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Structure and properties of carboxylato-telechelic polyisoprene

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The effects of molecular weight, type of neutralizing cation and excess neutralizing agent on the structure and properties of carboxylato-telechelic polyisoprene have been studied. In particular, the effects of cation valence and cation size were studied for group IA and IIA elements, for which the bonding to the carboxylate anion is primarily ionic. It was found that increasing cation valence and decreasing cation size have the general effect of increasing the electrostatic association of the ion pairs, resulting in a more elastic stress–strain response. Neutralization with zinc(II) and nickel(II), elements of the first transition series that form less ionic, more coordinative complexes with the carboxylate ion, resulted in materials with quite different mechanical properties. The zinc-neutralized material displayed rather poor mechanical properties, while the nickel-neutralized material was much stronger. Materials neutralized with aluminium(III) or titanium(IV) were observed to display a wide range of properties depending upon the amount of cation incorporated. It was determined that at least four times the stoichiometric amount of titanium(IV) is necessary to crosslink the material effectively. Materials of higher number-average molecular weight (33 000 vs. 15 000) displayed higher stresses and higher ultimate elongations owing to the development of a more extensive entanglement network. Finally, small-angle X-ray scattering studies of the $\bar{M}_n$ = 15 000 and 33 000 materials indicate that an ionic peak is observed for the $\bar{M}_n$ = 15 000 materials but is generally not observed for the $\bar{M}_n$ = 33 000 materials even with 100% excess neutralizing agent. The position of this peak is essentially unaffected by the type of neutralizing agent used. Analysis of the tail region of the scattering curves indicates that the interface between the ionic and non-ionic regions is sharp.

(Keywords: polyisoprene; structure; mechanical properties; neutralization; carboxylato-telechelic ionomers; small-angle X-ray scattering)

INTRODUCTION

Elastomeric ionomers have recently attracted interest owing to their potential as thermoplastic elastomers, i.e. elastomers that flow at elevated temperatures yet retain their elastic nature and network structure upon cooling. The properties of elastomeric ionomers are a direct result of the ionic network structure, which, in turn, is dependent upon such factors as the type of ionic groups attached to the polymer and their concentration, the neutralizing ion, the extent of neutralization, the molecular weight and the molecular architecture. Thus, by modifying these variables, as well as variables such as chain flexibility, one may create materials with a wide range of properties.

Lundberg and coworkers[1–9] have prepared sulphonated EPDM materials (terpolymers of ethylene, propylene and a non-conjugated diene monomer, typically ethylidene norbornene) and have studied both their bulk and solution properties. MacKnight and coworkers have studied the properties of polypentanamers containing carboxylate[10], phosphonate[11,12] and sulphonate[13,14] groups. Polyurethane ionomers have been studied by Dietrich, Keberle and Witt[15] and also by Cooper and coworkers[16–19]. In all of these materials, the ionic groups are distributed randomly along the chain. This random distribution results in an ionic network with a broad range of molecular weights between crosslinks. Telechelic ionomers, i.e. ionomers with the ionic groups located only at the chain ends, offer the opportunity to control the molecular weight between ionic crosslinks. In addition, a telechelic ionomer with the same ionic content as a random ionomer generally has a much lower molecular weight. This results in a significant modification of the rheological properties[20,21], substantially decreasing the viscosity at processing temperatures owing to the reduction in molecular entanglements[22]. Clearly, this represents a tremendous potential advantage for telechelic

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ionomers. In addition, study of these model systems is lending further insight into the fundamental structure–property behaviour of ionomers.

Otocka, Hellman and Blyler[23] first studied the properties of carboxyl-terminated polybutadiene. Wilkes, Kennedy and coworkers have more recently studied the solid-state mechanical[24–29], melt rheological[20,21] and solution[30–32] behaviour of a unique series of sulphonated polyisobutylene telechelic ionomers. Broze, Jérôme, Teyssié and coworkers[33–51] have investigated the structure and properties of carboxylato-telechelic ionomers based on polybutadiene and polyisoprene. Tant *et al.*[46] have recently reported the initial results of mechanical property studies of the carboxylato-telechelic polyisoprene. In this paper we present the results of further studies on the morphology and mechanical properties of carboxylato-telechelic polyisoprene, including the effects of molecular structural variables upon small-angle X-ray scattering as well as stress–strain, creep, stress relaxation, thermomechanical and dynamic mechanical properties

