Detection of sub-glass transition events in amorphous polymers using differential scanning calorimetry

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The variation of the heat capacity (C_p) as a function of temperature has been measured for a sample of poly(di-cyclo-octyl itaconate) using a differential scanning calorimeter. Two inflexions in the C_p–T curve have been detected. One, observed at 390K has been assigned to the glass–rubber transition, the other, located at 140K, is a consequence of intramolecular motion in the pendant cyclo-octyl rings. The heat capacity contribution calculated from the partition function describing a series of cyclo-octane conformers agreed closely with the experimental values associated with this lower inflexion, and supported our interpretation of the molecular origins of this transition.

Keywords Measurement; heat capacity; differential scanning calorimetry; sub-glass transition; poly(dicyclo-octyl itaconate); ring conformational changes

INTRODUCTION

Differential scanning calorimetry (d.s.c.) is widely used to detect the major transitions in polymers such as the melting temperature and the glass transition temperature T_g. In amorphous polymers the long range cooperative motion associated with T_g causes a relatively abrupt discontinuity in the heat capacity–temperature curve (C_p–T) and the extent of this change in C_p may be used for quantitative characterization of the system under study[1,2]. Outside the glass transition temperature region only slow monotonic changes in the C_p–T curve have been observed and studies of molecular motion in the glassy state have never relied, to any appreciable extent, on heat capacity studies. It has been claimed[3], however, that transitions in the liquid state can be detected using C_p–T data.

We have recently completed a study of the thermo-mechanical properties of two series of polymers, one based on the di-*n*-alkyl[4,5], and the other on the di-cycloalkyl[6,7], esters of itaconic acid. In the former, dynamic mechanical methods revealed a substantial relaxation in the glassy state of those derivatives with side chains of seven to eleven carbon atoms, which was ascribed to independent microbrownian motion of the side chains. This process appeared to be decoupled from the main chain motion which occurred at higher temperatures. More significantly, this sub-glass relaxation was clearly seen as a major inflexion in the C_p–T curve and bore all the characteristics of a second glass transition, even though it appeared at temperatures lower than the conventional, main chain, glass–rubber transition, where the sample softened. Since these polymers have an extremely high side chain density and as the side chains are less polar than the main backbone, these structures may be regarded as a type of comb polymer, or even copolymer, in which the side chains do not become entangled with the main chains of adjacent molecules to any significant extent, because of the effective shielding. The polymers then behave almost as two phases in the glass and the ease of detection of side chain motion is not so surprising.

In the second series containing the pendant cycloalkyl units, the dynamic mechanical spectra also reveal major damping peaks in the glassy state. It has been postulated that these are caused by conformational changes in the pendant ring systems which are entirely intramolecular in nature. The various conformers, available to a ring system, exist at different energy levels and the contribution to C_p from these conformational isomers can be calculated from statistical thermodynamics. It can be demonstrated that the magnitude of the C_p contribution is proportional to the number of energy levels available to the system, and so it should be possible to observe the consequence of these conformational changes on the C_p–T curve if the contribution to C_p is large enough to avoid being submerged in the broad background resulting from all the other vibrational contributions.

Conformational changes in cyclo-octane have been extensively studied both experimentally and theoretically[8–11], so that both the number and relative energies of the stable conformers are known with reasonable certainty. Dynamic thermomechanical studies[6] of poly(di-cyclo-octyl itaconate) have shown that intramolecular motion in the pendant cyclo-octyl units gives rise to an intense mechanically active process at ~175K and 1 Hz. This polymer should then provide an example of a system in which there is a significant contribution to the C_p–T curve in this temperature region and so was selected for this investigation.

