

Poly(alkyl itaconates): 4. Glass and sub-glass transitions in the di-alkyl ester series, methyl to hexyl

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Diester of itaconic acid were polymerized by both bulk and emulsion techniques to produce a series of samples with ester chain lengths ranging from methyl to hexyl. These were characterized by measuring the molecular weight, density, glass and sub-glass transitions. D.s.c. and dynamic mechanical methods were used to investigate the transition phenomena. The glass transition temperature was found to be a function of the ester side-chain length, and decreased as the side chain increased in length. Several mechanical damping maxima were located in the thermochemical spectra and specific molecular relaxation processes have been tentatively assigned to each. Comparison of these polymers with the poly(alkyl methacrylates) highlighted the strong similarities in properties.

INTRODUCTION

The poly di-alkyl esters of itaconic acid bear a close structural resemblance to polymers in the alkyl methacrylate series; this has encouraged an extensive study, part of which has already been reported¹⁻³, of the physical properties of these materials. As control of the glass transition temperature (T_g) is a subject of continuing interest, an examination of the molecular motions occurring in the amorphous state of poly(di-alkyl itaconates) should provide useful information in this area.

One method of altering T_g is to effect plasticization of the polymer. This can be achieved either by adding a low molecular weight compound to the polymer to form a physical mixture or by means of 'internal' plasticization. The latter method, which has been used by a number of workers⁴⁻⁸ involves incorporation of flexible pendant groups on the main polymer backbone; these then act in a manner similar to the small-molecule additives by pushing the chains further apart and thereby producing a change in T_g , generally a decrease. The main advantage of this technique is that the pendant groups are covalently bonded to the chain as opposed to the additive which can be lost by evaporation or leaching.

It is normally observed that, as the chain length of the pendant group increases, the T_g decreases, but the magnitude of this effect depends largely on the nature of the side chain with respect to the main chain. Thus in the poly(vinyl n-alkyl ethers)⁴ T_g is decreased by 34K as the alkyl side chain lengthens from methyl to n-butyl, whereas a much larger decrease of 83K is observed for poly(chloroacrylic esters)⁵ of comparable alkyl chain lengths. Similarly, large decreases in T_g of 110 and 67K have been found for esters of poly(methacrylic acid)⁶ and poly(acrylic acid)⁷ ranging from methyl to hexyl. It appears that the depression of T_g is most obvious when the flexibility of the side chain is substantially greater than the main chain.

Poly(di-alkyl itaconates) can be regarded as having a basic poly(alkyl methacrylate) structure in which one hydrogen of the α -methyl group has been replaced by an additional ester chain. This immediately increases the proportion of side-chain units to the main chain in the polyitaconates and comparative studies should show whether this effects the results of 'internal' plasticization. One might expect comparable or greater decreases in T_g as a function of the ester group length if this analogy is valid, and if so then these polymers could also be regarded as possible alternative materials to the acrylate and methacrylate polymers.

EXPERIMENTAL

Monomer preparation

Dialkyl itaconic acid esters were prepared by refluxing a mixture of itaconic acid (1 mole) and the appropriate alcohol (3 moles) in benzene for 6 h in the presence of sulphuric acid as catalyst. After cooling the reaction mixture, distilled water was added. The benzene layer, containing the diester, was separated and washed repeatedly with water to ensure removal of unreacted acid and any monoester which may have formed. The ester solution was dried overnight, then vacuum distilled to obtain the crude product. Further purification was effected by fractional distillation under vacuum. Products were examined by n.m.r. to ensure that no residual acid groups were present.

Polymerization of di-alkyl itaconates

Poly(di-alkyl itaconic acid esters) were prepared by bulk polymerization in glass tubes, sealed under vacuum, using α, α' -azobisisobutyronitrile as initiator. Reaction temperatures varied from 318 to 353K depending on the molecular weight required, and reactions were terminated at moderate conversions to avoid the formation of excessively broad molecular weight distributions. The reaction mixture was diluted with benzene, and the polymer isolated by precipi-

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Table 1 Characterization of poly(di-alkyl itaconates). Densities, molecular weights, and glass transition temperatures measured by d.s.c.

