Poly(alkyl itaconates): 8. Observations of dual glass transitions and crystallinity in the dialkyl ester series diheptyl to di-eicosyl

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A series of poly(di-n-alkyl itaconic acid esters) with side chain lengths from 7 to 20 carbon atoms have been prepared. For derivatives with chain lengths of 7 to 11 carbons, two glass transition temperatures have been detected. The transition occurring at the lower temperature T_g^2 originates in the side groups and is a result of the independent cooperative relaxation of the alkyl side chains, while that observed at higher temperatures T_g^1 reflects the glass–rubber transition of the main chain backbone and the cooperative motion of the total molecule. Derivatives with chain lengths $\geqslant 12$ carbon atoms display melting temperatures T_m, and measurement of the enthalpy of fusion ΔH_f indicates that side chain crystallization takes place with part of each side chain entering into a regularly packed hexagonal lattice.

INTRODUCTION

Interest in the polydialkyl esters of itaconic acid has arisen because of their close similarity to the poly(alkyl methacrylates) and has intensified since the discovery that itaconic acid can be made easily in large economical quantities. In a previous paper[1] the physical properties of the lower members of the dialkyl series, methyl to hexyl, were examined. Identification of the glass transition temperatures shows that the flexible alkyl side chains produced internal plasticization of the samples and paralleled comparable trends in the poly(alkyl methacrylates).

In most respects this part of the dialkyl itaconic acid ester series behaved as might have been expected by displaying properties similar to the alkyl methacrylates, but investigation of the higher members in the dialkyl itaconates has revealed interesting behaviour which is not mirrored in any other polymers to date and which is described here.

EXPERIMENTAL

Polymer preparation

Dialkyl itaconic acid esters with side chain lengths C_7 to C_{20} were prepared by esterification of itaconic acid using the appropriate alcohol[1]. Bulk polymerizations using α,α'-azobisisobutyronitrile as initiator were carried out under vacuum and were stopped at moderately low conversions to prevent broadening of the molecular weight distributions. The reaction mixtures were dissolved in benzene and the polymer isolated by precipitation using methanol as non-solvent. Emulsion polymerizations were found to be more satisfactory. Potassium persulphate was used as the initiator at temperatures of ~333 K and the polymer was isolated by precipitation in methanol. Samples were purified by repeated dissolution and reprecipitation before drying and storing *in vacuo*.

Characterization

Unfractionated samples were used throughout. Molecular weights were determined by light scattering (M_w) and viscosity (M_v) and all samples had sufficiently large values of M_w to ensure that parameters such as the glass transition temperature T_g, attained their asymptotic value. The densities of polymers up to C_{12} were measured at 296 K using a density gradient column which was calibrated using glass floats of known density.

Differential scanning calorimetry (d.s.c.)

D.s.c. thermograms were obtained for each polymer using 10–15 mg of rigorously dried material. The instrument was a Perkin–Elmer DSC-2 fitted with a scanning autozero. Helium was used as purge gas for measurements below 200 K, otherwise dry nitrogen was used. Scanning rates of up to 20 K min^{-1} were employed and the instrument was calibrated regularly with metal standards. The extrapolated onset of the baseline shift was taken as an indication of T_g, while the melting temperature T_m was measured from the peak of the appropriate endotherm.

Dynamic mechanical measurements

Dynamic thermomechanical spectra were obtained using two techniques. A torsional braid analyser[2] (t.b.a.) was used to obtain the polymer response at a nominal frequency of 1Hz. Composite samples were prepared by impregnating a glass fibre braid with polymer thereby allowing polymers which are mechanically weak at ambient temperatures to be handled easily[1,3]. Because the nature of the composite sample does not allow precise measurements of its geometry, the data obtained are non-absolute. They are displayed as the mechanical damping index ($1/n$), which is proportional to the logarithmic decrement, and as the relative rigidity ($1/p^2$), which is proportional to the complex modulus. Here, p is the time taken per oscillation of the composite, and n is the number

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Table 1 Characterization data for poly(di-n-alkyl itaconates)

