Poly(alkyl itaconates): 6. Ionomers based on butyl- and heptyl-itaconic acid esters

J. M. G. Cowie and Zia Haq*
Department of Chemistry, University of Stirling, Stirling FK9 4LA, UK
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Copolymers of mono- and dialkyl itaconates, with less than 55 mol % of the monoalkyl unit in the chain, were prepared and studied as potential ionomers. Salt formation raised the glass transition temperature only marginally, but changed some of the physical properties in a much more dramatic fashion. The copolymers were converted from soft, tacky substances in the unionized state to tough, non-tacky materials after salt formation as a result of ionic crosslinking in the matrix. Electron micrographs of one system revealed that ionic clusters of about 2 nm diameter were formed in the bulk polymer when the number of ionized groups in the chain reached 7 to 8 in every hundred methylene units.

INTRODUCTION

Interest in the properties of ionic polymers[1] has increased in the past 10 years and, in particular, attention has centred on copolymers which have a predominantly hydrocarbon backbone with a small percentage of pendant carboxyl groups placed randomly along the chain. This latter group has been given the general name 'ionomers'. Desirable property changes can be effected in polymers, such as polyethylene if they incorporate a small amount of an acid in the chain and if the acid groups are then partly or totally ionized. This salt formation can lead to intermolecular interactions which alter the supermolecular structure and the properties of the material[2–4]. Such changes arise from the crosslinking action of the ions introduced into the polymer matrix which act as tie points for the chains and impede their freedom of movement. Extensive ionization tends to lead to ionic cluster formation in the matrix thereby imparting a two phase character to the polymer. The crosslinks formed also have the additional feature of being thermally labile and this facilitates processing and fabrication.

Most of the work reported to date has been concerned with the salts of ethylene–carboxylic acid copolymers[1,5–7] and styrene based copolymers[8–10] although some other structures have been examined less extensively[11–13]. As a further aspect of our work on copolymers of itaconic acid esters[14] a study of the effect of introducing ions into structures based on these monomers was begun and our initial findings are reported here. Control of the carboxyl content in such copolymers can easily be effected and the resulting materials also present an interesting structural variation in that they contain relatively long side chains and consequently may differ in behaviour from the ionomers described by other workers.

The systems selected for the initial investigation include a medium and long side chain to provide variation in this factor and are poly(monobutyl-co-dibutyl itaconate) and poly(monoheptyl-co-diheptyl itaconate). As the range of combinations available in forming similar copolymers is extensive, these were selected as intermediate structures lying between the possible extremes of ester side chain lengths.

EXPERIMENTAL

Monomers

The preparation of mono- and dialkyl esters was as described in detail in previous publications in this series[15,16].

Sample preparation

Poly(monobutyl-co-dibutyl itaconate) [poly(MBI-co-DBI)] and poly(monoheptyl-co-diheptyl itaconate) [poly(MHpI-co-DHpI)] samples with varying concentrations of the monoalkyl comonomer were prepared by emulsion polymerization. Potassium persulphate was used as the initiator (0.5 wt %) and the emulsifier was sodium lauryl sulphate (2.5%). Temperatures were maintained in the range 328–331K in order to avoid undesirable side reactions which have been observed at higher temperatures[17]. Reaction times of 2 to 5 h were found to be suitable for the butyl copolymers giving conversions of 9 to 13% in the time. Similar conversions were achieved in 2 to 3 h for the heptyl copolymers. Samples were separated from the reaction mixture by coagulation with methanol and were purified by repeated dissolution in chloroform and reprecipitation with methanol cooled in dry ice, until all traces of emulsifier and other impurities were removed. The copolymers were finally dried *in vacuo* for several days.

Composition analysis

The concentration of the monoester in each copolymer was estimated by non-aqueous titration of the carboxyl groups with sodium hydroxide, using a pH meter. Because the neutralization reaction was often slow the change in pH was followed on a recorder. The solvent medium for the butyl copolymers was methanol, while a 50/50 mixture of ethanol–butanol was used for the heptyl copolymers.

