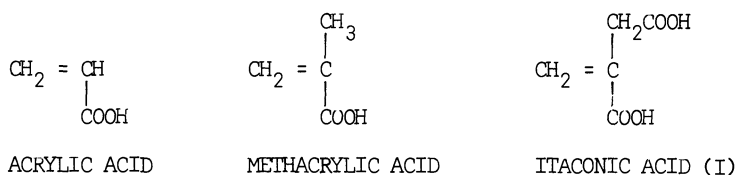PHYSICAL PROPERTIES OF POLYMERS BASED ON ITACONIC ACID

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Abstract - Mono and diesters of itaconic acid have been prepared
using linear, branched or cyclic alkane structures. These have
been homo and copolymerized to produce a wide range of polymers
with differing properties. These range from polyacids to polydiesters
to ionomeric structures. Their physical behaviour has been examined
and is reviewed herein.

INTRODUCTION

Many of the monomers used in today's polymer industry are derived from oil, and attractive
alternatives are now being sought which are obtained from a readily renewable source. One
such monomer is itaconic acid (I), a dicarboxylic acid, with an external methylene group,
which is structurally similar to acrylic and methacrylic acids.

$$CH_2 = CH \quad\quad CH_2 = \underset{\underset{COOH}{|}}{\overset{\overset{CH_3}{|}}{C}} \quad\quad CH_2 = \underset{\underset{COOH}{|}}{\overset{\overset{CH_2COOH}{|}}{C}}$$
$$|$$
$$COOH$$

ACRYLIC ACID   METHACRYLIC ACID   ITACONIC ACID (I)

The acid itself has been known since 1837 when it was isolated as a by-product in the
pyrolysis of citric acid (1), but while some interest was shown in its potential as a
monomer and polymers were prepared from its derivatives, it remained commercially non
viable until quite recently. Interest was rekindled in itaconic acid when it was found that
it could be produced in substantial quantities by means of a fermentation process. The
first report on this aspect was by Kinashita (2) who found that the fungus Aspergillus
Itaconicus produced itaconic acid by fermenting sugars. An improved process was later
reported by Calam et alia (3) who found that Aspergillus Terreus produced improved yields
of the acid under surface culture conditions and eventually 40% to 50% yields were achieved
using submerged culture techniques (4-6). Large scale fermentation processes using
molasses as the carbohydrate source have now been developed. While itaconic acid can be
polymerized in aqueous solution using potassium persulphate as initiator (7,8) it is not a
particularly easy reaction and has not been widely used. Improved yields and molecular
weights can be obtained if the anhydride is used with subsequent hydrolysis of the polymer
to the polyitaconic acid (9). More success is achieved when attention is turned to the
derivatives of the acid and in this context we shall be concerned with mono- and diesters
of the parent acid. Esterification of itaconic acid was first reported in 1873 (10) and
ester polymerization has been reviewed by Tate (9). It has been found that mono-esteri-
fication can be controlled with relative ease and that attack is almost exclusively on the
carboxyl unit attached through the methylene unit. This means that one can prepare both
mono and diesters and either homopolymerize or copolymerize the monomers thereby opening up
a large number of possible combinations and of course possible variations in physical
properties.

POLY(MONOALKYL ITACONATES)   COPOLYMERS (IONOMERS)   POLY(DIALKYL ITACONATES)
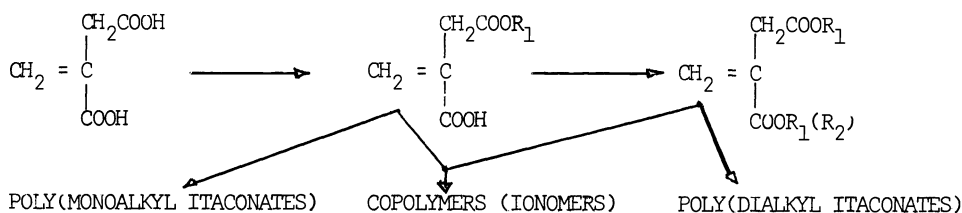
The polymers open to study when R = alkyl group thus range from polyacids, to ionomeric structures, to fully esterified structures which bear some resemblance to the poly(alkyl-methacrylates) and therefore display properties of some interest.

EXPERIMENTAL TECHNIQUES

Monomer preparation. (a) Monoesters with alkyl chain lengths from methyl to decyl were prepared by adding the appropriate alcohol (3 moles) to itaconic acid (1 mole). Freshly distilled acetyl chloride was added dropwise to the warm mixture to catalyse the reaction and the mixture was refluxed for 15 minutes. Unreacted alcohol was rapidly removed, under reduced pressure and the monoester rich fraction remaining was purified by fractional distillation. Longer ester chain lengths (octyl and higher) were separated by cooling the mixture, from which they crystallized. Several purification steps were necessary to ensure freedom from itaconic acid and anhydride impurities (11).

(b) Dialkyl itaconic acid esters were prepared by refluxing a 3/1 (alcohol/acid) mixture in benzene for six hours using sulphuric acid as catalyst. The reaction mixture was washed with water to remove unreacted acid and monoester, and the product was fractionally distilled under reduced pressure to obtain the pure material (12).

Polymerization. Both emulsion and bulk polymerization techniques were used. Monoalkyl mono-mers were melted into the reaction vessel and mixed with an equal volume of aqueous sodium lauryl sulphate emulsifier. Potassium persulphate was used as the initiator and the reaction was carried out in an agitated sealed flask at 323K to 343K for up to 40 hours. Addition of methanol separated the polymer which was thoroughly washed, purified by reprecipitation, and dried. The method was also used for dialkyl polymers. Bulk polymerization of the latter using azobisisobutyronitrile as initiator was also successful. When copolymers were prepared the emulsion technique was used exclusively. Molecular weights of all the polymers were measured by light scattering (11).