EXPERIMENTAL

Experimental details of the synthesis and neutralization of carboxylic acid polyisoprene can be found in previous publications[36,43]. Carboxylato-telechelic polyisoprenes were anionically prepared with an $\bar{M}_n$ of either 15 000 or 33 000, a heterodispersity ($\bar{M}_w/\bar{M}_n$) lower than 1.2, and a mean number of carboxylic acid groups per chain of 1.95. The ratio of 3,4/1,2 isoprene microstructure was 65/35. Neutralizations were carried out in solution under strictly anhydrous conditions by adding the stoichiometric amount of the alkaline or alkaline-earth alkoxide. Reactions were driven to completion by distilling off the alcohol product. Neutralization with nickel(II) and zinc(II) was also performed in solution by using nickel and zinc acetate as the metal reagent. Since metal acetates are much less water-sensitive than metal alkoxides, anhydrous conditions are no longer required. The metal acetate was used in stoichiometric amounts (one Ni or Zn per chain) and the acetic acid formed was distilled off[51]. Neutralization with aluminium(III) and titanium(IV) was also accomplished in solution under non-anhydrous conditions. As reported earlier by Jérôme *et al.*[41,43], water is needed in order to promote the desired crosslinking reaction. In fact, an excess of aluminium(III) or titanium(IV) alkoxide is required. The result is not a truly intermolecular ionic bond, but a carboxylato metal oxohydroxide type of intermolecular bridge[48,49]. The materials were carefully dried under vacuum at 50–60°C for several days.

Films of about 0.6 mm thickness were prepared for structural and mechanical property investigations by compression moulding at 100–120°C followed by cooling in room-temperature air. Care was taken during compression moulding to minimize the moulding time and thus the potential for crosslinking. The fact that the materials were, in some cases, remoulded several times without adverse effects on properties suggests that crosslinking did not occur to any appreciable extent. Dogbone-shaped samples, measuring 5.75 mm long in the linear region (10 mm overall) and 2.55 mm wide, were cut from these films.

Small-angle X-ray scattering (SAXS) experiments were conducted using an automated Kratky slit collimated camera. X-rays were obtained from a Philips PW1316/91 Cu tube operated at 40 kV and 20 mA by a Philips PW1729 generator. Cu Kα radiation with a wavelength of 15.4 nm was obtained from a copper target after nickel foil filtering. The scattered intensity was monitored by a one-dimensional position-sensitive detector (M. Braun–Innovative Technology Inc.). SAXS curves shown in the figures are smeared data, while Bragg spacings discussed in the text were calculated from the desmeared curves.

Stress–strain experiments were performed on an Instron model 1122 at room temperature (approximately 23°C). Experiments were conducted at a constant strain rate of 100% $\min^{-1}$ based on the initial length of the linear portion of the sample, unless otherwise stated. Instantaneous permanent set was determined by cyclic loading and unloading at the same time to increasing strain levels in increments of 50% elongation. The end of the unloading cycle and the beginning of the next loading cycle was taken at the point where stress reached zero. The instantaneous permanent set was defined as the elongation at the end of each cycle. Later statements concerning instantaneous set also refer to this same definition. The per cent hysteresis for a given cycle was calculated as the ratio of the area bounded by the loading–unloading curves to the total area under the loading curve multiplied by 100. These areas were determined using an electronic digital planimeter.

Long-term stress relaxation experiments were performed on a Tensilon/UTMII (Toyo Measuring Instruments Co. Ltd) because of the excellent stability of this instrument over long periods of time. Samples were strained to 25% at a strain rate of 400% $\min^{-1}$. The decay in stress was monitored for up to 10^4 min.

Creep experiments were conducted at room temperature by applying a load and monitoring the time-dependent sample deformation by one of two methods. In the first, the distance between two gauge marks located within the linear region of the dogbone specimen was monitored with a cathetometer. The other method made use of a linear voltage displacement transducer (LVDT). To maintain a constant initial stress among samples, a 4 g load was applied to a 20 mil (0.02 inch, 0.05 cm) thick sample and was adjusted appropriately for other sample thicknesses. The creep compliance, $D(t)$, was calculated using the relationship

$$D(t) = \varepsilon/\sigma = \varepsilon(A/F) = \varepsilon(A_0/\lambda F) \qquad (1)$$

where ε is the strain, σ is the engineering stress, A is the instantaneous cross-sectional area, A_0 is the original cross-sectional area, F is the measured force and λ is the extension ratio. All creep data were obtained at extension ratios less than 1.20. It is noted that in our previous paper[46] equation (1) was expressed incorrectly, although the actual data were correct.