EXPERIMENTAL

Monomer preparation and polymerization

Di-cyclo-octyl itaconate was prepared by conventional acid catalysed esterification of itaconic acid with cyclo-

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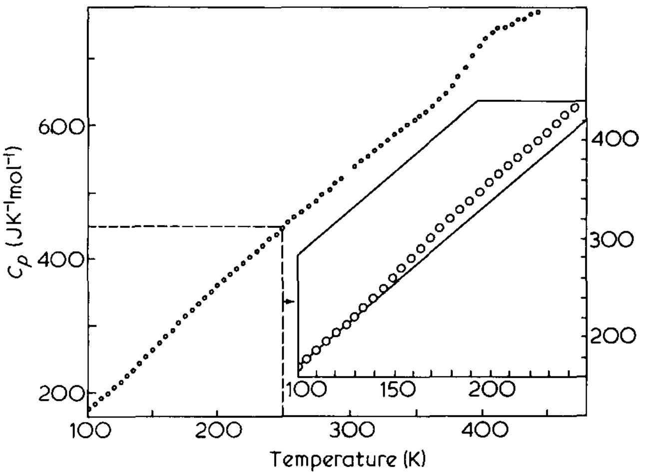

Figure 1 **Heat capacity of poly(di-cyclo-octyl itaconate) as a function of temperature. C_p is in units of J K^{-1} per mole of polymer repeat unit. Detailed primary data are available and can be obtained on request**

octanol. The pure monomer was separated on a silica column using chloroform as eluant. Polymerization was carried out in bulk at 323K using α,α'-azobisisobutyronitrile as initiator. The polymer was precipitated twice from chloroform solution into methanol and its purity checked using both infra-red and n.m.r. spectroscopy. The number average molecular weight, determined by membrane osmometry in toluene as solvent, was 1.8×10^5 g mol^{-1}.

Heat capacity measurement

The heat capacity, C_p, of poly(di-cyclo-octyl itaconate) (PDCyOI) was measured using a Perkin Elmer DSC-2 fitted with a low temperature accessory and scanning auto zero. All measurements were made at a scanning rate of 20K min^{-1} over the temperature range 90–470K. Below 300K, helium was used as purge gas while nitrogen was used for temperatures in excess of this. Pure samples of mercury, gallium, indium and lead were used for temperature calibration and this was monitored at frequent intervals throughout the series of measurements.

Values of C_p were determined at 5K intervals by comparing the recorded output for a sample of PDCyOI (29 mg) with that for a standard sapphire sample. Both were measured relative to the baseline established for an empty pan of the same weight as that used for both polymer and sapphire. Polymer, sapphire, and baseline scans were run consecutively while making sure that the level of liquid nitrogen coolant, used during sub-ambient runs, was always maintained at a constant level to minimize drift. The C_p values quoted are an average of six separate determinations over the 90–300K range and of two determinations over the 300–470K range. The reproducibility of the measured C_p was $\pm 2.5\%$ at 110K, improving to $\pm 1\%$ at 170K to 230K and finally $\pm 0.5\%$ at 300K and above. All measurements on the polymer sample were made after quenching from 470K at a rate of 320K min^{-1}, to the appropriate starting temperature. Variations in the thermal treatment of the sample (e.g. slow cooling) did not appear to alter the C_p significantly in the low temperature region of interest, although some changes were noted in the glass transition region.

Dynamic mechanical measurements

The damping characteristics of PDCyOI were measured as a function of temperature and frequency using a Rheovibron viscoelastometer DDVIIC. The sample was supported on a glass fibre strip using a technique described previously[12] and examined over a temperature range 120K to 273K. The apparent activation energy $\Delta H^{\ddagger}$ of a damping process was estimated using the Arrhenius equation.

RESULTS AND DISCUSSION

The experimental values of C_p evaluated at 5K intervals for PDCyOI are plotted in *Figure 1* and the 1 Hz damping thermogram[6] is shown in *Figure 2* for comparison. It can be seen that there is a reasonably close correspondence between the temperature of the maximum of the major damping peak ($\sim$410K) and the obvious glass transition inflexion at $\sim$390K on the C_p–T curve. The magnitude of this inflexion $(\Delta C_p)_g$ is 50 J K^{-1} mol^{-1}, referring to the repeat unit molar mass of 350 g mol^{-1} of the polymer. Below T_g the C_p–T curve displays a noticeable, but much smaller, inflexion between 140 and 190K, which can be more clearly seen in the insert to *Figure 1*. This inflexion is located in the temperature range covered by the lesser damping peak located in the glassy state of PDCyOI.