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* Present address: Unilever Research Ltd, Port Sunlight, Cheshire, UK.

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Table 1 Glass transition temperatures for unionized and ionized copolymers of itaconic acid esters measured by d.s.c. and t.b.a.

		T_g (K)			
Copolymer	Composition (mol %)	D.s.c.	T.b.a.	D.s.c.	T.b.a.
Poly(MBI-co-DBI)	5.7/94.3	287	–	289	–
Poly(MBI-co-DBI)	9.5/90.5	294	301	297	305
Poly(MHpI-co-DHpI)	11/89	254	257	256	258
Poly(MHpI-co-DHpI)	16/84	258	262	262	262

Polysalt preparation

Salts of the various copolymers were prepared by titration with sodium or caesium hydroxide using the method described above. Solutions were stirred overnight to ensure complete neutralization and the polysalt was isolated by solvent evaporation. Final drying was carried out under vacuum.

Characterization

The dynamic thermomechanical spectra were measured using both torsional braid analysis (t.b.a.) and the Rheovibron viscoelastometer DDV-II-C. In t.b.a. the sample is supported on a glass fibre braid which gives added strength to the polymer and allows one to investigate the behaviour of the material in temperature ranges where the polymer is mechanically weak. The method is non-absolute and only relative values of the modulus and damping are obtained[18]. When absolute measurements were required, and these were necessary when the effects of ionization on the modulus were to be assessed, the Rheovibron was employed and samples were unsupported strips of polymer cut from cast films.

Differential scanning calorimetry (d.s.c.)

The glass transition temperature (T_g) was also located by means of a Perkin–Elmer DSC-2. Thermograms were measured at a scan speed of 20 K/min, and the T_g was located as the point of intersection of the baseline with the extrapolated sloping portion of the thermogram resulting from the baseline shift which is experienced during this transition.

Electron microscopy

Copolymer films were either solvent cast or mechanically pressed and sections of about 100–150 μm thickness were cut using an LKB ultratome. Sections were floated onto copper grids and examined in a Jeol JEM 100C transmission electron microscope with a standard resolution of 0.14 nm. Samples were viewed and photographed at 200 000 magnification.

RESULTS

Glass transition temperatures

It has been demonstrated for other systems that the enhancement of the desirable properties, arising from ionomer formation, tends to diminish once the percentage of ionized groups in the polymer matrix exceeds about 6 in every hundred methylene units[4]. The copolymers examined here were restricted to a composition range in which the monoester incorporated in the chain was normally less than 55 mol %.

The sodium salts of poly(MBI-co-DBI) containing 5.7 and 9.5 mol % of the monobutyl monomer were examined by d.s.c. and t.b.a., and T_g located in each case. Comparison with the unionized copolymers showed that only a marginal increase in T_g of 2 to 3K was obtained as a result of salt formation. Similar small increases in T_g (see *Table 1*) were found for the sodium salts of two poly(MHpI-co-DHpI) samples containing 11 and 16 mol % of the monoheptyl unit in the chains. There does appear to be a tendency for this difference to be accentuated as the ionic content of the copolymers increases, but this aspect could not be pursued further in these systems as the T_g in copolymers containing higher proportions of monoester is difficult to locate. This is a result of the dehydration reaction which occurs around 440K and either masks the T_g or changes the chemical structure of the copolymer before the transition can be observed[14].

Thermomechanical response

The dynamic thermomechanical damping spectra of the ionized copolymers are virtually identical with those obtained from the unionized samples. Above the glass transition there is some indication of a decrease in the damping level, suggesting that ionization leaves the glassy state essentially unaffected but influences the response in the rubber-like region above T_g. This is illustrated in *Figure 1*. A high level of damping in this region would indicate that the polymer, in this case the unionized copolymer, tends to behave like a viscous liquid, while a decrease in the damping suggests a more rubber-like response. This behaviour is consistent with the suggestion that the polysalt structure is stabilized by ionic crosslinks and the physical appearance of the materials bears this out. The unionized copolymers tend to be soft and very tacky with good adhesive qualities, but this is changed after salt formation when the material is transformed into a tough, leathery substance with little or no tackiness.