Polymer	$10^{-5} M_w$	Density* (g/cm ³)	T_g (K)
Poly(dimethyl itaconate) PDMI	2.7	1.3082	368
Poly(di-ethyl itaconate) PDEI	2.0	1.2027	331
Poly(di-n-propyl itaconate) PDPrI	4.9	1.1485	307
Poly(di-n-butyl itaconate) PDBI	2.6	1.0706	285
Poly(di-n-pentyl itaconate) PDPI	2.0	1.0525	278
Poly(di-iso-pentyl itaconate)	—	—	280
Poly(di-n-hexyl itaconate)	2.8	1.0398	255
Poly(di-2-ethyl hexyl itaconate)	—	—	257

* All densities were measured at 296 K

tation, with petrol ether for the lower esters, and methanol for the higher esters. Polymer samples were purified by reprecipitation and finally dried *in vacuo* at 330K.

Additionally, samples of the poly(di-methyl itaconate) (PDMI), and poly(di-n-butyl itaconate) (PDBI), were prepared by emulsion polymerization at 328K. Potassium persulphate was used as initiator and sodium lauryl sulphate was the emulsifier. Reaction times of up to 24 h were used. The polymers were coagulated by addition of diethyl ether, then purified by repeated reprecipitation from acetone solution.

Characterization

Molecular weights. Weight-average molecular weights (M_w) of the unfractionated polymers were measured by light scattering⁸ and the data are gathered in Table 1. In all cases the values of M_w are sufficiently large to ensure that T_g will have attained its asymptotic value.

Differential scanning calorimetry (d.s.c.). Polymer samples (10–15 mg) were dried for two days prior to examination in a Perkin–Elmer DSC-2. The instrument was equipped with a low temperature mode and helium was used as a purge gas when samples were examined at temperatures below 200K. Thermograms were measured between 100 and 500K at scan rates of up to 20 K/min. The glass transition was located as a base-line shift on the thermogram and T_g estimated from the point of intersection of the base line with the extrapolation of the sloping portion of the curve resulting from the base line shift. Regular calibration of the instrument was carried out using metal standards.

Torsional braid analysis (t.b.a.). The dynamic mechanical behaviour of each sample was measured as a function of temperature using a torsional braid analyser^{9,10}. The nominal frequency of this instrument is approximately 1 Hz and the temperature range covered was 80–550K. Samples were prepared for measurement by impregnating a glass fibre braid with the polymer. This was achieved by soaking the braid in a polymer solution (10–15% w/v) for about 2 h, then drying the braid under tension (70 g) for 24 h *in vacuo* at room temperature. Glass braid supports were purchased initially from Chemical Instruments Corporation, but latterly they were made in the laboratory from material supplied by Jones Stroud Insulations. These braids were first cleaned thoroughly by immersion in chromic acid for seven days to remove unwanted surface coatings on the glass fibres which interfere with measurements. This treatment was followed by repeated washing of the braids in hot distilled water followed by drying at 380K before use.

The polymer–braid composite was suspended in the

sample chamber which was continually flushed by a nitrogen stream (flow rate 20 cm³/min). Cooling was effected by the rapid circulation of nitrogen gas through tubes surrounding the sample chamber. In order to attain temperatures as low as 80–100K, the flow rate of the gas, which was precooled in liquid nitrogen before entering the instrument, had to be maintained at 20 dm³/min. The sample was allowed to equilibrate for at least 30 min at the lowest temperature before commencing measurement. The temperature was then allowed to rise slowly by gradually reducing the flow rate of the cooling gas. When the thermal scan was continued above ambient temperatures the nitrogen flow was stopped in the cooling coils and a programmed heater was used to control further increases in temperature. As the specimen is a composite, the polymer geometry is irregular and cannot be defined; thus only relative values of the elastic shear modulus and the loss modulus can be obtained. This is adequate when only comparative studies are being carried out. The data have been expressed in terms of the mechanical damping index ($1/n$), where n is the number of oscillations occurring between two arbitrarily chosen boundary amplitudes in the decay wave. This is directly proportional to the logarithmic decrement and describes the damping characteristics of the samples. Decay curves were measured at 2.5 min intervals and approximately 200 data points were collected to construct each thermogram. These are plotted as $-\log(1/n)$ against temperature.

Rheovibron. The dynamic thermomechanical behaviour of the polymers was measured at four additional frequencies of 3.5, 11, 35, and 110 Hz using a Rheovibron viscoelastometer model DDV-II-C. Polymers were supported on strips of glass-fibre filter paper and again only a relative value of $\tan \delta$ was measured over a temperature range which encompassed the glass transition temperature.