It seems reasonable to assume that this inflexion represents the onset of a new contribution to C_p which is inactive below 140K and may be associated with the intramolecular motions in the cyclo-octyl ring which we assigned previously to the corresponding damping peak in the dynamic mechanical spectrum[6].

One can attempt to quantify this new contribution to C_p, in the temperature range 140K to 190K, by determining the differences $(\Delta C_p)_t$, between a linear extrapolation of the C_p–T curve from below 130K and the experimental curve, as shown in *Figure 1*.

There are of course limitations to this approach. The extrapolated line is based on data which only extend down to 100K and the behaviour of the 'baseline' underlying the inflexion is unknown and may not be completely linear. Nevertheless it was considered that a reasonable estimate could be made on these assumptions and it was decided to investigate the derived values of $(\Delta C_p)_t$ from the onset of the inflexion up to 280K, based on such a linear extrapolation.

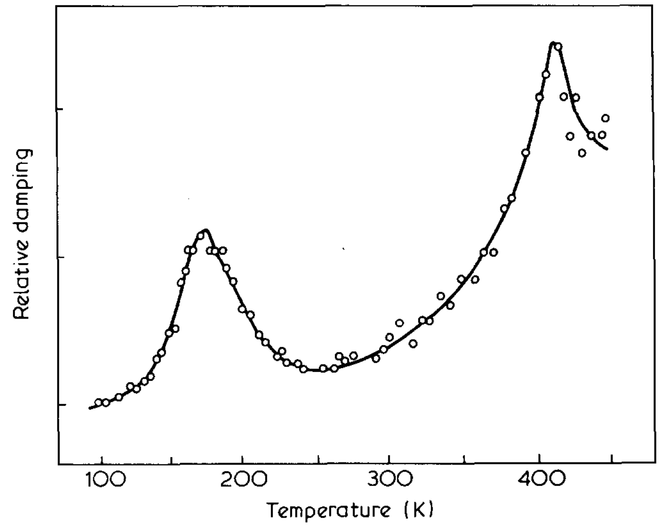

Figure 2 **Relative mechanical damping thermogram for poly(di-cyclo-octyl itaconate) as a function of temperature. Taken from ref. 6**