The physical effect is seen more clearly if one examines the modulus and damping curves of the unsupported films measured on the Rheovibron. In *Figure 2* the complex modulus (E^*) and the damping (tan δ) are shown as a func-

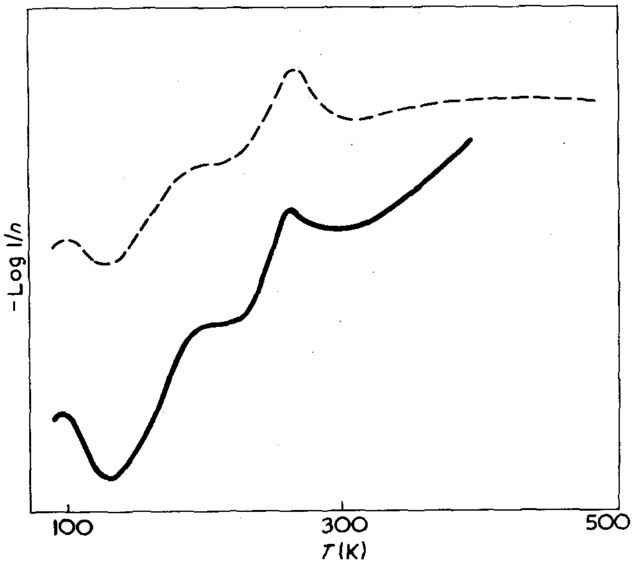

Figure 1 Comparison of loss curves from t.b.a. measurements for unionized (——) and ionized (– – – –) poly(MHpI-co-DHpI) containing 16 mol % of monoheptyl units

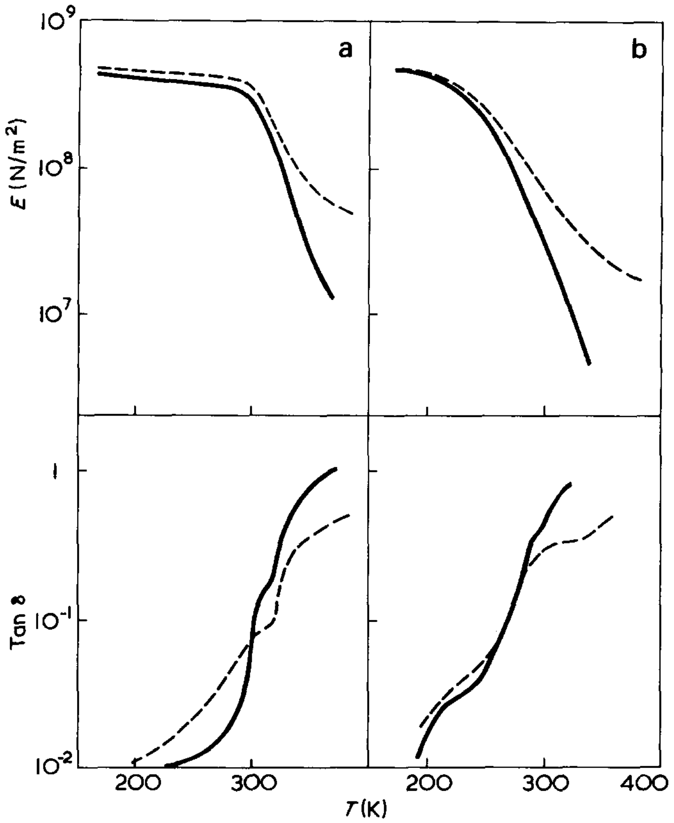

Figure 2 Modulus and tan δ curves plotted as function of temperature. (a) Poly(MBI-co-DBI) containing 9.5 mol % monobutyl itaconate and (b) poly(MHpl-co-DHpl) containing 16 mol % of monoheptyl itaconate