Dynamic mechanical properties were measured using a Polymer Laboratories Dynamic Mechanical Thermal Analyzer, which was operated in the shear mode at a frequency of 10 Hz. Scans were made from −150 to 180°C at a scan rate of 5°C $\min^{-1}$. The shear storage modulus was calculated and then plotted as a function of temperature. D.m.t.a. experiments were performed under a nitrogen atmosphere.

Thermomechanical analysis was performed using a Perkin–Elmer TMS-2. The temperature range from −100°C to softening (up to 300°C) was scanned at a heating rate of 10°C $\min^{-1}$, and the penetration of a probe under a 10 g load was monitored. T.m.a. experiments were also performed under a nitrogen atmosphere.

RESULTS AND DISCUSSION

Structural studies by small-angle X-ray scattering (SAXS)

Small-angle X-ray scattering is a powerful technique that provides information regarding the morphology of a material based upon differences in the local electron density. For a two-phase system, the scattering theory has been well developed and has been discussed elsewhere[52–55]. SAXS is routinely applied to obtain information regarding the spatial correlation between regions of similar electron density over distances of 200–5000 nm as well as the nature of the interfacial region between phases. Ionomers are generally considered to be made up of at least two phases, an ionic phase resulting from the association of the ionic groups dispersed within a non-polar matrix consisting of the non-polar chain material. If the chains are crystallizable, then a third phase made up of polymer crystallites may be present. For the materials of interest here, crystallinity is not present in the undeformed materials and only a two-phase model needs to be considered. The differing electron density of the ionic regions and the non-polar matrix provides the contrast for application of SAXS.

The SAXS profiles of carboxy-telechelic polyisoprene (PIP) of $\bar{M}_n = 33\,000$ neutralized to different levels are shown in *Figure 1*. The numbers 1, 2, 4 or 6 in this and later figures refer to the amount of neutralizing agent used, i.e. 1 = 100% or end point neutralization, 2 = 200% etc. For the Na(I) and Mg(II) ionomers (curves A to D in *Figure 1a*), no evidence of an 'ionic peak' is observed. Since its first observation, the presence of an ionic peak has been considered evidence of the aggregation or clustering of many ions[56]. The absence of an ionic peak may result from a lack of cluster formation, the lack of long-range periodicity between the ionic aggregates, an electron density difference between the phases that is too small to provide adequate scattering, or a low concentration of ionic groups. The ionic content of these ionomers is quite low, being about 0.4 ionic groups per 100 isoprene repeat units. Hence, the absence of the ionic peak for these materials may be due to the low concentration of ions as well as perhaps a lack of adequate long-range order. These results, then, do not oppose the presence of a network structure. Mechanical property results to be presented in this paper clearly indicate that the ionic groups in these materials do associate quite strongly. Some of the scattering curves for these ionomers display a distinct upturn at low angles similar to that observed by others for many different ionomer systems. It has been recently proposed that this 'zero-angle scattering' is due to the ionic groups being inhomogeneously distributed throughout the material[57]. While this is certainly not the only possible explanation, it does appear to be the most likely. It should be noted as well that the zero-angle scattering increases with addition of excess neutralizing agent. It is not clear why the Ti(IV) material displays much more scattering than the other materials although this may reflect the higher electron density of Ti relative to the other counter ions.

The scattering profile for the stoichiometrically neutralized aluminium(III) ionomer of $\bar{M}_n = 33\,000$ is shown by curve A in *Figure 1b*. Again, an ionic peak is not observed. With the addition of 100% excess neutralizing agent, there is an upward shift in the scattering curve but a clear peak is still not discernible. However, with increasing levels of excess neutralization, the development of a distinct ionic peak is observed (curves C and D). The desmearing procedure of the smeared scattering profile was carried out using Vonk's program[58]. The desmearing procedure usually shifts the scattering profile to higher scattering angles or smaller *d* spacings. As aluminium(III) ions beyond the stoichiometric amount are added to the system, these excess ions probably associate with the ionic regions in the material. Additional aluminium(III) ions result in an increase in the intensity of the scattering peak, probably due to the fact that the additional ions act to increase the square of the electron density difference between the ionic and non-ionic phases.