Poly(itaconic acid ester)	10^5 M_w	Density[b] kg m^{-3}	T_g^2/K D.s.c.	T_g^2/K T.b.a.	$\Delta H^{\ddagger 2}$ kJ mol^{-1}	T_g^1/K D.s.c.	T_g^1/K T.b.a.	$\Delta H^{\ddagger 1}$ kJ mol^{-1}
Diheptyl (PDHpl)	4.3	1012.3	188	195	230	250	255	141
Di-octyl (PDOl)	4.0	997.7	191	198	166	253	240	123
Dinonyl (PDNI)	3.0	983.7	197	205	154	262	270	120
Didecyl (PDDI)	3.1	981.8	210	210	–	270	270	–
Diundecyl (PDUI)	8.0	980.5	218	217	–	275	265	–
Didodecyl[a] (PDDol)	2.2	979.2	(235)	225	111	–	–	–
Di-oleyl	–	–	–	–	–	195	–	–

[a] Exhibits a melting temperature, see *Table 2*
[b] Measured at 296K

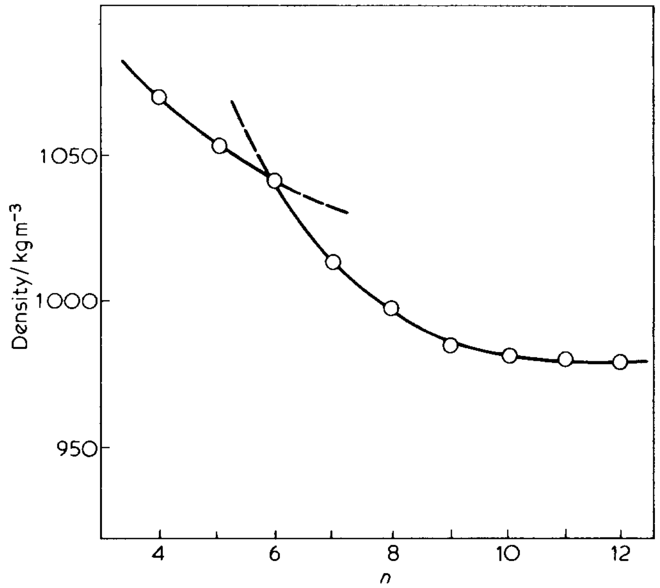

Figure 1 Densities of poly(dialkyl itaconates) as a function of side chain length *n*, measured at T = 296K

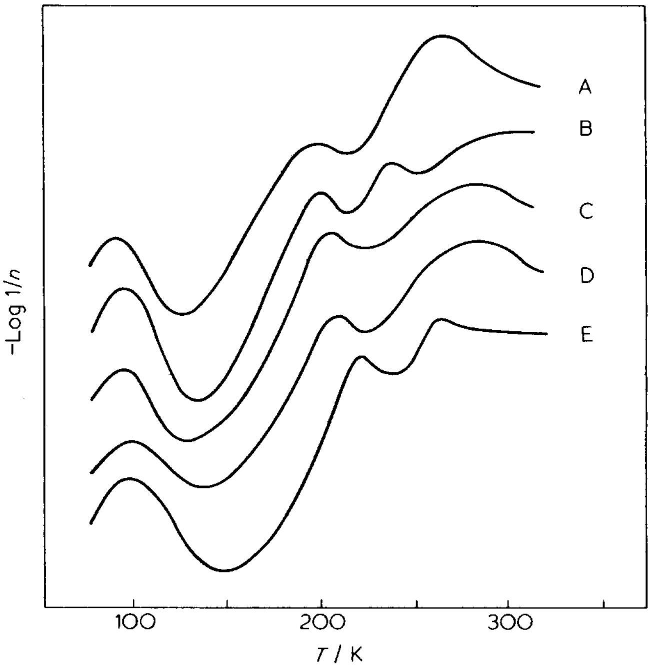

Figure 2 T.b.a. damping spectra for: A, diheptyl; B, di-octyl; C, dinonyl; D, didecyl; E, diundecyl; derivatives of poly(itaconic acid)

of oscillations occurring between two fixed boundary amplitudes in the decay wave.