Analysis of copolymer composition. When the comonomers were a pair of mono and diesters the copolymer composition was established by non aqueous titration of the free carboxyls in the chain. Copolymers prepared from a pair of diesters were analysed using nmr spectroscopy. Typical assignments used are shown in Figure 1 which shows the spectra for dimethyl and di-heptyl itaconates. The latter is typical of the longer side chain esters. Relative proportions of the comonomers were estimated by comparing the areas of the methylene absorptions between 0.9 and 2.3 ppm and the methoxy or oxymethylene absorptions between 3.4 and 4.5 ppm (13).
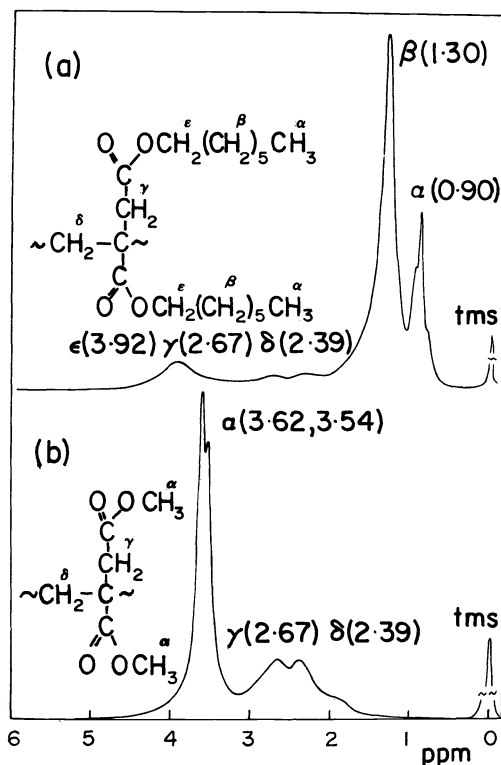

Fig. 1. Nmr spectra for poly(di-n-heptyl itaconate), upper curve, and poly(dimethyl itaconate), lower curve, showing peak assignments.

Differential scanning calorimetry (dsc). Phase transitions, such as melting and glass
transitions can be conveniently measured by dsc. The instrument used was a Perkin-Elmer
DSC-2 equipped with facilities to allow low temperature measurements and to maintain base
line stability. Polymer samples (10-15mg) were dried for two days prior to examination and
the usual temperature range for the thermogram was 100K to 500K. At low temperatures the
purge gas used was helium, but nitrogen was adequate for temperatures above 200K. Several
scan rates were possible but rates up to 20K min^{-1} were most commonly used. The instrument
was regularly calibrated with metal standards. Endothermic peaks typify melting but the
glass transition is seen as a shift in base line. The glass transition temperature T_g
could be estimated from the point of intersection of the base line with the extrapolated
sloping portion of the curve arising from the base line shift.

Dynamic mechanical analysis. The thermomechanical response of the sample was determined
using two techniques thereby giving measurements of a range of frequency from about 1Hz to
110Hz. The low frequency spectra were obtained using a torsional braid analyser (12,14)
over a temperature range 80-550K. This is a particularly useful instrument when the samples
to be measured are mechanically weak or liquid at normal temperatures, as the polymer is
supported on a glass braid. This is achieved by soaking the braid in a polymer solution
(10-15% w/v) for about 2 hours, after which the braid is dried under tension (70g) in vacuo.
The polymer braid composite is suspended in the sample chamber under nitrogen and attached
to an inertial disc. At intervals of 2-4K the braid is subjected to a torsional motion and
the decay curve is recorded. As the specimen is a composite, the polymer geometry is
irregular and ill defined, consequently only relative values of the elastic shear and loss
moduli can be obtained. Data are therefore expressed as the mechanical damping index (1/n)
where 'n' is the number of oscillations occurring between two fixed but arbitrarily chosen
boundary amplitudes in the decay wave, and as the relative rigidity ($1/P^2$), where P is
obtained by dividing the time required for a number of oscillations to take place, by that
number. The former is proportional to the logarithmic decrement, the latter to the complex
modulus. Measurements at 3.5, 11.0, 35 and 110Hz were obtained using a Rheovibron visco-
elastometer model DDV-II-C. Mechanically strong polymers were measured directly using strips
of polymer film and the weaker ones were supported on cellulose filter strips (12).

POLY(MONO-n-ALKYL ITACONIC ACID ESTERS)

The polymers prepared were all hard brittle solids which were soluble in a variety of
alcohols. When the dsc thermograms were examined, they were found to be relatively
featureless except for a pronounced endotherm beginning at 430K. With the exception of the
poly(mono-decyl itaconate) no evidence of T_g could be found in these polymers even above the
endotherm. This indicated that some fundamental change was taking place in this region.
The mono-decyl polymer displayed a T_g at 315K, below the endotherm temperature but this was
the only one detected. Much more information can be derived from the thermomechanical
spectra and representative curves of the damping index as a function of temperature for four
samples are shown in Figure 2. Each example contains more than one spectrum and these
illustrate the effect of thermal recycling on the mechanical behaviour.
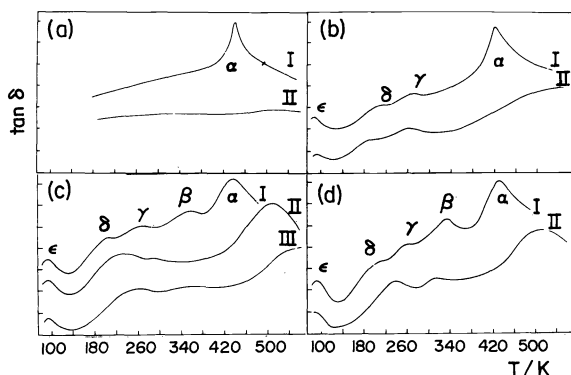

Fig. 2. Temperature dependence of mechanical damping index (1/n)
for (a) poly(monomethyl itaconate), (b) poly(mono-n-butyl itaconate),
(c) poly(mono-n-nonyl itaconate) and (d) poly(mono-n-decyl itaconate).
Curve I - initial scan; curve II - first thermal cycle;
curve III - second thermal recycle.