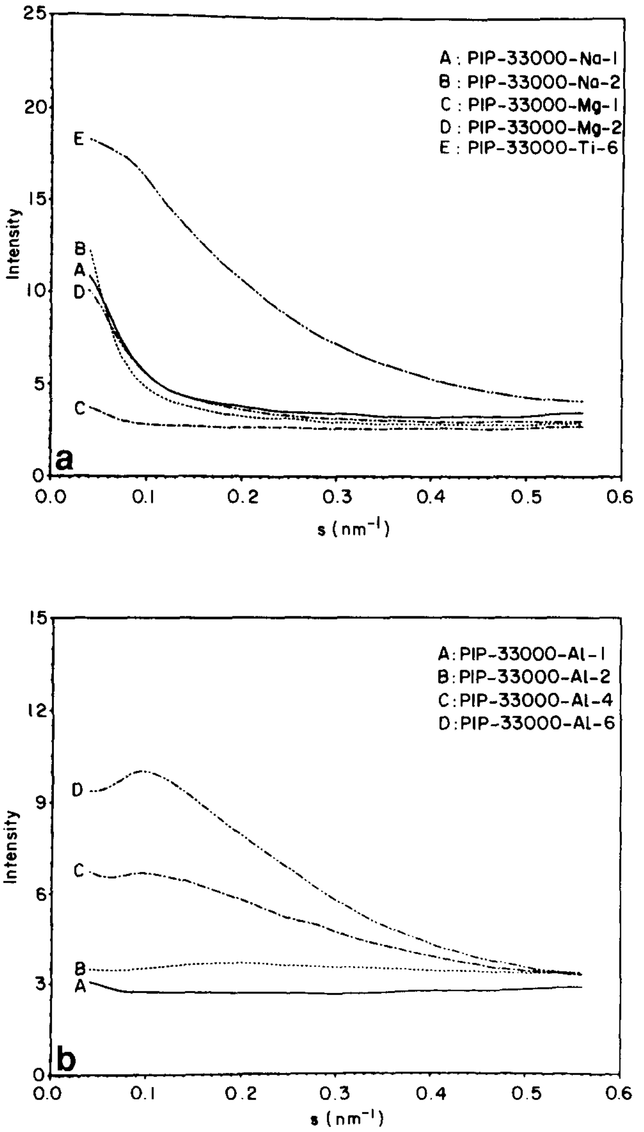

Figure 1 Smeared small-angle X-ray scattering curves for PIP-3300-M-X ionomers: (a) Na(I), Mg(II) and Ti(IV) ionomers; and (b) Al(III) ionomers

SAXS curves for the $\bar{M}_n = 15\,000$ carboxy-telechelic polyisoprene neutralized stoichiometrically with potassium(I), magnesium(II) and barium(II) are shown in *Figure 2*. In contrast to the curves for the $\bar{M}_n = 33\,000$ materials, each of these curves displays the characteristic 'ionic peak', which has historically been considered evidence of the presence of clusters. The fact that the peak is observed for the $\bar{M}_n = 15\,000$ ionomers but not the $\bar{M}_n = 33\,000$ ionomers is probably the result of the

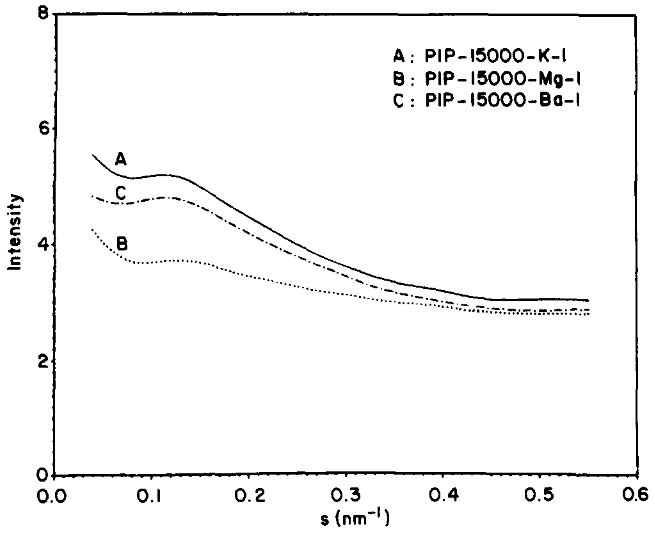

Figure 2 Smeared small-angle X-ray scattering curves for PIP-15000-M-X ionomers neutralized with K(I), Mg(II) and Ba(II)

higher concentration of ions in the lower-molecular-weight materials as well as perhaps a more periodic long-range order. The nature of the cation, however, has very little effect on the periodic spacing between the ionic domains. Desmeared *d* spacings determined from the scattering curves are about 7 nm for these materials.