The polymer response at four different frequencies, 3.5, 11, 35 and 110 Hz, was measured using a Rheovibron viscoelastometer model DDV IIC. Again the polymer was supported, this time on cellulose filter strips[4], and data are expressed in terms of the apparent damping (tanδ) as a function of temperature.

It has been demonstrated[3] that the dynamic mechanical response of supported polymer samples does not differ significantly from that of the unsupported sample and that the resulting spectra are essentially identical. By obtaining data at different frequencies, it is possible to estimate the apparent activation energy $\Delta H^{\ddagger}$ of a given process from the Arrhenius equation.

RESULTS AND DISCUSSION

Density

The densities of poly(dialkyl itaconate) samples, measured at a temperature above the T_g of each, are listed in *Table 1*. There is a general decrease in density as the length of the side chain increases. A discontinuity is also evident lying between the hexyl and heptyl derivatives, as seen in *Figure 1* where density is displayed as a function of side chain length. At side chain lengths C_{11} and C_{12} the density approaches an asymptotic limit just prior to the point at which crystallinity in the itaconates becomes evident.

Dynamic mechanical spectra

The thermomechanical response of the poly(dialkyl itaconates) with side chain lengths C_7 to C_{12} are shown in *Figure 2*, plotted as the mechanical damping index *versus* temperature. Three main features can be identified.

A high intensity damping peak is seen to occur in the 250–270 K temperature range which can be identified with a glass transition on comparison with d.s.c. thermograms. A second damping peak lying adjacent to, but at a lower temperature than, the high temperature peak, corresponds to a second glass transition and these will be discussed more fully in the next section. Peak temperatures are summarized in *Table 1*.

All samples exhibit a common γ damping peak centred on a temperature of $T_\gamma \sim 100$ K. Previous work[1,5] had indicated that damping processes in this region appear when there is a side chain in the polymer containing the sequences +O–C–C–C+ or +C–C–C–C+. The process is thought to involve restricted motion in this unit which could be rotation about the middle (C–C) bond when the

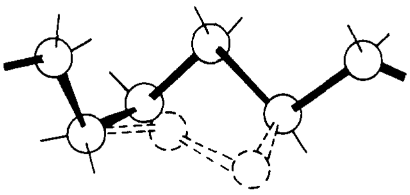

Figure 3 Proposed relaxation process involving a $ttg^- \rightarrow g^-tt$ conformational change in the alkyl side chains occurring at a temperature of ~100K

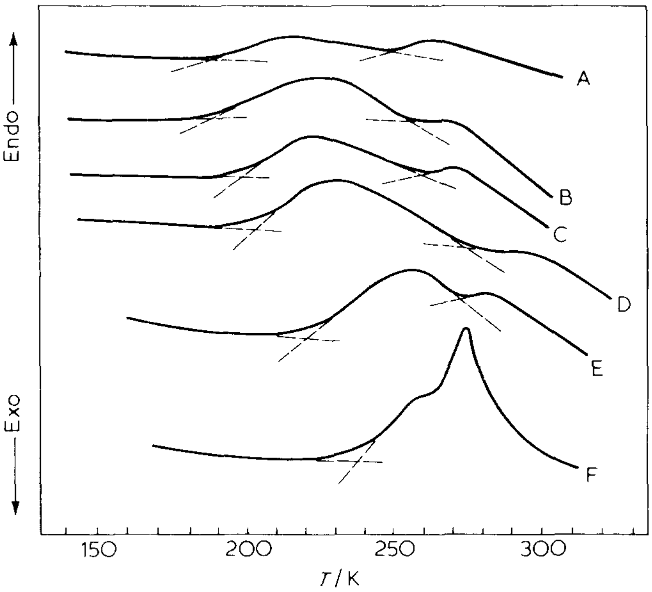

Figure 4 D.s.c. thermograms for: A, diheptyl; B, di-octyl; C, dinonyl; D, didecyl; E, diundecyl; F, didodecyl, derivatives of poly(itaconic acid), showing two T_g transitions in A–E and the melting endotherm in sample F

chains are relatively short[5], or by a mechanism similar to that described by Boyd and Breitling[6] known as the 'flip–flop'. The latter is a modification of the Boyer[7] crankshaft motion, but without requiring colinearity of the stem bonds. The sequence transformation is $(tg^+tg^-t) \rightarrow (tg^-tg^+t)$ and has an activation energy with the required order of magnitude. An alternative process[8,9] which also has an appropriate $\Delta H^\ddagger$ (see equation 1) involves the elementary migration of a *gauche* bond two positions along the chain, as shown in *Figure 3*. This is a simple local $(ttg^-) \rightarrow (g^-tt)$ sequence change which can be accommodated without significant disturbance of adjacent groups in the chain. These mechanisms are the ones most likely to account for the γ damping peak.