This is most clearly shown for poly(mono-methyl itaconate) which displays a large damping
peak at about 440K, but when the braid is cooled and then reheated this disappears. The
phenomenon is not quite so clear cut for the other polymers as the number of thermal re-
cycles necessary to eliminate this peak increased as the length of the alkyl chain increased.
This suggests the process is retarded by the longer alkyl side chains. Additional damping

peaks also appeared at lower temperatures and these are summarised in Table 1.

TABLE 1:   Damping peaks present in dynamic thermomechanical spectra
            of poly(mono-n-alkyl itaconates)

Polymer	T_α/K	T_β/K	T_γ/K	T_δ/K	T_ε/K
Monomethyl	435	-	-	-	-
Mono-n-butyl	430	-	240	190	95
Mono-n-heptyl	435	-	248	195	95
Mono-n-octyl	440	-	248	190	95
Mono-n-nonyl	440	360	250	195	95
Mono-n-decyl	440	327	255	195	95

There is a remarkable consistency of temperature at which each of the peaks is detected in each polymer suggesting that the molecular origins are common to all.

Interpretation. The ε-transition was observed in poly(mono-n-alkyl itaconates) only when the alkyl chain contained four or more atoms. This damping peak appeared at 95K and was unaffected by thermal recycling. It is reasonable to assume that this is caused by a molecular motion originating in the alkyl side chain, similar to that observed in poly-(alkyl methacrylates) (15,16). The movement will entail either simple rotation about -(C-C)- bonds of the type suggested by Shimizu et alia (17) and outlined in Figure 3
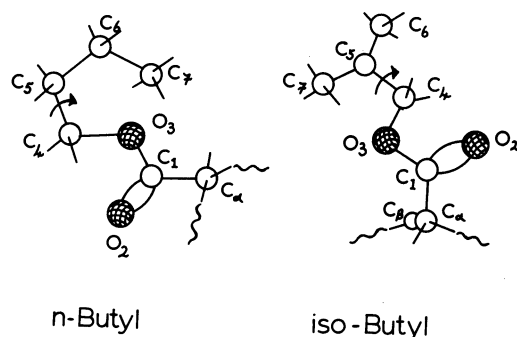

n-Butyl   iso-Butyl

Fig.3.   Possible bond rotations in n-butyl and iso-butyl side chains.

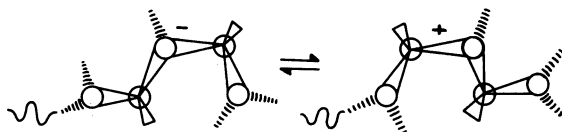or perhaps an elementary migration of a gauche bond by one position (18) as shown in Figure 4.

Fig.4.   Possible motion in alkyl side chain involving a
         tt g⁻t → t g⁺t   conformational change.

The transition which is seen in the range 180-200K (the δ-transition) may be a composite peak. Several workers (19,20) have found evidence of damping maxima in other polymers centred on this temperature region which they were able to attribute to the -COOH group and possibly the water associated with it. Some evidence to support this is found in the damping spectra of a series of poly(monobutyl-co-dibutyl itaconates). On examination of the spectra in Figure 5 one can see that the δ-peak vanishes as the mole % of monobutyl itaconate in the copolymer decreases, suggesting that it is associated with the presence of the carboxyl group.

The picture is not quite so clear with the higher esters. While here the carboxyl group and associated water may play a part in the damping process; inspection of the damping behaviour of a series of poly(monoheptyl-co-diheptyl itaconates), shown in figure 6, suggests that this damping peak actually increases as the content of monoheptyl itaconate decreases. Subsequent work on the dialkyl derivatives, which will be outlined later, has shown that this is due to cooperative motion in the alkyl side chain. This peak appears to be a composite of two possible processes in these polymers.
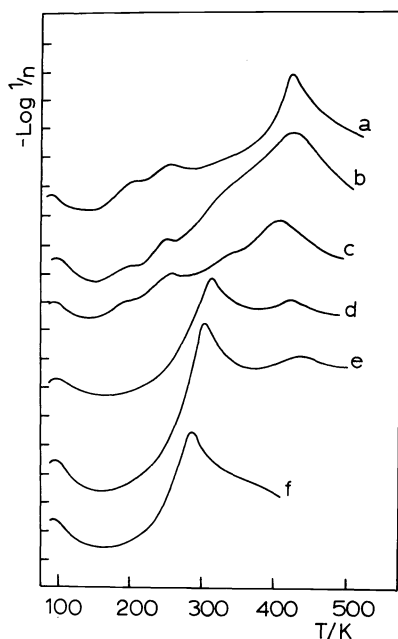
Fig.5. The temperature dependence of the
mechanical damping index for a series of
poly(monobutyl-co-di-butyl itaconates).
Curve (a) poly(monobutyl itaconate).
Copolymers containing (b) 45.6 mole;
(c) 36.5 mole %; (d) 14.7 mole %;
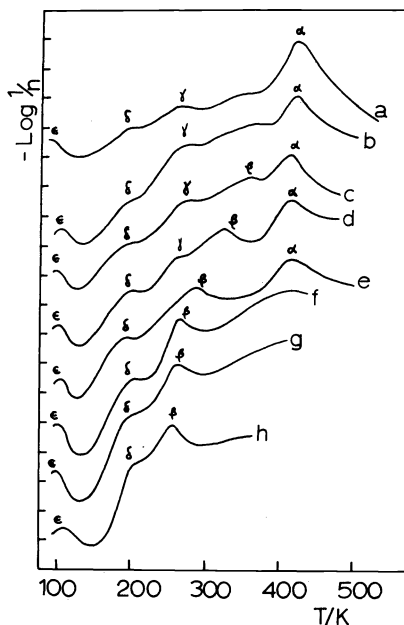(e) 9.5 mole % of monobutyl itaconate;
curve (f) poly(dibutyl itaconate).