tion of temperature for both ionized and unionized samples. For both types of copolymer there is a marked increase in the modulus of the ionized samples in the rubbery plateau region and this is accompanied by a decrease in the damping levels in the same temperature range. The damping peaks arising from the glass transition are not particularly well-defined in either case as the specimen tension cannot be maintained properly above T_g where the onset of viscous flow is beginning to appear in the sample. In this respect the support provided by the glass braid in the t.b.a. measurements is more suitable for accurate location of the T_g.

Partial ionization

The extension of the rubber-like plateau, manifest by an increase in E^* in the modulus–temperature curves, is found to be progressive and a function of the amount of ionization in the sample. This is illustrated in *Figure 3* which shows the change in modulus as a sample of poly (MHpI-co-DHpI) containing 30 mol % of the monoheptyl monomer was ionized in stages up to 100%. As the salt formation progresses and more ionic crosslinks are introduced into the sample, the modulus also increases. This is less pronounced in the glassy region but becomes greater in the temperature range 300 to 450K, until the modulus of the fully ionized copolymer in this region is almost 10 times greater than that of the unionized sample.

While modulus enhancement is proportional to the content of ionized groups in the copolymers, unlimited increases may become counter-productive. It has been observed that fully ionized copolymers containing larger proportions of the monoheptyl units begin to exhibit brittle qualities or tend to become less tractible and more difficult to press mould.

Electron microscopy

A number of electron micrographs were taken of sections of films cast from copolymer salts. One such series, in *Figure 4*, shows samples of poly(MBI-co-DBI) and its caesium salts prepared from samples containing from 9.5 to 55 mol % of the monobutyl monomer. In *Figure 4a* the micrograph depicts a sample of composition (9.5 MBI: 90.5 DBI) which is unionized, but without differential staining techniques an accurate interpretation of the structure is difficult. Comparisons can be made which are more helpful and *Figure 4b* shows the corresponding caesium salt. The structure now seems to be more compact, suggesting the beginnings of a light crosslinking in the material. As the darker centres of high electron density are likely to contain the caesium ions, these are well dispersed throughout the matrix at this stage. When the carboxyl content of the copolymer is increased to (30 MBI: 70 DBI), the caesium salt (shown in *Figure 4c*) seems to show a suggestion of chain-like structures developing in which the darker ionic centres are lined up giving a cross-hatched appearance to the micrograph. A further increase in monobutyl content to 55 mol % leads to a significant structural change. The caesium salt has formed distinct aggregates or domains within the matrix of about 1 to 2 nm diameter. This suggests that clustering of the ionic centres has taken place, forming a two phase system in the polymer matrix. The structure bears some resemblance to the microphase separation experienced in some block copolymer systems.