Density. A density gradient column was used to estimate polymer densities at 296K. The gradient was created from water and aqueous sodium chloride solutions and glass floats of known density were used to calibrate the column. Small pieces of polymer film (~1 mm²) were dropped into the gradient and their resting position determined using a cathometer. Densities were obtained by interpolation.

RESULTS AND DISCUSSION

D.s.c. thermograms

The thermal response of each polymer in the range 100 to 500K was measured by d.s.c. The thermograms are relatively featureless except for a base-line shift corresponding to T_g . The results are shown in Table 1 and the T_g s are plotted in Figure 1 as a function of the number of carbon atoms in the ester side chain. As expected the flexible hydrocarbon chain acts as an 'internal' plasticizer for the molecule and produces a general decrease in T_g as the ester chain lengthens. An interesting comparison can be made here between the itaconates and the alkyl methacrylates. The corresponding values of T_g for the poly(alkyl methacrylate)* series, methyl to hexyl, are also plotted in Figure 1 and correlate closely with the itaconates. Apart from minor

* The glass-transition temperatures and density data for the poly(alkyl methacrylates) are drawn from the *Polymer Handbook* (Brandrup and Immergut), 2nd edition.

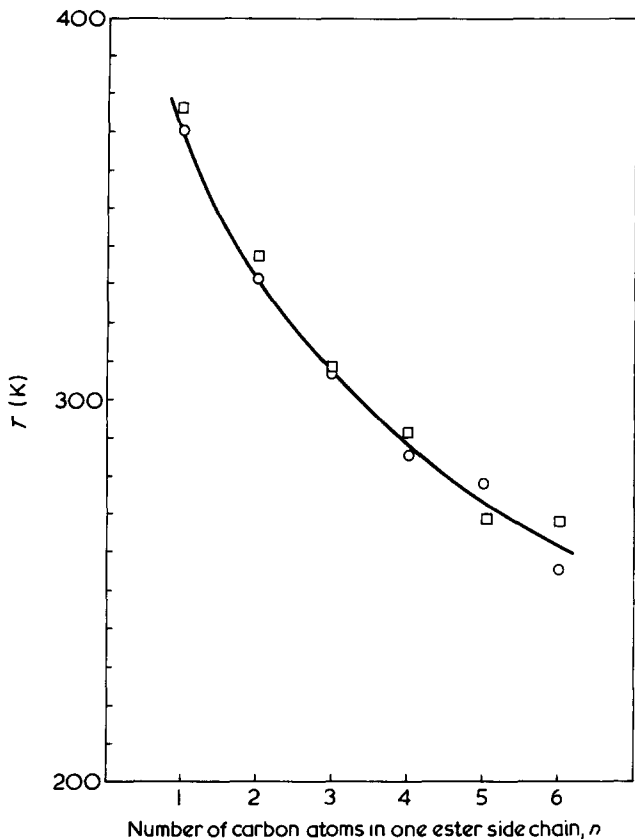


Figure 1 Variation of T_g as a function of the number of carbon atoms in the ester side chain: ○, polyitaconates; □, poly(alkyl methacrylates)

differences, the addition of a second ester chain to the monomer unit does little to enhance the depression of T_g , and the variation of T_g from methyl to hexyl esters in both series can be represented approximately by the same curve.

Density measurements indicate that the specific volumes of the poly(alkyl itaconates) are less than the methacrylates*, indicating a difference in chain-packing efficiency in the amorphous state, but again this appears to have little effect on the relative magnitudes of T_g . As the densities of the itaconates are greater, the plasticizing effect of the extra side chains may be offset by the closer packing of the chains in the solid with the implied reduction in available free volume.

Dynamic mechanical response

The t.b.a. thermal spectra for the six di-*n*-alkyl polymers are shown in Figure 2, while that of atactic poly(methyl methacrylate) (PMMA) is shown in Figure 3 for comparison. Three distinct damping maxima can be identified; they are designated α , β , and γ in order of decreasing temperature. Each polymer exhibits a prominent α -damping peak which is identified as the glass transition region, and the temperature of the damping maxima are recorded in Table 2. These values, obtained at less than 1 Hz, compare favourably with the values of T_g obtained from d.s.c. measurements and follow the trend shown in Figure 1. The physical appearance of the polymers at room temperature also confirms this interpretation; PDMI is a hard glassy solid, PDBI is rubbery, and PDHI is a highly viscous liquid.