D.s.c. thermograms

Examination of the thermal behaviour of this series of polymers shows that they can be divided into two general groups. The first includes the members from diheptyl to diundecyl which can be distinguished by the fact that they display two baseline shifts in the d.s.c. thermograms indicative of two glass–rubber transitions. There is a tendency for the base lines to appear curved in the d.s.c. spectra. We have noticed that (dC_p/dt) before an inflection for a glass transition is usually greater than after for the poly(itaconates) and this baseline slope change has also been observed for several other polymers too. In this case it tends to give the impression that maxima appear between the two baseline shifts. The second group encompasses samples with side chains longer than didodecyl, where the dominating feature is a melting endotherm with no suggestion of a glass transition whatsoever. The didodecyl derivative itself exhibits a large melting endotherm with some suggestion of a glass transition close to the onset of the melting process.

Returning to the first group, the thermograms in *Figure 4* clearly show the existence of two glass transitions and it is also clear that the transition at the lower temperature involves the greater change in heat capacity. This is confirmed by quantitative measurements. Designating the glass transition at the higher temperature T_g^1 and that for the lower T_g^2, we find for poly(diheptyl itaconate) that $\Delta C_p = 0.10\ \mathrm{J\,K^{-1}\,g^{-1}}$ at T_g^2 and $\Delta C_p = 0.067\ \mathrm{J\,K^{-1}\,g^{-1}}$ at T_g^1. Similarly for the dioctyl derivative, $\Delta C_p = 0.286\ \mathrm{J\,K^{-1}\,g^{-1}}$ for the T_g^2 transition and $\Delta C_p = 0.076\ \mathrm{J\,K^{-1}\,g^{-1}}$ for T_g^1.

Clearly, if two glass transitions exist for these molecules we must identify the underlying causes. Comparison of the T_g values with those obtained for earlier members of the series[1] is best carried out by plotting T_g against the number of atoms in the side chain as shown in *Figure 5*. The values of T_g for methyl to hexyl derivatives are more closely in line with the T_g^1 for the higher derivatives, suggesting that this can be associated with the long range cooperative motion of the whole polymer molecule. The depression of T_g is retarded as the side chain increases and T_g^1 actually increases slowly. This type of behaviour has been reported for a series of poly(vinyl n-alkyl ethers) where a minimum T_g was observed at the octyl derivative[10]. This is believed to be due to developing crystallinity or order in the samples as the side chain lengthens, which tends to raise the sample T_g. Other workers[11,12] have found that fluorine-substituted acrylates and esters of poly(acrylic acid) behave in the same way, but the data for poly(alkyl methacrylates) are contradictory. Rogers and Mandelkern[13] found T_g to decrease monotonically for samples up to dodecyl methacrylate, while others suggest the T_g decreases then increases as the side chain lengthens.

In order to examine how T_g might be affected if crystallinity was absent, a sample of poly(di-oleyl itaconate) was prepared. The double bond, located near the