Analysis of the tail region of the scattering curve provides information concerning the state of phase separation and, in particular, the interface between phases. For the ionomers that do not display an ionic peak (all curves in *Figure 1a* and curves A and B in *Figure 1b*), it was estimated that the observed contribution to the tail region was essentially due to thermal background scattering. Hence, no further quantitative analysis could be made. Since the tail region was nearly flat for all of the ionomers, thermal density fluctuations were estimated using Bonart's method[59–61]. The estimated contribution due to thermal density fluctuations or background scattering was then removed from the scattering profile. *Table 1* gives the interfacial or diffuse boundary thickness values estimated by different methods. The estimated interfacial thickness for all materials was found to be less than 0.2 nm, irrespective of the method used for determination. This suggests that the interfacial region between the ionic and non-ionic phases is very sharp. A similar conclusion was also reached by Williams *et al.*[62] for both polybutadiene- and polyisoprene-based telechelic ionomers.

Bonart[59,60] has shown that the degree of phase separation can be estimated from the different ratios of the mean electron density fluctuations in the system. To estimate the theoretical electron density difference, $\Delta\rho_c^2$, the electron density of the individual phases must be known. For ionomers, estimation of the electron density of the ionic phase is difficult since the location of the unassociated or free ions is not known. The electron density of the ionic phase was, however, approximated by using the electron density of the corresponding metal hydroxide. Also, the presence of excess ions further complicates the determination of the different ratios mentioned above. In fact, the electron density variance determined experimentally was found to be about three times more than that calculated from theoretical considerations, assuming complete phase separation between the ionic domains and the polyisoprene chain. Therefore, the analysis developed by Bonart to determine the nature of ion aggregation could not be applied to these ionomers.

Mechanical properties of $\bar{M}_n = 15\,000$ ionomers

It is well known from electrostatics that the attractive force, F, between an anion of charge e_a and a cation of charge e_c is directly proportional to the product of these charges and varies inversely with both the dielectric constant of the medium, ε, and the square of the ion separation distance, a, i.e.

$$F = (1/\varepsilon)(e_a e_c/a^2) \qquad (2)$$

It is thus apparent that the two variables of importance in this case are the charge or valence of the neutralizing cation and its size (since radius determines a), assuming a primarily electrostatic or ionic interaction and equivalent steric effects. The force of attraction should then increase with increasing valence and decreasing radius of the cation. However, it is found that this general rule holds only within a particular group of the periodic table, and generally cannot be applied across groups[44,46,51]. Even within groups IA and IIA, which form highly ionic complexes, the size of the cation can sterically influence the number of carboxylate groups that can associate. The presence of polar molecules such as water can also affect the strength of ionic association. Furthermore, as far as divalent cations are concerned, a sharp distinction has to be made between the essentially ionic alkaline-earth carboxylates and the less ionic and more coordinative transition-metal carboxylates[47]. For the latter bonding situation, the carboxylate group is an electron donor (ligand) interacting with the metal cation, which is electron-deficient. Coordinative complexes are then built up and the coordination number of the cation (number of ligands donating electron density) is of prime importance in the association process[63].

In order to investigate the effect of cation type upon mechanical properties, a carboxy-telechelic polyisoprene of $\bar{M}_n = 15\,000$ was end point neutralized with seven different monovalent and divalent cations. The cations chosen were Na(I) and K(I) from group IA of the periodic table, Mg(II), Ca(II) and Ba(II) from group IIA, and Ni(II) and Zn(II) from the first series of transition metals. *Figure 3* shows the stress–strain behaviour at a strain rate of 100% min^{-1} for the $\bar{M}_n = 15\,000$ carboxy-telechelic polyisoprene neutralized stoichiometrically with Na(I), K(I), Mg(II), Ca(II), Ba(II), Ni(II) and Zn(II).

Table 1 Diffuse boundary thickness values estimated from different methods for carboxy-telechelic PIP ionomers

	Interfacial thickness, σ (nm)			
Sample	Bonart	Exponential	Koberstein	Ruland
PIP-33000-A1-1	–	–	–	–
PIP-33000-A1-2	–	–	–	–
PIP-33000-A1-4	0.08	0.06	0.06	0.01
PIP-33000-A1-6	0.06	0.05	0.03	0.04
PIP-15000-K-1	0.14	0.09	0.10	0.06
PIP-15000-Mg-1	0.17	0.10	0.11	0.0
PIP-15000-Ba-1	0.0	0.02	0.02	0.0