A pronounced shoulder (the β -relaxation) can be seen in PDMI, PDEI, and PDPrI, lying in the temperature range 230–280K. This appears in the same region as the β -relaxation in PMMA although in the itaconate polymers the shoulder

is somewhat broader. This damping maximum is independent of ester chain length in the alkyl methacrylates and has been attributed to rotation of the alkoxy carbonyl group linking the side chains to the polymer backbone^{11–13}. The transition is also assigned to this group rotation in the polyitaconates because of the similarities. The broadening of the β -relaxation shoulder can be explained by the presence of two types of ester linkage in the itaconate chains. As one of these is separated from the main chain by a methylene group it may undergo rotation more readily and so extend the temperature range over which the relaxation occurs.

No definite β -dispersion could be detected in the PDBI spectrum as the α -damping peak is spread over a temperature range which encompasses the β -peak. Consequently the secondary side group motion is enveloped in the damping process arising from the glass transition for this sample and cannot be resolved. As PDPI and PDHI also have glass transitions in this general temperature range or lower, only the α -damping peaks are observed.

At lower temperatures a third peak, the γ -transition, is observed in all samples with ester chains containing more than three carbon atoms. There is some indication that damping in the PDPrI begins to increase below 100K but our measurements could not be extended to confirm the existence of a damping maximum at such low temperatures.

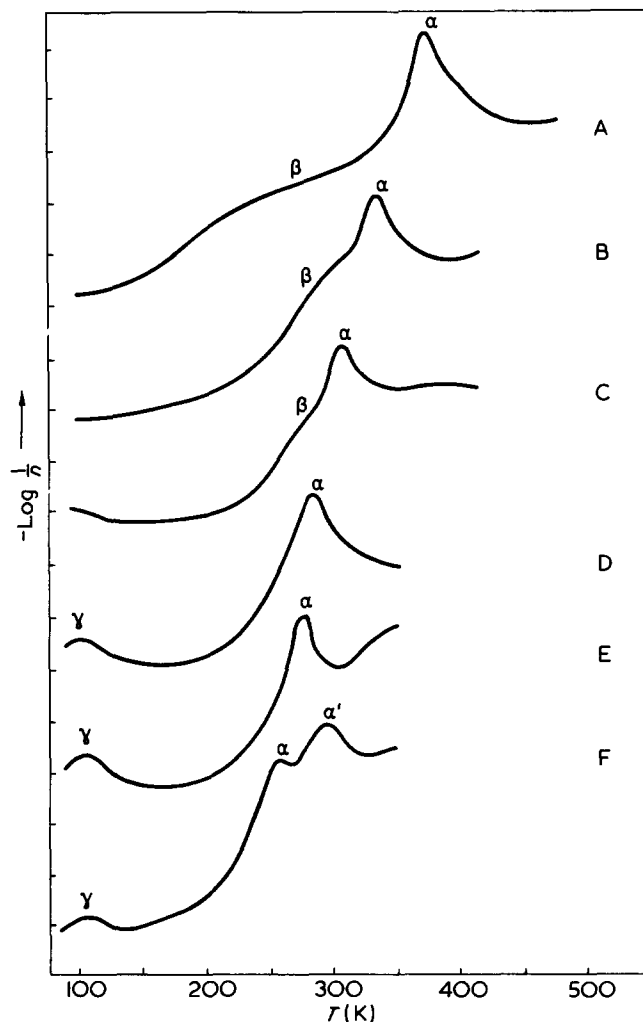


Figure 2 T.b.a. thermomechanical spectra for poly(di-*n*-alkyl itaconates). The $-\log(1/n)$ scale is in arbitrary units, and curves are displaced vertically with respect to one another, for clarity. A, PDMI; B, PDEI; C, PDPrI; D, PDBI; E, PDPI; F, PDHI

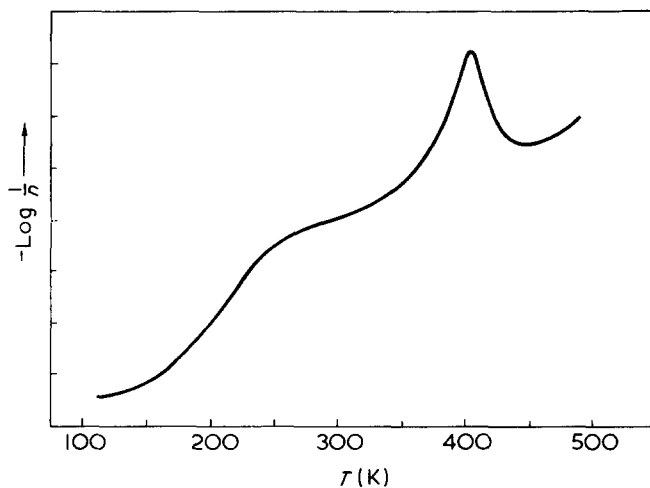


Figure 3 T.b.a. thermomechanical spectrum of poly(methyl methacrylate)