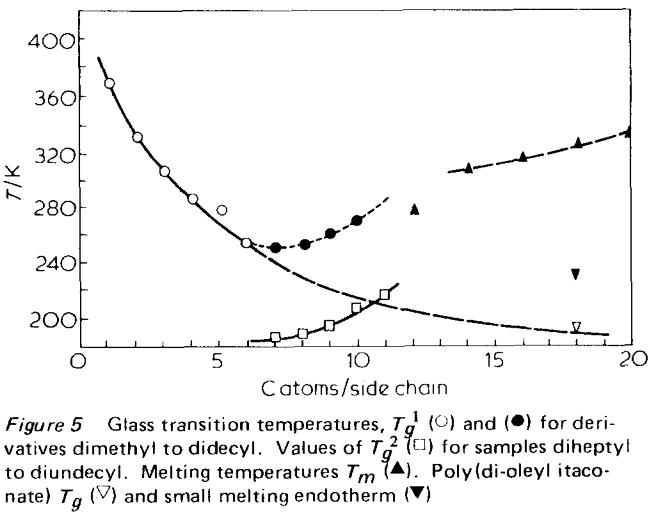

Figure 5 Glass transition temperatures, T_g^1 (○) and (●) for derivatives dimethyl to didecyl. Values of T_g^2 (□) for samples diheptyl to diundecyl. Melting temperatures T_m (▲). Poly(di-oleyl itaconate) T_g (▽) and small melting endotherm (▼)

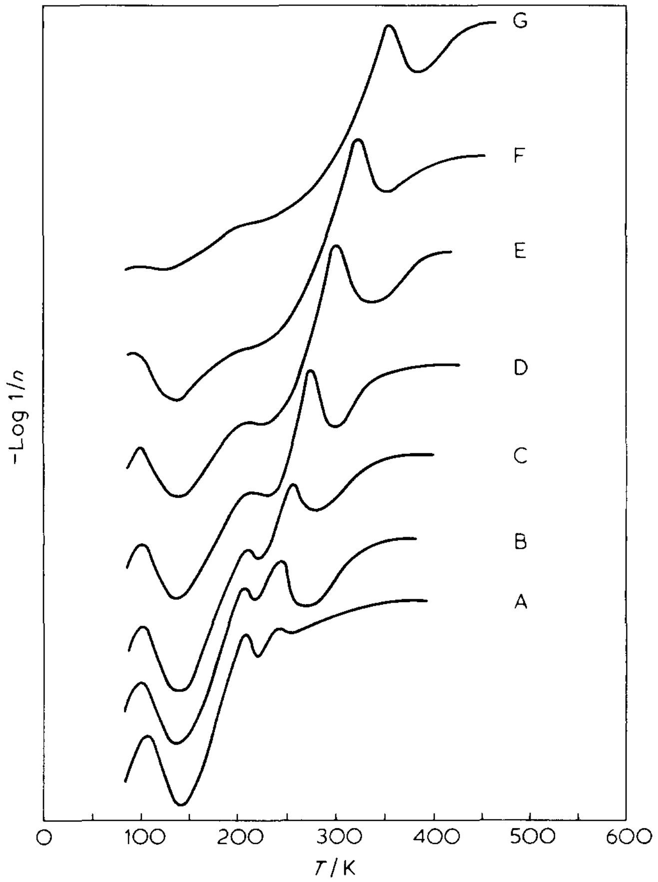

Figure 6 T.b.a. damping thermograms for poly (dimethyl-co-di-octyl itaconate). Sample A is poly (di-octyl itaconate); the remaining are copolymers with mol % di-octyl units of: B, 93.4; C, 77.95; D, 56.1; E, 36.0; F, 21.7; G, 8.4

centre of the side chain prevents extensive crystallization by disrupting the symmetry of the side chain and the polymer showed a T_g at 195 K. A reasonable extrapolation of the data which encompasses this point is shown by the broken line in *Figure 5*. A small melting endotherm was also detected in the d.s.c. spectrum and this is also located on the diagram but at a temperature well below that of the corresponding poly(di-octadecyl itaconate).

As crystallinity eventually develops in the poly(dialkyl itaconates) when side chain lengths of $C \geqslant 12$ are reached, the increase in T_g^1 may be a reflection of a move towards ordering in the side chains. This is not clear from density measurements and in this case it may be increased entanglements in the system which affect T_g^1 and cause the rise.