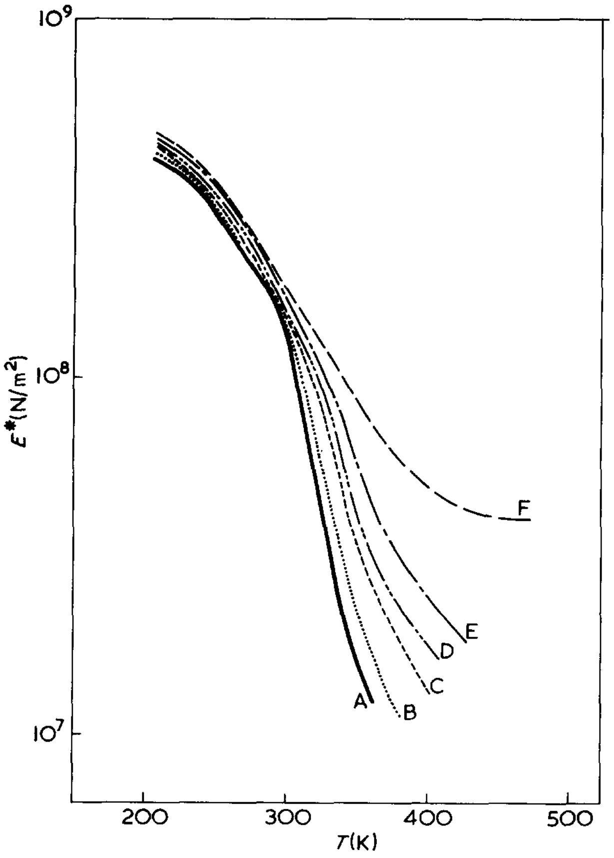

Figure 3 Effect of ionization on the modulus of poly(MHpl-co-DHpl) containing 30 mol % of the monoheptyl unit. A, Unionized; B, 17%; C, 33%; D, 50%; E, 68%; F, 100% ionized

