer backbone thus calculated:

$$C_p(\mathrm{J\,K^{-1}\,mol^{-1}}) = -60.953 + 1.6346T - 5.8634 \times 10^{-3}T^2 + 13.02 \times 10^{-6}T^3 \tag{7}$$

This is strictly valid between 100 and 210K, which are the limits of the experimental data from which it is derived.

All but two of the frequencies for use in equation (6) were obtained from the infra-red spectra of the polymers and are shown in *Table 1*. The last two frequencies per CH_2 group are those that describe methylene sequences twisting and bending modes, and values were chosen to provide the fits shown by the full curve in *Figures 6* and *7*. These are reasonably close to the frequencies of the corresponding acoustical modes in polyethylene employed by Dole[11] in his calculation of the C_p–T curve for this polymer.

In the case of poly(dicyclododecyl itaconate) the theoretical curve provides a good description of the experimental data up to ~250K, above which temperature the curvature in the C_p–T data is overestimated. For poly(dicyclodecyl itaconate) the theoretical curve, which is approximately quadratic in behaviour, cannot be fitted satisfactorily to the data over any appreciable temperature range, and the two low frequencies in the vibrational spectrum have been so chosen to obtain a fit below ~140K and thus provide a basis for extrapolation into the region of the shallow inflection in the data. The differences between the experimental data and this curved form of extrapolation are then taken to represent the heat capacity contribution (ΔC_p) from the pendant cyclodecane rings. An alternative set of ΔC_p values may be obtained on the basis of the linear extrapolation, also shown in *Figure 6*, and the two sets of ΔC_p values are plotted in *Figure 8*.

Table 1 Modes and frequencies used to evaluate equation (6) for pendant cycloalkane rings

Mode	Frequency (cm^{-1})	No. of modes
C–H stretch	2850	2 per CH_2 + 1 per CH
C–C stretch	950	1 per CH_2 + 1 per CH
C–H twist	1300	1 per CH_2
C–H wag	1300	1 per CH_2
C–H bend	1430	1 per CH_2
C–H rock	750	1 per CH_2
C–O stretch	1200	1 per ring
C–H rock	1300	1 per CH
–$(CH_2)_n$– twisting and bending	390 and 135 for poly(dicyclodecyl itaconate) 550 and 80 for poly(dicyclododecyl itaconate)	per CH_2

The purely thermodynamic arguments leading to the heat capacity contributions shown in *Figure 1* ignore the existence of energy barriers between the lowest energy conformer 'ground state' and the higher energy ones. If it is assumed that all the systems achieve their ground states on cooling, and all other states are to be isolated by insurmountable barriers, then no heat capacity change with temperature would be observed. As before[2] we treat the problem of energy barriers between states by defining a temperature T_a at which any conformer is no longer isolated from the ground state and becomes 'active' in the thermodynamic sense. The contributions to C_p can then be calculated over temperature ranges between successive T_a's, where T_a is given by[2,12]

$$T_a(\mathrm{K}) = \Delta E^{\ddagger}/0.27 \tag{8}$$

with $\Delta E^{\ddagger}$ the energy barrier in kJ mol^{-1}. The available conformers for poly(dicyclodecyl itaconate) and poly(dicyclododecyl itaconate) are listed in *Table 2* and the theoretical contributions to the heat capacities of the two polymers from their pendant rings are shown in *Figure 8*.

The analysis reveals that the heat capacity contribution to the C_p–T behaviour of poly(dicyclododecyl itaconate) is roughly wedge-shaped with virtually no abrupt onset. This, and the fact that the overall contribution is much smaller than that observed in poly(dicyclooctyl itaconate), implies that d.s.c. measurements would be unlikely to detect any identifiable changes or discontinuities in the C_p–T curve—which is indeed the case (*Figure 7*).

The calculated contribution for poly(dicyclodecyl itaconate), on the other hand, is somewhat larger with a