What then is the origin of T_g^2 which also increases from ~188 K in the heptyl derivative to ~218 K in the undecyl derivative? The T_g^2 transitions has all the characteristics of a glass–rubber transition and evidence points to it originating in the alkyl side chains of the polymers. This is best illustrated by reference to work on itaconate copolymers. The t.b.a. spectra of random copolymers prepared from dimethyl itaconate with comonomers, diheptyl[14], dioctyl and dinonyl itaconate all show the same general trends, typified by the damping curves for the dimethyl/dioctyl copolymers shown in *Figure 6*. The corresponding d.s.c. spectra show a similar picture[14]. The copolymer T_g can now be traced through the series as the major damping peak appearing at the highest temperature and relating eventually to T_g^1 in the dioctyl itaconate. The T_g^2 is not present in the dimethyl polymer or copolymers with high dimethyl content. It can be identified with the central damping peak in the poly(dioctyl itaconate) spectrum appearing at 198 K and on following this through the copolymer series it is seen to diminish in intensity as the mol % of the dioctyl itaconate unit decreases, eventually disappearing at a composition of ~10 mol % dioctyl in the copolymer. The diheptyl and dinonyl copolymers also behave in this way. This damping peak, associated with T_g^2 is clearly associated with a relaxation process in the octyl side chains. This interpretation is consistent with the relative magnitudes of ΔC_p associated with each transition. The larger values of ΔC_p measured for T_g^2 are reasonable to expect, as the proportion of the polymer existing as side chain becomes progressively larger when the side chain lengthens. The change in heat capacity resulting from cooperative motion of the backbone at T_g^1 will be correspondingly smaller as the side chains will be already moving cooperatively in the matrix.

The apparent activation energies $\Delta H^{\ddagger}$ for the T_g^2 transitions in poly(diheptyl itaconate) is ~200 kJ mol^{-1} and that for the T_g^1 transition is ~145 kJ mol^{-1}. Both are of the correct order of magnitude for major relaxation processes. We can estimate $\Delta H^{\ddagger}$ expected for a secondary relaxation from the approximate relation

$$\Delta H^{\ddagger}/\mathrm{kJ\ mol^{-1}} = 0.252\ T_{\max}/\mathrm{K} \qquad (1)$$

proposed by Heijboer[15], which is valid at a frequency of 1 Hz. Here, $T_{\max}$ is the temperature at the maximum of the damping curve. Experimental values for $\Delta H^{\ddagger}$ are shown in *Figure 7* for the itaconate series. A smooth curve can be drawn through data for $\Delta H^{\ddagger}$ associated with T_g^1 for dimethyl through to dinonyl itaconate. Comparison with data drawn from the literature for the apparent activation energies of the glass transitions in the poly(alkyl methacrylate) series reveals a similar trend with increasing side chain length. When $\Delta H^{\ddagger}$ for the T_g^2 process is examined it

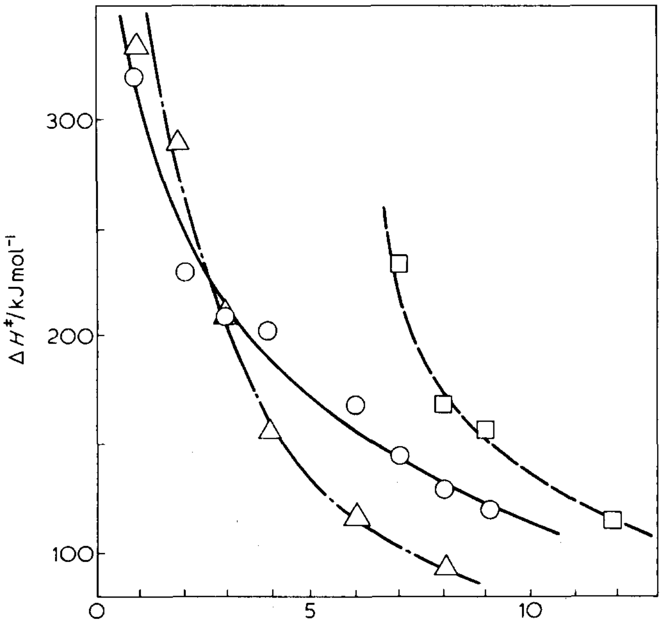

Figure 7 Apparent activation energy $\Delta H^{\ddagger}$ as a function of side chain length n for (○) poly(n-alkyl) itaconates) at T_g^1 and (□) at T_g^2. Poly(alkyl methacrylates) at T_g are represented by (△)

is found that these are generally higher and appear to be associated with a separate process. Thus the results all point to the existence of two distinct relaxations taking place, both of which have the characteristics of a glass–rubber transition. The diheptyl to diundecyl derivatives exhibit two T_gs: T_g^2 arises from a cooperative relaxation the alkyl side chains which appears to be decoupled from the main chain, while T_g^1 marks the transition of the whole polymer molecule from the glass to the rubber-like state.