Fig.6. Torsional braid thermograms for
curve (a) poly(monoheptyl itaconate), curves
(b-g) copolymers containing 92.8, 83.7, 56.5,
43.8, 34.2 and 20.6 mole % of monoheptyl
itaconate (comonomer diheptyl itaconate),
curve (h) poly(di-heptyl itaconate).

The transition lying in the 240-260K temperature range is comparable to that found in poly-
(alkyl methacrylates) by Heijboer (21) and others (22,23). This is believed to be due to
the rotation of the alkoxycarbonyl group. Only two polymers exhibit a β-peak which can be
associated with the glass transition temperature, namely the nonyl and decyl derivatives.
All others appear to possess T_g which lies either under or above the damping peak at 430K
which is common to all the mono alkyl itaconates. This is a major event, consistently
observed in the temperature range 430-450K irrespective of the derivative studied. The peak
tends to disappear or be reduced in intensity if the sample is thermally recycled suggesting
that it may have a chemical origin. Weight loss curves, obtained in a nitrogen atmosphere
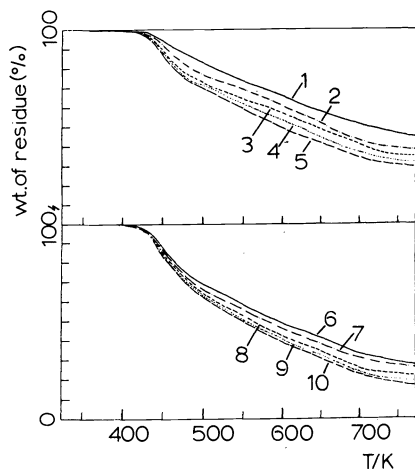at a heating rate of 10K min^{-1}, are shown in Figure 7 for ten of the polyacids.

Fig.7. Thermogravimetric analysis curves for poly(mono-alkyl
itaconates). Curves 1 to 5, methyl to pentyl esters and
curves 6 to 10, hexyl to decyl esters.

The initial weight loss begins around 430K, the temperature at which the damping peaks and the dsc endotherms were observed. Polymers continued to lose weight until around 800K, where the rate appeared to slow down; at this point the loss in weight was approximately proportional to the length of the ester side chain. Analysis of the volatile produts evolved at 470K revealed the presence of water and the alcohol appropriate to the particular polymer i.e. for poly(monomethyl itaconate), methanol was detected. Some carbon dioxide and a small quantity of ketene could be isolated when analysis at slightly higher temperatures was carried out. In a separate experiment using only the monomethyl derivative, thermal treatment at 435K resulted in the rapid expansion of the sample into a foam with a white open structure, many times the volume of the original polymer. The gases evolved, which were responsible for the foaming process were analysed by glc and in the mass spectrometer, and were found to be methanol and water. The infrared spectrum of the foamed polymer, see Figure 8, showed new absorptions at 1780 cm^{-1} and 1855 cm^{-1} which are indicative of five-membered anhydride rings and absorptions at 1805 cm^{-1} and 1755 cm^{-1} characteristic of six or
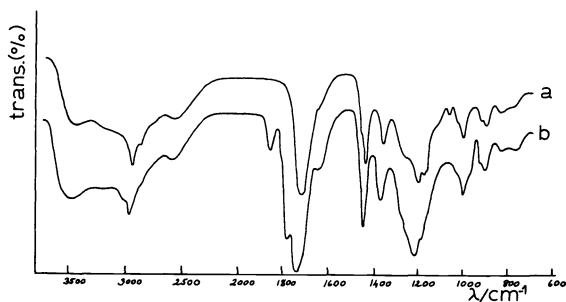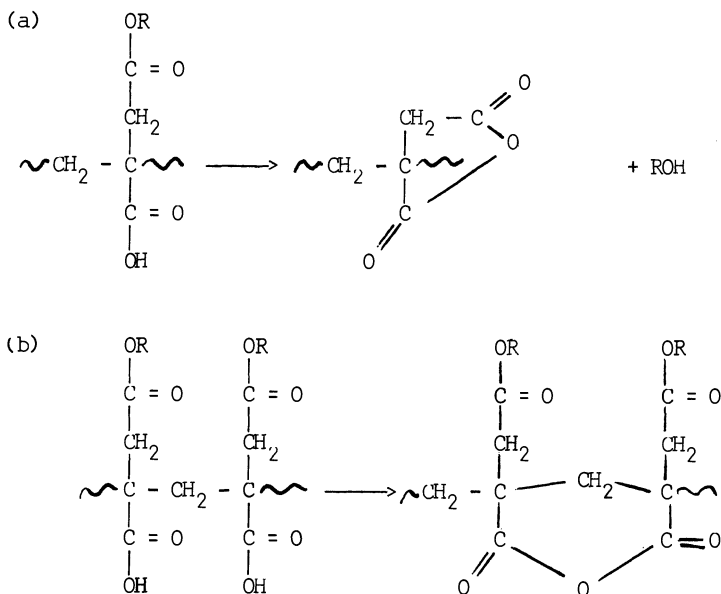

Fig.8. Infrared spectra of poly(monomethyl itaconate) before (solid line) and after (broken line) heating at 470K for 15 mins.

even seven-membered anhydride rings. Consideration of these data leads one to the conclusion that the process is then a dehydration/de-esterification reaction either of an inter or intramolecular nature involving reactions of the type:

(a)

(b)

This changes the character of the polymer by introducing ring structures into the chain which will undoubtedly raise the glass transition temperature of this thermal product above that of the parent polyacid. The product is, in effect, a copolymer of the original polymer and the new anhydride units. The resultant foaming is most efficient in the methyl derivative and becomes less dramatic as the alkyl chain length increases. This is reflected in the much slower elimination of the damping peak by thermal recycling suggesting that the dehydration/de-esterification is slowed down, perhaps by the shielding of the appropriate groups by the longer alkyl chains.