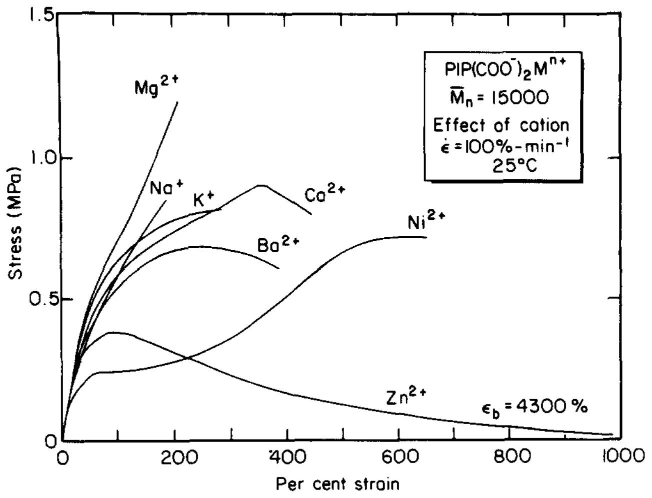

Figure 3 Stress–strain curves for $\bar{M}_n = 15000$ carboxy-telechelic polyisoprene end point neutralized with various monovalent and divalent cations

Materials neutralized with cations from group IA, i.e. Na(I) and K(I), behave somewhat differently in that the Na(I) material displays a linear stress–strain response while the stress–strain curve for the K(I) material shows more curvature and reaches a slightly higher strain. This difference apparently results from the fact that the radius of Na(I) (9.9 nm) is smaller than that of K(I) (13.3 nm), resulting in a higher attractive force and thus a stiffer material. Based on only two cations from group IA, this conclusion has to be considered cautiously. Indeed, the dynamic mechanical properties of a series of alkaline carboxylato-telechelic polybutadienes ($\bar{M}_n = 4600$) suggest a similar conclusion[47]. In this series, the material neutralized with Na(I) displayed a higher degree of association and a more thermally stable ionic network than the material neutralized with the larger K(I) cation. However, a material neutralized with Li(I), a smaller cation, was found to be more weakly associating, suggesting that steric considerations may play a role as well. That is, a very small cation may not allow the association of as many carboxylate groups, thus decreasing the functionality of the ionic aggregate. Thus, one must consider not only the electrostatics of the problem but the steric ability of ionic groups to coordinate with the cation.

Considering now the materials neutralized with cations from group IIA, i.e. Mg(II), Ca(II) and Ba(II), a similar trend is observed. The stress–strain curve of the material neutralized with Mg(II), the smallest cation in the series, is quite linear, suggesting a nearly elastic response, and reaches the highest ultimate stress of any of the materials. Both Ca(II) and Ba(II) are larger than Mg(II), and the materials neutralized with these two cations display a viscous or yielding response at higher elongations. The fact that the Ca(II) material reaches higher stresses than the Ba(II) material may be the result of its smaller radius (9.9 nm), and thus stronger interaction of the ion pairs, as compared to Ba(II) (13.4 nm). In the series of materials neutralized with alkaline-earth cations, both the mechanical properties reported here and the dynamic mechanical properties reported earlier[38,39,44] support the general idea that the strength of interaction of the dipoles, which increases as the ionic radius decreases, controls the response of the materials.

As expected, the two materials neutralized with cations from the first series of transition metals (Ni(II) and Zn(II)) display quite different behaviour owing to their less ionic, more coordinative character. At low strains (<40%) the stress–strain behaviour of the Zn(II) material is similar to that of the others. At about 40% elongation the material yields and begins to flow, with stress decreasing until failure finally occurs above 4000% strain. The behaviour of the Ni(II) material is much more interesting. While the stress–strain curve deviates from the others at very low strain, it reaches a short plateau and then increases again. The stress at break is similar to those of materials neutralized with group IA and IIA cations (except Mg(II)), while the ultimate strain is much higher. *Table 2* compares the ultimate stress and ultimate strain of the materials neutralized with different cations.