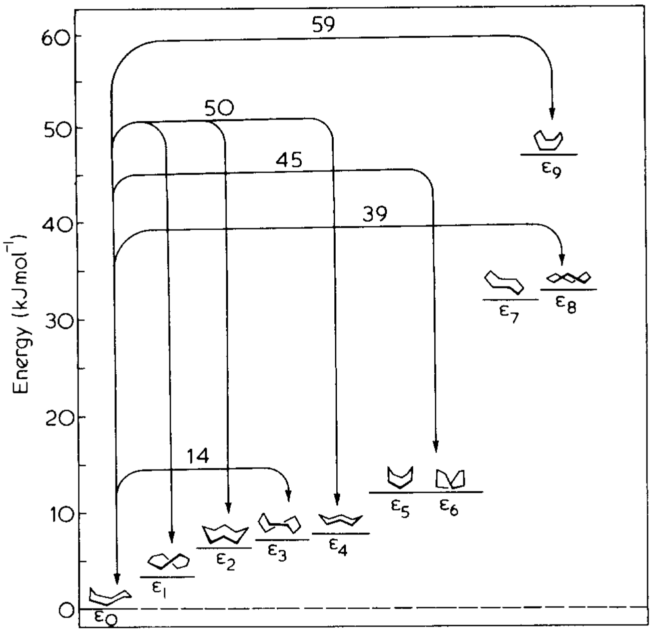

Figure 3 Energy level diagram for cyclo-octane conformers. The boat–chair, BC, conformer is taken as ground state $\varepsilon_0 = 0$ with the energy barriers in kJ mol^{-1} indicated on the diagram for conversion to the higher energy conformers ε_1 to ε_9. These are–
ε_1 (twist–chair–chair TCC) = 3.3 kJ mol^{-1}
ε_2 (crown Cr) = 6.3 kJ mol^{-1}
ε_3 (twist–boat–chair TBC) = 7.1 kJ mol^{-1}
ε_4 (chair–chair CC) = 7.5 kJ mol^{-1}
ε_5 (boat–boat BB) = 11.7 kJ mol^{-1}
ε_6 (twist–boat TB) = 11.7 kJ mol^{-1}
ε_7 (chair C) = 31.4 kJ mol^{-1}
ε_8 (twist–chair TC) = 32.3 kJ mol^{-1}
ε_9 (boat B) = 47.0 kJ mol^{-1}

Cyclo-octane is known to undergo a number of conformational interconversions[9] and the relative conformational energies and barriers to interconversion have been calculated by Anet and Krane[11]. An energy diagram based on their results is shown in *Figure 3* and it can be seen that apart from one low energy process, the boat–chair (BC)↔twist-boat–chair (TBC) conversion, the activation energy barriers range from 39 to 59 kJ mol^{-1}.

The value of $\Delta H^\ddagger$ obtained for the damping process centred on 175K was 46 ± 5 kJ mol^{-1} which corresponds closely to some of the energies for interconversions shown in *Figure 3*. It was proposed elsewhere[6] that at least three ring interconversions were occurring in the glassy state of PDCyOI, a BC↔TB, a BC↔BB, and a TBC↔TCC process, and that these were responsible for the observed damping. One can extend this concept and consider the contribution that all the conformers of the cyclo-octyl ring might make to C_p. This can be achieved if the conformers are taken to represent a series of energy levels which the molecule can occupy and the distribution over these levels is then estimated using the Boltzmann principle. A partition function Q can then be derived from

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

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

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

It has been shown[13] that for polymer systems the difference between C_v and C_p is very small and so one can make the approximation in equation (2). This can be recast as

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

Equation (3) can now be used to estimate C_p as a function of temperature for any system of i energy levels.

This purely thermodynamic treatment ignores the existence of energy barriers and if any of the energy levels in the system were isolated by an energy barrier too large to be overcome easily at the temperature in question one would not expect it to contribute. Thus if we are to treat the pendant cyclo-octyl rings in PDCyOI as a system comprising nine conformational energy states, some account must be taken of the energy barriers shown to exist between each pair. Heijboer[14] has demonstrated that the local energy barrier for a molecular process in a polymer glass can be related to the temperature of the damping maximum (T_m(K)) of that process measured at 1 Hz by

$$\Delta H^\ddagger(\text{kJ mol}^{-1}) = A[T_m(\text{K})] \qquad (4)$$

where A is a constant which has a value of ~0.27. One can then estimate values of T_m corresponding to the five energy barriers depicted in *Figure 3*. If the boat-chair (BC) conformer is now taken as the zero energy form ($\varepsilon_0 = 0$) then each T_m can be equated to the temperature T_a at which the relevant conformer is no longer separated by an energy barrier which is too large and so becomes 'active' in a thermodynamic sense also. The contributions to C_p can now be calculated over successive temperature intervals by considering that energy levels become available in the order outlined in *Table 1*.