Some thermal stability can be gained by converting the polyacid to a polysalt but this tends to bind water more readily and makes the degradation pattern difficult to follow. The

dehydration reaction does, however, tend to be curtailed by this neutralization procedure, but this has not yet been studied in detail.

POLY(DI-ALKYL ITACONIC ACID ESTERS)

Formation of a series of dialkyl derivatives of polyitaconic acid creates materials which have a close structural resemblance to poly(alkyl methacrylates). This suggests that they may display similar properties and are well worth examining in some detail. Because derivatives with up to 20 carbon atoms in the alkyl side chain have been prepared and because there are significant changes in behaviour with increasing chain length the dialkyl derivatives will be dealt with initially in groups for convenience.

Methyl to hexyl derivatives. Results of the torsional braid analysis of the polymers as a function of temperature are shown in terms of the damping response in Figure 9. The most prominent feature is the damping arising from the glass transition and the temperatures of
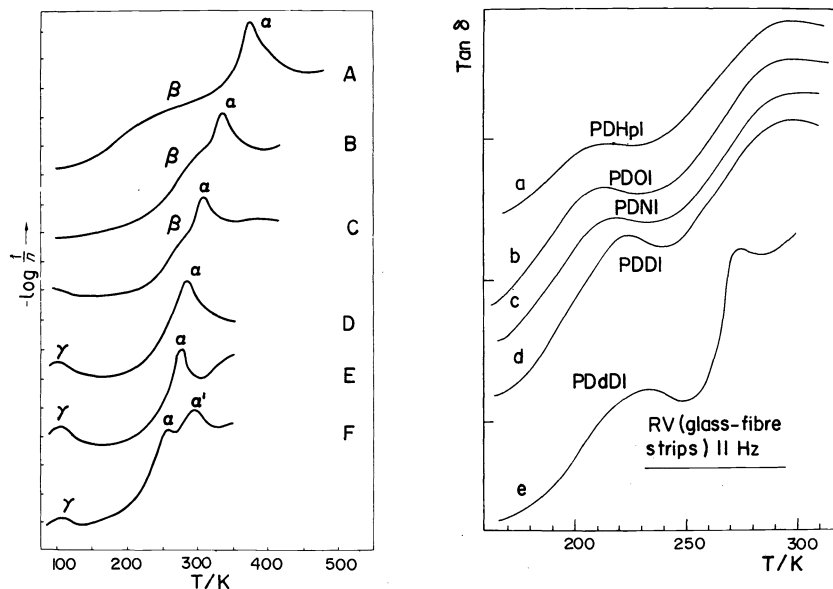

Fig.9. Thermomechanical damping spectra for poly(di-n-alkyl itaconates).
Left: Top to bottom, methyl to hexyl.
Right: Top to bottom, heptyl to dodecyl.

the peak maxima correspond closely to T_g measured by dsc. The data are summarised in Table 2. Here two branched derivatives are included for comparison.

TABLE 2: Densities; T_g and its apparent activation energy, for poly(di-n-alkyl itaconates)

Polymer	Density (296K) (g/cm^3)	T_g/K (d.s.c.)	$\Delta H^{\ddagger}$ kJ mol^{-1}
DiMethyl	1.3082	368	320
DiEthyl	1.2027	331	230
Di-n-Propyl	1.1485	307	208
Di-n-Butyl	1.0706	285	202
Di-n-Pentyl	1.0525	278	–
Di-iso-Pentyl	–	280	–
Di-n-Hexyl	1.0398	255	165
Di-2-Ethyl Hexyl	–	257	–

The most important response which is clearly seen is the internal plasticizing by the alkyl side chain in these polymers and this mirrors closely the behaviour of the corresponding poly(di-alkyl methacrylates).

Heptyl to undecyl derivatives. The decrease in T_g with increasing alkyl chain length is monotonic until the heptyl derivative is reached and here an apparent change in physical behaviour occurs. Examination of the dsc thermograms for the heptyl to undecyl poly-diesters shows the existence of two apparent glass transitions, characterised by a base line shift. The data are summarized in Table 3.

TABLE 3: Transition temperatures for poly(dialkyl itaconates) with side chain lengths greater than six carbon atoms

Polymer	Tm/K	T_g^1/K	$\Delta H^{\ddagger}$ (kJ mol^{-1})	T_g^2/K	$\Delta H^{\ddagger}$ (kJ mol^{-1})
Di-heptyl	–	250	140	188	200
Di-octyl	–	253	120	191	165
Di-nonyl	–	262	120	197	155
Di-decyl	–	270	–	210	–
Di-undecyl	–	(275)	–	218	–
Di-dodecyl	267	–	–	(225)	–
Di-tetradecyl	299	–	–	–	–
Di-hexadecyl	318	–	–	–	–
Di-octadecyl	329	–	–	–	–
Di-oleyl	(252)	192	–	–	–
Di-eicosyl	341	–	–	–	–