The effect of strain rate on the stress–strain behaviour sheds further light upon the effectiveness of the various cations in crosslinking the chains. A stronger network resulting from stronger ionic bonding would be expected to result in less strain-rate dependence owing to less chain slippage. A weaker ionic network would experience more chain slippage and thus more strain-rate dependence. *Figure 4* shows the strain-rate dependence for the materials neutralized with Na(I) and K(I). Clearly, strain rate has a more significant effect for the K(I) material than for the Na(I) material, again indicating that Na(I) associates more strongly owing to its smaller size. Although not shown, a similar trend was observed for the effect of strain rate on the stress–strain behaviour of materials neutralized with Mg(II), the smallest group IIA cation studied, and Ba(II), the largest group IIA cation studied. Again, the effect of cation size was clear. The stress–strain behaviour of the Mg(II) material showed very little dependence on strain rate, while the strain-rate dependence of the Ba(II) material was significant. Thus Mg(II), the smallest group IIA cation, provides stronger ionic bonding. When the alkaline and alkaline-earth carboxylates are compared, the effect of valence, and therefore the charge of the metal cation, is not very obvious. Although K(I) is monovalent and its ionic radius is similar to that of the divalent cation Ba(II), the mechanical properties of the material neutralized with K(I) are quite similar to those of the material neutralized with Ba(II). *Figure 3* indicates that the K(I) material displays a somewhat stronger resistance to deformation than the Ba(II) material. In spite of a difference in the ionic radius, the same conclusion can be drawn for the Na(I)/Mg(II) pair. Since electroneutrality of the system requires that a divalent cation is associated with two carboxylate end-groups, any favourable effect due to an increase in the cation charge might be counterbalanced by problems in associating larger ion pairs.

The effect of strain rate upon the response of the two materials neutralized with the transition metals Ni(II)

Table 2 Ultimate stress and ultimate strain of $\bar{M}_n = 15000$ PIP neutralized with various cations

Cation	Ultimate stress (MPa)	Ultimate strain (%)
Na	0.85	170
K	0.82	280
Mg	1.20	210
Ca	0.80	450
Ba	0.61	385
Ni	0.72	660
Zn	0	4300

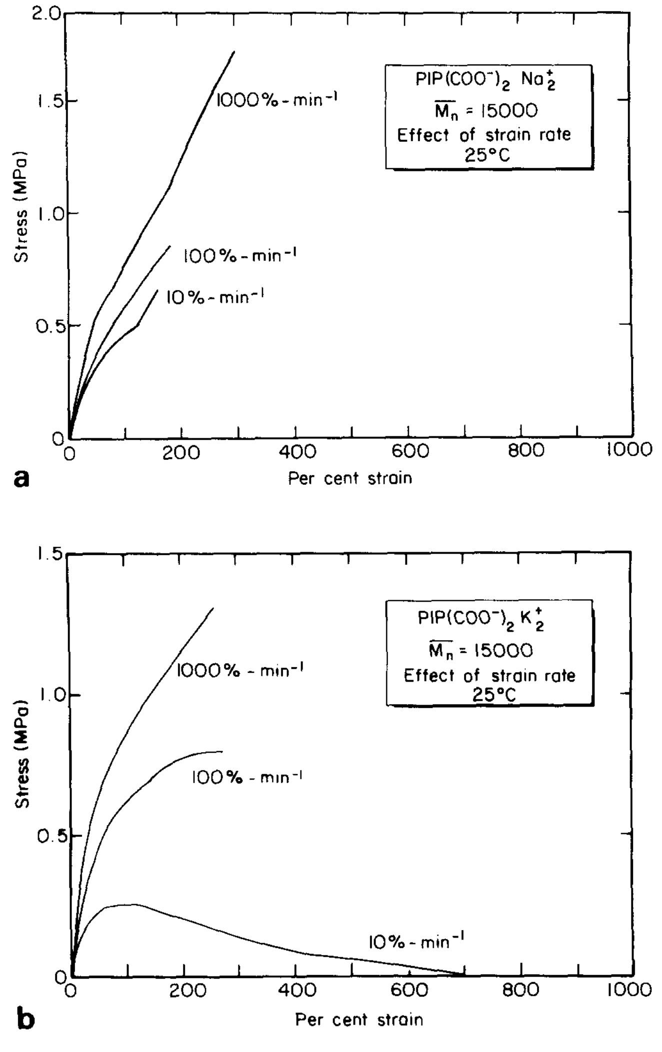

Figure 4 Effect of strain rate on stress–strain behaviour of $\bar{M}_n = 15000$ materials end point neutralized with (a) Na(I) and (b) K(I)

and Zn(II) is not shown. However, it was found that, while both show a substantial dependence on strain rate, they are nonetheless quite different. The Zn(II) material yields and then flows with constantly decreasing stress at the two lowest strain rates, indicating very little resistance to the deformation. For the Ni(II) material, stress increases at all strain rates until fracture occurs, indicating that the ionic crosslinks remain quite effective even at high extensions and possibly suggesting a more rapid re-formation of ionic association during any ion hopping that occurs.