Table 2 Damping maxima in dynamic mechanical spectra of poly(di-n-alkyl itaconates)

Polymer	T_α (K)	T_β (K)	T_γ (K)
PDMI	378	260–270	—
PDEI	328	~280	—
PDPrI	308	~280	—
PDBI	290	—	95–110
PDPI	274	—	100–110
PDHI	254	—	100–110

The γ -transition is found between 95 and 110K and molecular relaxations have been observed in this region for a number of other polymers. Several workers^{5,13–16} have detected a similar loss peak in the poly(alkyl methacrylate) and poly(chloro-alkyl methacrylate) series, when the alkyl chain was propyl or larger.

The transition was absent in the branched esters poly(isopropyl methacrylate)⁵ and poly(*t*-butyl methacrylate)¹⁶, where there was no linear four-atom grouping in the side chains. Similarly a dynamic loss peak around 120K (110 Hz) was found in spectra of poly(pentene-1) and poly(4-methyl pentene-1)^{17–19} but not in poly(3-methyl pentene-1)¹⁷. Shimizu *et al.*²⁰ carried out a detailed analysis of this relaxation process and reached the conclusion that side chains with sequences of (C–C–C–C), or (O–C–C–C), would rotate in this temperature range if there was no steric hindrance to the rotation of the central (C–C) bond. This differs slightly from the Shatzki 'crankshaft' mechanism²¹ and is more like the Boyer suggestion²². From this one can conclude that the γ -mechanism in the polyitaconates arises from the alkyl side chain relaxing independently of the oxycarbonyl group.

One further damping peak, designated α' , appears only in the PDHI sample, and is either absent or not readily detected in the other samples. This is centred around 285K, which is above the T_g of the polymer, but its nature is not at all clear at present. Gillham and Boyer²³ have located, by means of both t.b.a. and d.t.a., a T_{II} transition lying above T_g in polystyrene. The ratio T_g/T_{II} was found to be about 0.9, which is comparable to the data for PDHI. While the d.s.c. thermograms hint at the possibility of two transitions at 255 and ~275K in first-run samples of PDHI, the

Table 3 Apparent activation energies ΔH^* for glass transition in poly(di-n-alkyl itaconates)

Polymer	ΔH^* (kJ/mol)
PDMI	320
PDEI	230
PDPrI	208
PDBI	202
PDPI	—
PDHI	165

the main evidence for the existence of the α' peak comes from the t.b.a. curves (Figure 2). Further investigations are in progress to determine its exact cause.

Apparent activation energies for T_g

The frequency dependence of the temperature (T_{max}) of the α -damping peak maximum was measured at 3.5, 11, 35, and 110 Hz. Apparent activation energies ΔH^* were estimated from plots of log (frequency) against $1/T_{max}$ and are shown in Table 3. There is a general decrease in ΔH^* with increasing ester side chain length which mirrors the decrease in T_g . Average values of ΔH^* reported for comparable alkyl methacrylate polymers²⁴ range from somewhat larger values for the lower esters (e.g. PMMA, $\Delta H^* \sim 340$ to 420 kJ/mol) to smaller values for the higher esters [e.g. poly(hexyl methacrylate), $\Delta H^* \sim 125$ kJ/mol]. This suggests that the presence of two ester side chains on the monomer units in the polyitaconates begins to affect the cooperative chain motion only in the higher esters.

Side chain branching

Two samples, in which a branch point had been introduced into the side chain, were also examined. The T_g appears to be altered only slightly in both cases; in poly(di-iso-pentyl itaconate) the T_g is only marginally higher than the PDPrI, as is the poly(di-2-ethyl hexyl itaconate) in comparison with PDHI.

CONCLUSIONS

The poly(di-n-alkyl itaconates), as might be expected, exhibit many of the properties associated with the poly(alkyl methacrylate) series. Glass transition and sub-glass mechanical damping peaks are similar in both series when equivalent esters are compared. The presence of a second ester chain attached to each monomer unit in the itaconates appears to have little effect on the observed relaxation processes when the molecular weight of the polymer is large enough to ensure that the asymptotic value of T_g pertains.

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