Similarly two damping peaks can be seen in the mechanical spectra (Fig.9) which might correspond to these transitions, a fact which is confirmed by the use of copolymer samples whose examination aid the interpretation immensely. This was achieved by preparing a series of poly(dimethyl-co-di-n-heptyl itaconate) copolymers and studying them by dsc and tba. The dsc thermograms in Figure 10A show only one T_g for poly(dimethyl itaconate) but the gradual appearance of a second T_g, as the diheptyl content increases is quite evident. The data are summarized in Figure 10B and show the expected trend for copolymer T_g's in the upper curve substantiating the value of 250K as the expected T_g for the poly diheptyl ester. This is the temperature at which the upper damping peak appears in the tba spectrum. The lower T_g
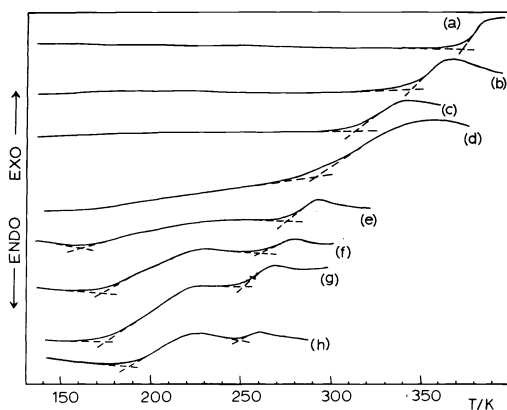

Fig.10A: Dsc curves for (a) poly-(dimethyl itaconate) (h) poly(diheptyl itaconate) and varying copolymer compositions curves (b-g).
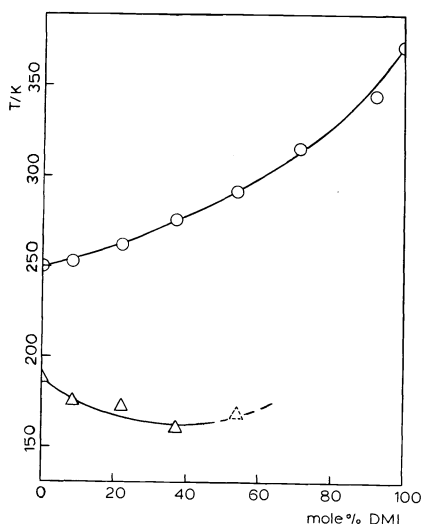
Fig.10B: Upper T_g (-O-) and lower T_g (-Δ-) as a function of mole % dimethyl itaconate in the copolymer.

must originate in a part of the molecule other than the main backbone and indications are that this must be the side chains. This corresponds to the lower damping peak in the tba spectrum. Reference to Figure 6 where the damping spectra for poly(monoheptyl-co-diheptyl itaconates) are displayed shows a build up of the damping peak corresponding to the lower transition as the content of heptyl side chains in the copolymer increases. Similarly, damping spectra for the poly(dimethyl-co-diheptyl itaconates) show a similar increase in this lower damping peak as the diheptyl content of the copolymer grows (13). The same observations were made for the octyl, nonyl and decyl derivatives and it is proposed that these polymers all display two T_g's, the lower one represents co-operative motion of the alkyl side chains which move independently of the main chain, and the upper T_g represents co-operative motion of the whole polymer molecule including the main backbone chain (24). These trends are summarized in Figure 11. The upper T_g decreases with increasing side chain length until C7, then swings upwards, while the lower T_g always increases but is only seen

between C_7 and C_{11}. The increasing T_g's reflect the increasing tendency for the side chains to order and crystallize and this finally becomes evident in polymers with side chains C_{12} and higher, where distinct melting endotherms dominate the response of the polymers.
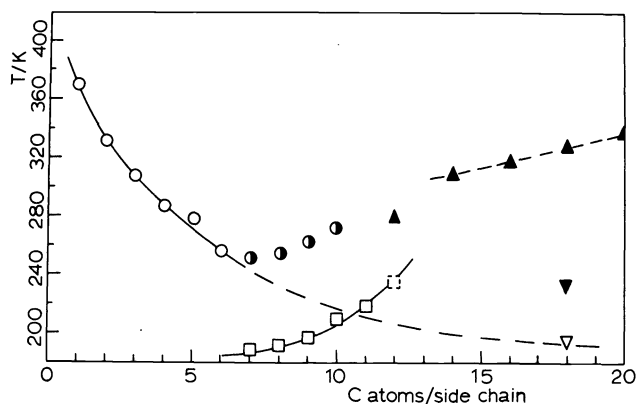

Fig.11. Transitions in poly(dialkyl itaconates) as a function of the length of the alkyl chain. Circles and squares represent glass transitions, filled V triangles represent melting transitions. Open triangle represents T_g of poly(dioleyl itaconate).

Further evidence to support the idea that the lower transition is a glass transition comes from a study of the apparent activation energies for the process. These were found to range from 150 to 200 kJ mol^{-1} for the lower transition which is very much larger than one would expect for a secondary transition taking place in this temperature range, i.e. 40 to 50 kJ mol^{-1} (25).

Docecyl to eicosyl derivatives. Polymers containing alkyl ester side chains of twelve or more singly bonded carbon atoms displayed pronounced melting points but no T_g. There is a linear relationship of Tm with alkyl chain length, except for the C_{12} derivative where there is some slight suggestion of a lower T_g to be found in the dsc traces. This implies that crystallinity is not fully developed in this sample. Side chain crystallinity has been studied in other polymers and Jordon et alia (26) have suggested that an alkane chain in excess of nine carbon atoms is required before the side chain can enter a crystal structure. In the polyitaconates there is only evidence of a melting transition in the C_{12} and higher derivatives, but the tendency towards some kind of order in the side chains in samples C_8-C_{11} does appear to raise the value of the glass transition above that expected for each sample. The extrapolation of the curve for the upper T_g, from the data for the lower poly-itaconates, drawn in Figure 11, clearly shows this deviation. The validity of this extrapolation was confirmed by preparing and measuring the glass transition temperature of a sample of poly(dioleyl itaconate). This structure is a chain of 18 carbons with a double bond exactly placed in the middle of the chain where it effectively disrupts the tendency of the side chain to crystallise. The polymer was found to be predominantly amorphous, with only a small melting endotherm detected in the dsc thermogram at 250K. The T_g is 195K, which falls in the expected temperature region predicted by the extrapolated curve.