From these calculations a C_p–T curve consisting of five segments can be constructed and is shown in *Figure 4* where it can be compared with the experimental data, expressed in terms of ΔC_p per mole of cyclo-octyl units (i.e. $(\Delta C_p)_t/2$ as there are two cyclo-octyl units attached to each monomer). Two discontinuities are seen, one at 167K where ε_5 and ε_6 are included and a much larger one at 185K where ε_1, ε_2 and ε_4 enter the calculation. As one can see the theoretical curve is able to predict both the onset of ΔC_p and its magnitude with reasonable accuracy in spite of the approximations involved. Consequently it can be suggested that the coincidence of this theoretical treatment with the experimental curve allows one to identify the molecular processes responsible for the inflexion in the C_p–T curve at 140–190K in PDCyOI, as

Table 1 Progression of available conformers as a function of temperature using BC as a zero point

Temperature range (K)	$\Delta H^\ddagger$ (kJ mol^{-1})	T_a (K)	Energy levels available
0–52	–	–	–
52–144	14.0	52	ε_3
144–167	39.0	144	$\varepsilon_3 + \varepsilon_7 + \varepsilon_8$
167–185	45.0	167	$\varepsilon_3 + \varepsilon_5 + \varepsilon_6 + \varepsilon_7 + \varepsilon_8$
185–219	50.0	185	$\varepsilon_1 + \varepsilon_2 + \varepsilon_3 + \varepsilon_4 + \varepsilon_5 + \varepsilon_6 + \varepsilon_7 + \varepsilon_8$
>219	59.0	219	all

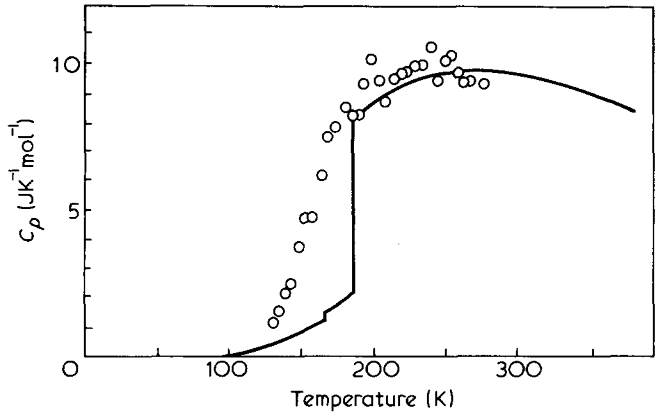

Figure 4 Comparison of calculated heat capacity contribution from cyclo-octane conformers with experimental data (open circles) $(\Delta C_p)_t/2$, both expressed as J K^{-1} per mole of cyclo-octyl units

the redistribution of pendant cyclo-octyl units among their energetically non-equivalent conformations.

It must be stressed, however, that PDCyOI does lend itself to this type of analysis as it satisfies two important criteria:

(a) there is a relaxation process in the glass which is mechanically active and produces an intense damping peak,

(b) the underlying molecular mechanism is one involving a substantial number of different energy states, with closely spaced activation energy barriers.

It would appear from our results that while mechanical activity and the contribution to C_p may have their origin in molecular motions involving the same part of the molecule, the magnitude of $(\Delta C_p)_t$ will depend mainly on the number of associated and available energy states. One must conclude that mechanically active processes will only be detected on the C_p–T curve, using our existing instrumentation, if the available energy states are sufficiently numerous. For example poly(di-cyclohexyl itaconate) and poly(cyclohexyl methacrylate) both exhibit damping peaks in the glass which have been ascribed to the chair–chair interconversion of the pendant cyclohexyl rings[15,16]. As this only involves two energy levels the maximum contribution to C_p is 3.65 kJ mol^{-1} and this is probably too small to detect unequivocally. Contributions of this magnitude would require a more sensitive detection system and greater experimental accuracy before becoming evident in a C_p–T curve. Nevertheless, it is believed that there are several other systems, with mechanically active relaxation processes occurring in the glassy state which may be observed using d.s.c. because the active portion of the molecule also possesses enough energetically non-equivalent conformers to give an appreciable $(\Delta C_p)_t$ in a restricted temperature range. These are now under investigation.

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