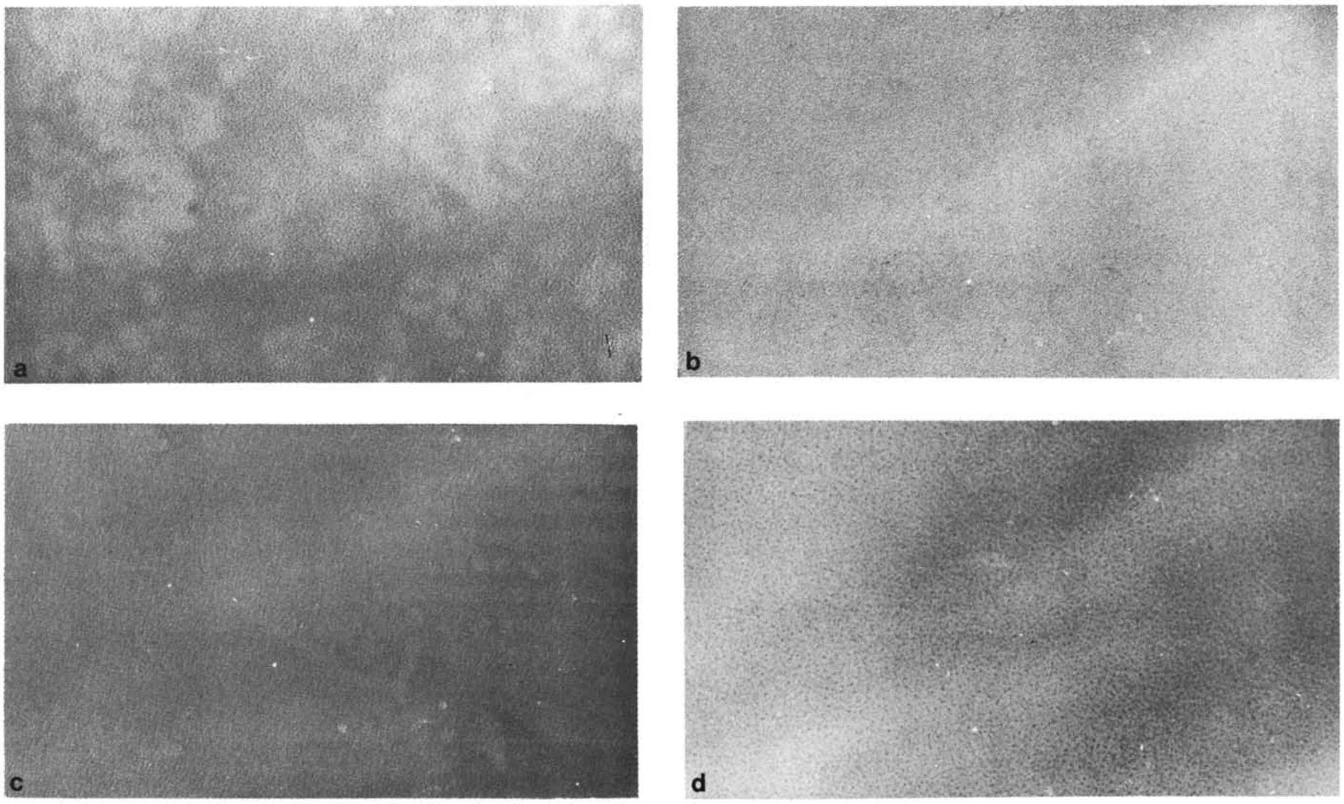

Figure 4 Electron micrographs for poly(MBI-co-DBI). (a) Unionized copolymer containing 9.5 mol % of MBI; (b) caesium salt of copolymer containing 9.5 mol % of MBI; (c) caesium salt of copolymer containing 30 mol % of MBI; (d) caesium salt of copolymer containing 55 mol % of MBI

DISCUSSION

The ability of ions to crosslink polymer chains is well established but the state of aggregation and ionic cluster formation in these polysalts is still an open question. A number of morphological models have been suggested which reflect the differing ideas on the distribution of ionic charges in the medium[1,19,20], but as they are mainly based on observation of ethylenic ionomers the models contain a crystallinity component which can be ignored when discussing the itaconate systems.

The simplest kind of ionic association is the formation of ion pairs, a process which will be highly probable in a medium with a low dielectric constant. Some workers[21-23] favour a structure in which ion pairs are randomly distributed throughout the ionomer. Others[19,24] consider a 'cluster' model to be more appropriate in which large ionic aggregates of about 10 nm diameter are embedded in the amorphous polymer matrix. A modified version of this model proposed by Marx *et al.*[20] pictures a random distribution of much smaller clusters, with diameters of about 1 nm, embedded in the polymer. This is supported by MacKnight *et al.*[25].

The evidence presented to support each of the models is individually quite convincing and an element of truth may exist in each. From our own results, the structure of the itaconate ionomers appears to vary with composition or the extent of ionization in the particular sample examined. The aggregation of ionic centres was observed to take place in acrylic acid–polyethylene ionomers when the copolymer contained 6% of ionized groups. The fact that aggregation was detected in poly(MBI-co-DBI) only when the mol % of the monoheptyl units reached 55 mol %, is rather misleading as this in fact represents much the same ratio of carboxyl group to methylene unit content (~7–8%) as with the acrylic acid–ethylene copolymer. The inclusion of the hydrocarbon side chains dilutes the concentration of carboxyl groups and allows easier control over the total content of ionizable groups.

The best description for the itaconate ionomers examined to date is that proposed by Marx and coworkers. When the concentration of ionized groups is high enough, small aggregates of approximately 2 nm diameter form randomly within the polymer matrix, but ion pair formation may well be the forerunner of this stage as the electron micrographs show no real evidence of significant clustering of the ionic centres at lower concentrations of carboxyl group. It remains to be seen whether larger concentrations of carboxyl group in these polysalts cause the smaller aggregates to coalesce and form the larger clusters proposed by Longworth and Vaughan[19]. We have, as yet, no evidence of this taking place.

The larger ionic clusters detected in *Figure 4d* probably contain up to ten ion pairs, but the increase in mechanical stability achieved by ionic crosslinking and the conversion of the relatively soft tacky copolymers into tough leathery materials after salt formation can be realized without forming these larger ionic aggregations. It may be that the significant property changes are brought about by the formation of ion pairs and that the larger cluster formation marks the end of significant property enhancement. This requires further investigation and a continuing study of these materials is being made.

The data presented here are sufficient to indicate that copolymers based on itaconic acid derivatives can form a potentially interesting group of ionomers but that more work is necessary if a proper understanding of their behaviour is to be obtained.

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