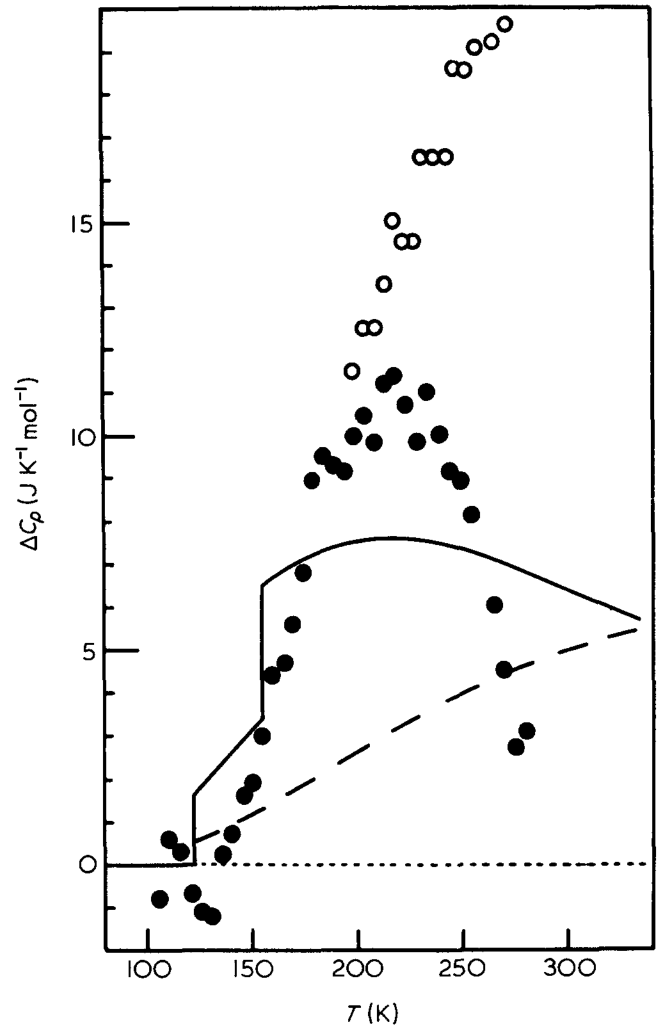

Figure 8 The differences (ΔC_p) between the experimental heat capacity of poly(dicyclodecyl itaconate) and the C_p–T extrapolation curve calculated from equations (6) and (7) (●), and the linear C_p–T extrapolation (○). The full curve is the theoretical contribution to the heat capacity from the set of cyclodecane conformers indicated in *Figure 3* and *Table 2*. The broken curve is the theoretical contribution to the heat capacity of poly(dicyclododecylitaconate) from the set of cyclododecane conformers indicated in *Figure 5* and *Table 2*

Table 2 Progression of available conformers as a function of temperature using lowest energy conformer as ground state

Temperature range (K)	$\Delta E\ddagger$ (kJ mol^{-1})	T_a (K)	Energy levels available
	Poly(dicyclodecyl itaconate)		
0–123	–	–	–
123–155	33.2	123	$\epsilon_2+\epsilon_3+\epsilon_4$
>155	42.0	155	$\epsilon_1+\epsilon_2+\epsilon_4$*
	Poly(dicyclododecyl itaconate)		
0–123	–	–	–
123–197	33.2	123	$\epsilon_1+\epsilon_2$
>197	53.3	197	$\epsilon_1+\epsilon_2+\epsilon_3$

* High energy ϵ_5 not used in calculation

relatively abrupt onset. The ΔC_p values obtained from the curved extrapolation fall in reasonably well with the theoretical contribution, especially at the onset of the inflection. The overall pattern of agreement, it must be admitted, is poorer than for poly(dicyclooctyl itaconate)^2 where not only the inflection onset was reproduced but also the absolute values of ΔC_p were accurately fitted over a wide temperature range. In this present case the calculation underestimates the size of the ΔC_p maximum and the rate at which ΔC_p decreases thereafter. The alternative set of ΔC_p values, evaluated from the linear extrapolation in *Figure 6*, correspond with those from the curved extrapolation up to 200K but then continue to increase, quite contrary to prediction.

These two opposing trends reflect the uncertainties in both methods of extrapolation. It is unlikely that strictly linear C_p–T behaviour holds over such a wide temperature range as examined here. Similar limitations also apply to the curved extrapolation since the temperature range available over which the chosen frequency spectrum reproduces the experimental data is small (105–140K), being limited by the lowest starting temperature