POLY ITACONIC ACID ESTERS CONTAINING RING SYSTEMS

A number of diesters of polyitaconic acid have been prepared with phenyl and saturated ring systems attached to the side chains and the main transitions detected are summarised in Table 4. When the rings are not attached through methylene units to the chain the T_g's are quite close, irrespective of ring size (5-8 atoms).
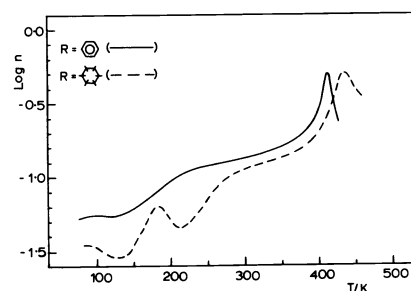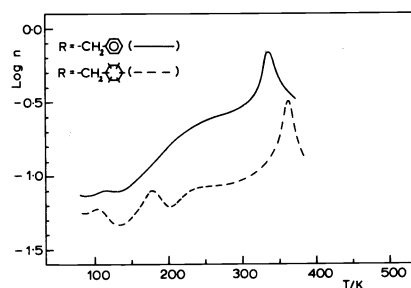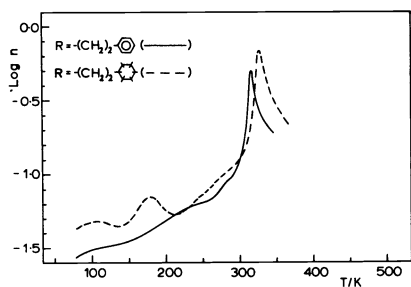
Spacing of the ring further away from the chain appears to lower T_g with the introduction also of more flexible units. The most significant feature is the difference between the saturated and aromatic ring systems. Distinct subglass relaxation processes are observed when saturated rings are included, which are not detected in the phenyl derivatives. This can be seen in Figure 12A where the cyclohexyl and phenyl derivatives are compared.

There is a pronounced damping maximum seen in each cyclohexyl derivative, which is missing in the phenyl polymer, around 185K. This has been identified as being due to the chair-chair transition taking place in the cyclohexyl ring, a conformational change which has an apparent activation energy of the correct order of magnitude (21). This intramolecular damping process which is confined to the ring system does not appear to reduce the brittle nature of most of these polymers. Equally substantial damping processes are detected in polymers

containing pentyl, heptyl and octyl rings and these are displayed in Figure 13A.
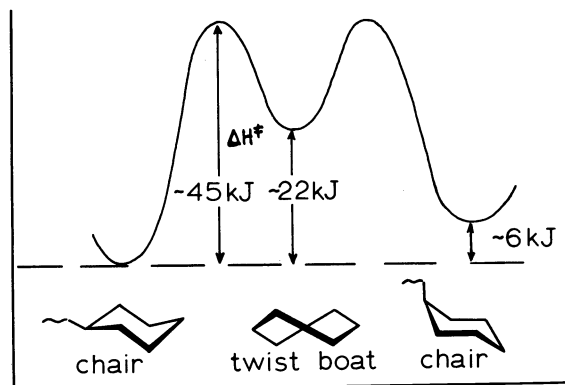
TABLE 4:   Glass and Sub Glass transition temperatures for poly(itaconic acid esters) containing ring systems

Side chain	T_g/K	Secondary Transitions	
		T/K	$\Delta H^{\ddagger}/kJ\ mol^{-1}$
Diphenyl	405	–	–
Dibenzyl	328	–	–
Diethylphenyl	308	–	–
Dipropylphenyl	265	–	–
Dicyclohexyl	417	185	65
Dimethylcyclohexyl	356	185	52
Diethylcyclohexyl	321	185	50
Dicyclopentyl	395	(221)	–
Dicycloheptyl	390	113	(20)
Dicyclooctyl	413	175	46

Fig.12A: Thermomechanical damping index curves for cyclohexyl and phenyl derivatives of polyitaconic acid.

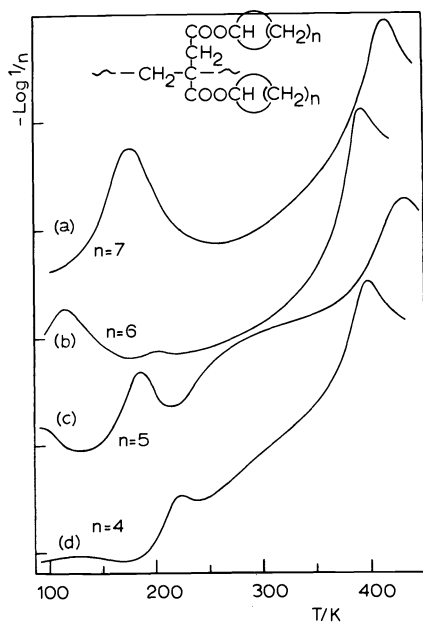Fig.12B: Proposed chair-chair transition for the cyclohexyl ring.

A

The damping in the cyclopentyl ester is hardest to explain as intramolecular changes here can best be effected by pseudo-rotation in the ring which has very low energy barriers to overcome. The most likely explanation is a rotation of the complete cyclopentyl ring system about the (O-ring) bond. For the cycloheptyl and cyclo-octyl derivatives a number of possible changes with the appropriate activation energy are shown in Figure 13B which are intramolecular in nature and involve conformational changes in the ring itself.