Independent side chain relaxation in poly(α-amino acids) has been reported by a number of workers[16–20]. In poly(n-alkyl-D-glutamates), Kajiyama *et al.*[18] observed a relaxation process involving the entire side chain around 293 K and concluded that this large scale motion was a glass transition, in spite of the fact that in these semicrystalline polymers the T_g for the whole molecule is expected at much higher temperatures >480 K. Pezzin *et al.*[19] arrived at similar conclusions from d.s.c. studies of a different group of poly(α-amino acids) in agreement with several other groups of workers. All postulate that there is a glass transition which is caused by the relaxation of the side chains, independent of the core of the polymer, but cooperatively with each other.

These systems are more clearly two phase with a crystalline region, normally incorporating the main chain, and an amorphous or disordered region in which the side chains are located. The itaconates are essentially amorphous up to the diundecyl derivative, but the evidence leads one to postulate a two phase structure in the polymer matrix with the side chains occupying one region and the polymer core in separate domains. Because of the length of the side chain and the regular, high density, 'comb' formation of the polymer, we cannot escape drawing comparisons between these and regular graft copolymer structures which are also capable of displaying two T_gs, particularly when the grafted side chain differs in flexibility from the backbone. This regular high density arrangement of side chains may be a key feature in determining the presence of two T_gs, as the related alkyl methacrylates show no evidence of comparable behaviour. Dilatometric studies by Haldon and Simha[21] have revealed multiple transitions in poly(alkyl methacrylate) glasses which are too small to associate with a major glass–rubber transition. It would appear that in this latter series of polymers the side chains and polymer backbone chains can intermingle freely in the matrix thereby impeding independent relaxation. In the itaconate series the much higher density of side chains, which tend to shield and encase the backbone, appear able to segregate themselves and form discrete regions separate from the core of the polymer and that the two domains are characterized by independent T_gs.

Crystallinity

It has been widely recorded that comb-like polymers with long paraffinic side chains exhibit side chain crystallization and this topic has been extensively reviewed by Plate and Shibaev[22]. Some doubt exists as to whether the main chain of the polymer is incorporated in the lattice, but evidence favours the concept that only the side chains are involved in the crystallization process for polymers with structures similar to those studied here.

Heats of fusion, ΔH_f, were measured for samples with side chain lengths $\geqslant 12$ carbon atoms, all of which exhibit melting endotherms in their d.s.c. thermograms. Samples were annealed for 16 h prior to measurement, cooled well below the annealing temperature then heated at 10 K min^{-1}. Each measurement was calibrated against an indium standard run under the same conditions immediately after each measurement, and values are quoted in *Table 2*. The data can be fitted by a first degree polynomial of the form[23]:

Table 2 Heats of fusion for long chain poly(di-n-alkyl itaconates)

Polymer	Annealing Temp./K	T_m/K (peak)	ΔH_f/ J g^{-1}	ΔH_f/ kJ mol^{-1}
Didodecyl	255	272	17.9	8.3
Ditetradecyl	285	306	26.0	13.6
Dihexadecyl	295	312	45.1	26.1
Di-octadecyl	310	326	64.2	40.8
Di-eicosyl	320	336	68.2	46.7

$$\Delta H_f/\text{kJ mol}^{-1} = A + Bn \qquad (2)$$

where n is the number of methylene units in the monomer side chains (including terminal methyl groups), A is a contribution from the chain ends, and B is the enthalpy of fusion per mole of CH_2 units.