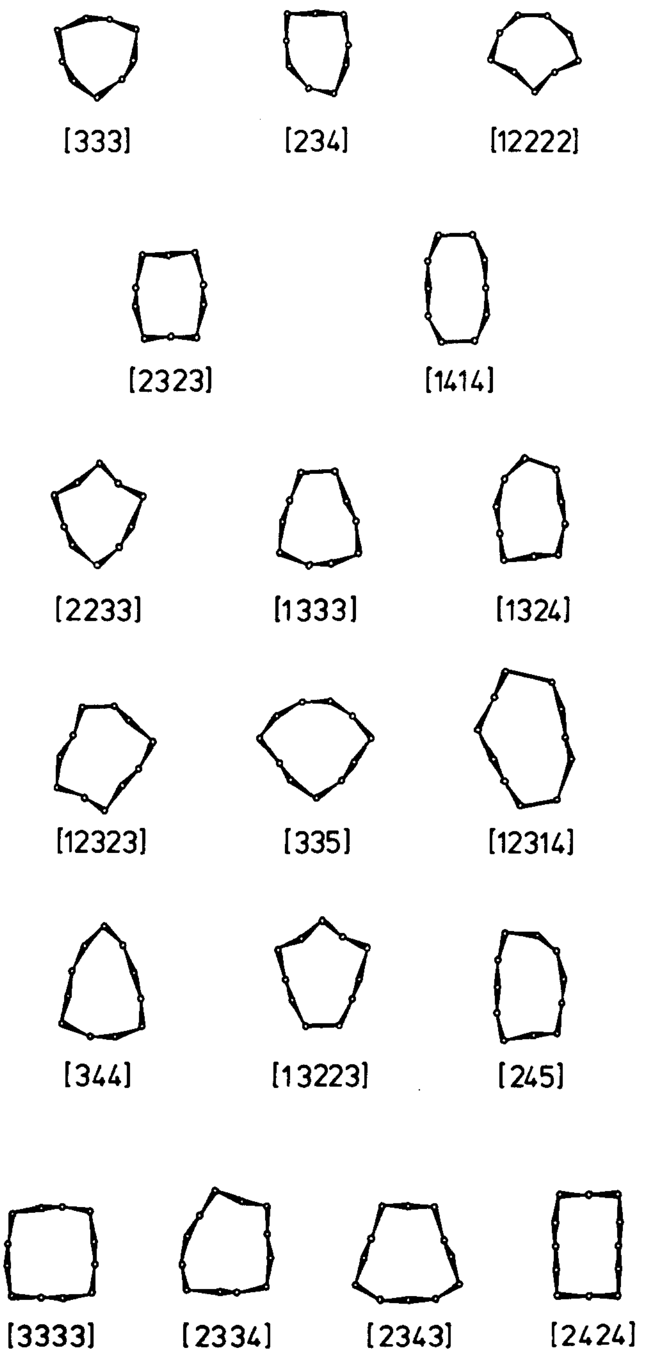

Figure 9 'Wedge' diagrams of the conformers used to calculate the heat capacity contributions from cycloalkyl rings. The energies of the conformers are listed in *Table 3*

Table 3 Energies, relative to lowest energy conformer, of the cycloalkane conformers used to calculate the contributions to C_V

C atoms per cycloalkane ring	Conformer	E (kJ mol^{-1})
9	[333]	0.0
	[234]	5.9
	[12 222]	11.8
10	[2323]	0.0
	[1414]	3.6
	[2233]	5.9
	[1333]	5.9
	[1324]	19.7
	[1243]	51.2
11	[12 323]	0.0
	[335]	0.0
	[12 314]	5.0
	[344]	5.0
	[13 223]	6.3
	[245]	11.3
12	[3333]	0.0
	[2334]	6.7
	[2343]	12.2
	[2424]	20.6

attainable. Although such an extrapolation has been used with success[1] for poly(di-n-alkyl itaconates) the ΔC_p values involved were an order of magnitude greater, and consequently less dependent on the choice of baseline. The shape of the theoretical contribution shown in *Figure 8* implies that 'baseline' behaviour with somewhat less curvature above 240K would be more appropriate and, as noted earlier, the calculation *via* equations (6) and (7) also overestimates the C_p–T *curvature for* poly(dicyclododecyl itaconate) in the same temperature range. It should also be recalled that equation (7), describing the C_p–T behaviour of the polyitaconate backbone, may not be applicable above 200K and this will also limit the validity of any extrapolation above this temperature.

It is concluded that d.s.c. can be used to detect molecular motions in the glassy state provided two criteria are met. First, a considerable number of non-equienergetic energy states must be accessible to the system with energies less than $\sim 15\,\mathrm{kJ\,mol^{-1}}$ and, secondly, the energy barriers between states must be surmountable over a relatively narrow temperature range. With this in mind, we feel that a d.s.c. examination of other members of the poly(dicycloalkyl itaconate) series for heat capacity changes corresponding to the known mechanically active relaxations involving pendant rings is not warranted. The usefulness of the statistical thermodynamic arguments in providing quantitative predictions of overall heat capacities is also limited by the need to define the contributions from all other sources. The use of equations such as (7) would seem a reasonable approach; however, this does imply that the heat capacity behaviour of a polymer backbone does not depend on the particular substituent 'environment' in which it finds itself—and this is probably not the case.

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