Fig.13A: Thermomechanical damping index curves for poly itaconic acid cyclopentyl, cycloheptyl and cyclo-octyl esters.

Fig.13B: Possible conformational changes in these systems.
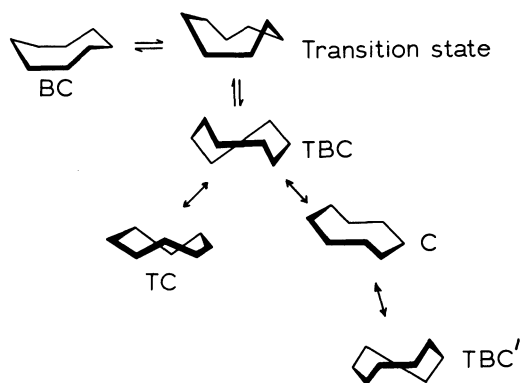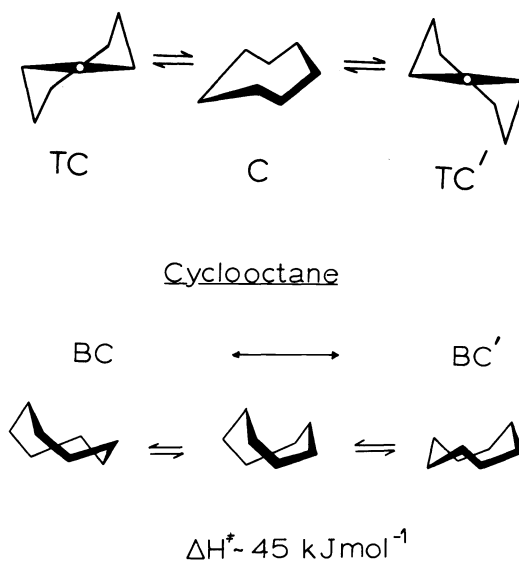
IONOMERIC STRUCTURES

Ionic polymers have elicited much interest in the past decade and copolymers of mono and diesters of itaconic acid present interesting possibilities in this area. The term 'ionomer' has been coined to describe materials composed of a hydrocarbon backbone containing pendant acid groups which can be neutralized to form salts. Some workers prefer to reserve the term for polymers containing less than 10 mole % salt groups thereby excluding the polyacids (which are potentially polyelectrolytes), described in an earlier section, from this group. Two combinations of mono and diester have been examined in an exploratory manner to ascertain the potential of this type of structure (27); poly(monobutyl-co-dibutyl itaconate) and poly(monoheptyl-co-di-heptyl itaconate) samples of varying composition together with their salts. The glass transition, as far as can be judged in these polymers, is raised by neutralization of the free carboxyl groups but not by significant amounts (27). What does alter significantly is that the parent polymers, which are often tacky and mechanically weak at ambient temperatures, become non-tacky and tough after ionization. This is illustrated effectively in Figure 14 where it can be seen that after the glass transition the modulus rises steadily as the extent of neutralization increases.

The introduction of ions into the structure leads to cross-linking of the chains and a much more stable tough rubberlike material above T_g. This is manifest in an increase in the modulus and the creation of a plateau region in the modulus curve partially resembling a cross-linked rubber plateau region. Alternatively, the effect can be magnified by increasing

the carboxyl group content and this is shown in Figure 15. The sodium salt of sample (4) has a modulus which is equivalent to the glassy state of the copolymer. This property enhancement is perhaps best achieved by holding the crosslinking levels down, as the higher levels often lead to brittle intractable structures. Results are sufficiently encouraging, however, to promote further work in this area.
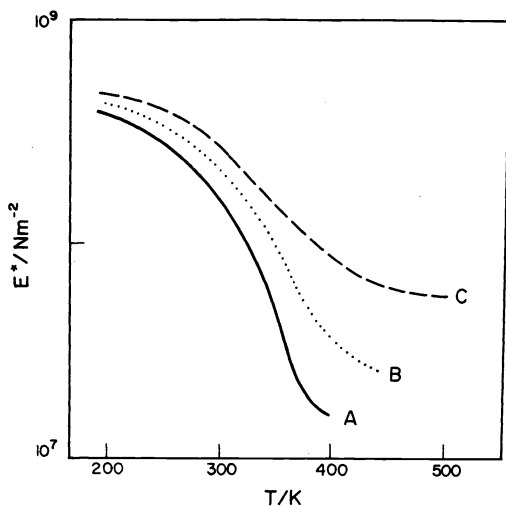

Fig.14. Modulus-temperature curves for a poly(monoheptyl-co-diheptyl) copolymer containing 30 mole % of monoheptyl units.
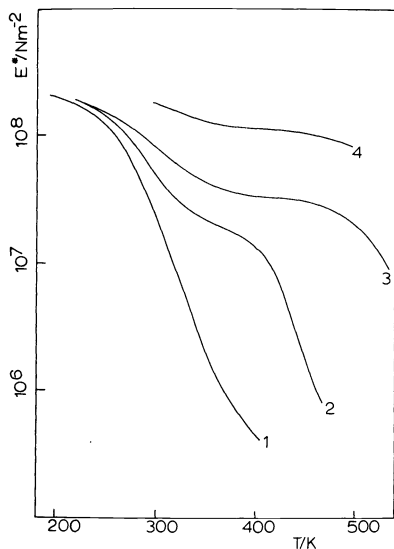Curves A - Unneutralized;   B, 50%;   C, 100% ionized.

Fig.15. Modulus-temperature spectra for the sodium salts of poly(monoheptyl-co-diheptyl itaconate) samples (1) 7 mole %; (2) 20.6 mole %, (3) 32.2 mole %, (4) 42.4 mole % monoheptyl in the copolymer.

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