From this B was found to be $\sim 2900 \pm 200$ J (mol CH_2)$^{-1}$ which is close to the value of 3028 J (mol CH_2)$^{-1}$ reported by Broadhurst[24] for the α-hexagonal$\rightarrow$liquid transition in n-alkanes. This type of packing of paraffinic side chains in a hexagonal lattice has been observed for other comb branched polymers[22,25] from both X-ray diffraction and spectroscopic studies. Jordan *et al.*[23] have proposed that the first 9 to 12 methylene units are not involved in the crystal lattice, but that any units in excess of this will pack in a hexagonal ordered arrangement. Our results indicate that $\Delta H_f = 0$ at $n \sim 22.5$, which is consistent with the fact that the didodecyl derivative ($n = 24$) crystallizes, but the diundecyl derivative ($n = 22$) does not, and tends to support the above model. Jordan also proposed an end-to-end arrangement of the crystallites, but Morawetz *et al.*[26] favour an intercalating structure with side groups pointing in opposite directions interlocking to form the side chain crystallites. Our present data are insufficient to allow comments on these detailed aspects at this stage, but work is proceeding in this area and will be reported later.

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REFERENCES

1 Cowie, J. M. G., Henshall, S. A. E., McEwen, I. J. and Velickovič, J. *Polymer* 1977, **18**, 612
2 Lewis, A. F. and Gillham, J. K. *J. Appl. Polym. Sci.* 1962, **6**, 422
3 Cowie, J. M. G. *Polym. Eng. Sci.* 1979, **19**, 709
4 Cowie, J. M. G. and McEwen, I. J. *Polymer* 1979, **20**, 719
5 Shimizu, K., Yano, O. and Wada, Y. *J. Polym. Sci. (Polym. Phys. Edn)* 1975, **13**, 1959
6 Boyd, R. H. and Breitling, S. M. *Macromolecules* 1974, **7**, 855
7 Boyer, R. F. *Rubber Chem. Technol.* 1963, **36**, 1303
8 Cowie, J. M. G. *J. Macromol. Sci. (B)* in press

9 Dale, J. *Acta Chem. Scand.* 1973, **27**, 1130

10 Schell, W. J., Simha, R. and Aklonis, J. J. *J. Macromol. Sci.* (*A*) 1969, **3**, 1297

11 Wiley, R. H. and Brauer, G. M. *J. Polym. Sci.* 1948, **3**, 647

12 Bovey, F. A., Abere, J. F., Rathman, G. B. and Sandberg, C. L. *J. Polym. Sci.* 1955, **15**, 520

13 Rogers, S. S. and Mandelkern, L. *J. Phys. Chem.* 1957, **61**, 985

14 Cowie, J. M. G., Haq, Z. and McEwen, I. J. *J. Polym. Sci.* (*Polym. Lett.*) 1979, **17**, 771

15 Heijboer, J. *Ann. NY Acad. Sci.* 1976, **279**, 104

16 Sugai, S. and Hikichi, H. *J. Appl. Phys. Jpn* 1963, **32**, 705

17 Hikichi, H. *J. Phys. Soc. Jpn* 1964, **19**, 2169

18 Kajiyama, T., Kuroishi, M. and Takayanagi, M. *J. Macromol. Sci.* (*B*) 1975, **11**, 121, 195

19 Pezzin, G., Ceccorulli, G., Pizzoli, M. and Pegion, E. *Macromolecules* 1975, **8**, 762

20 Hiltner, A., Anderson, J. M. and Borkowski, E. *Macromolecules* 1972, **5**, 446

21 Haldon, R. A. and Simha, R. *J. Appl. Phys.* 1968, **39**, 1890

22 Platé, N. A. and Shibaev, V. P. *J. Polym. Sci.* (*Macromol. Rev.*) 1974, **8**, 117

23 Jordan, E. F., Feldeisen, D. W. and Wrigley, A. N. *J. Polym. Sci.* (*A-1*) 1979, **9**, 1835

24 Broadhurst, M. G. *J. Res. Nat. Bur. Stand.* (*A*) 1962, **66**, 241

25 Magagnini, P. L., Andruzzi, F. and Benetti, G. F. *Macromolecules* 1980, **13**, 12

26 Hsieh, H. W. S., Post, B. and Morawetz, H. *J. Polym. Sci.* (*Polym. Phys. Edn*) 1976, **14**, 1241