Figures 5 and *6* show the stress relaxation and creep behaviour, respectively, for this series of materials. Again, as in the stress–strain experiments, the smallest cations studied in groups IA and IIA provided the most resistance to flow, as might be expected, assuming other factors remain unchanged. Network stability was greatest for the Mg(II) material. Again, for materials neutralized with group IA and IIA cations, network stability decreases with increasing cation size within each group. Keeping in mind the restrictions placed on the effect of the radius of alkaline cations, it is worth noting that a regular increase in the size of alkaline-earth cations by about 5 nm in going from Mg(II) (17.2 nm) to Ca(II) (22.3 nm) and finally to Ba(II) (27.8 nm) does not have a systematic effect on the mechanical properties. For instance, the Mg(II) material exhibits a much higher resistance to flow than the Ca(II) and Ba(II) materials, the behaviour of which is quite similar (*Figures 5* and *6*). Some general trends based on electrostatic interactions clearly emerge from these results, and they may serve at least as useful guidelines in predicting the mechanical properties of polymers containing metal carboxylates. Nevertheless, the apparent relationship between the strength of interaction of the dipoles and the ultimate mechanical properties is essentially qualitative. This relationship can be perturbed by other more subtle parameters affecting the mean degree of association of the ion pairs and possibly the entanglement of the ionically crosslinked chains[50]. Again, the limited effect of cation valence is illustrated by the stress relaxation and creep experiments, which progress very similarly for the Na(I)/Mg(II) and K(I)/Ba(II) pairs, respectively. The Zn(II) material relaxes more quickly than the others, partly because of its less ionic character. It is noted that the shapes of the stress relaxation curves are all very similar except that for the Ni(II) material. The rate of relaxation is high for this material at short times, but becomes much slower than for the other materials at longer times. The stress

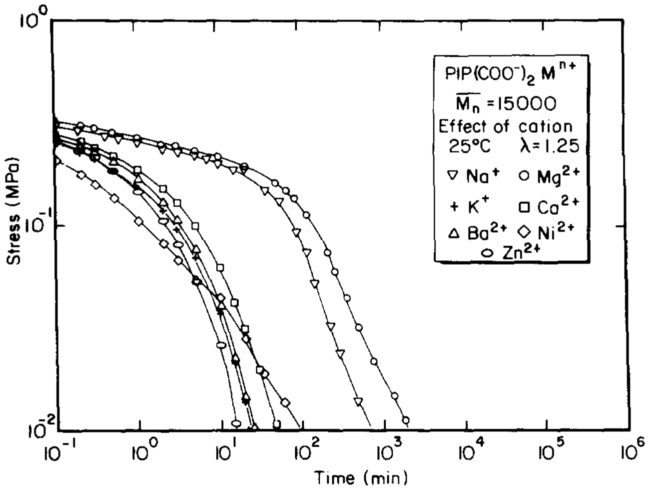

Figure 5 Stress relaxation curves for $\bar{M}_n = 15000$ carboxy-telechelic polyisoprene end point neutralized with various cations

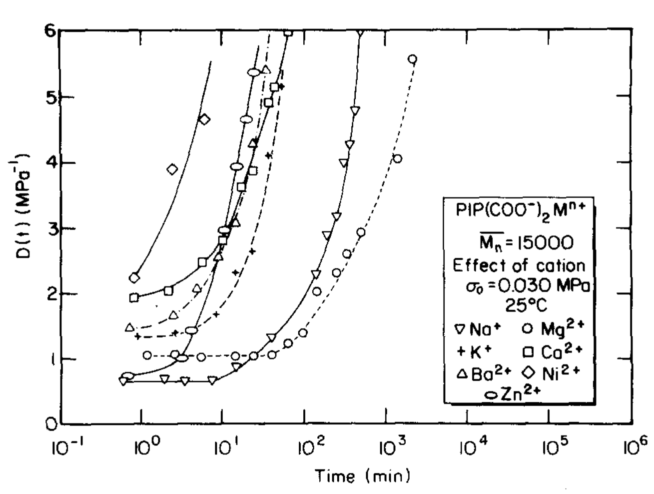

Figure 6 Creep curves for $\bar{M}_n = 15000$ carboxy-telechelic polyisoprene end point neutralized with various cations

relaxation curve for the Ni(II) material actually crosses the curves for all of the materials except Na(I) and Mg(II) during the time window studied. This supports the results of the stress–strain experiments, which show that the Ni(II) materials displays a behaviour that is very different from all of the others.

The results of thermomechanical (t.m.a.) experiments on these materials are shown in *Figure 7*. The flow regions of the two smallest cations, Na(I) and Mg(II), occur at the highest temperatures, with the Mg(I) network persisting to highest temperatures. The flow temperatures decrease with increasing cation size within groups IA and IIA. The Zn(II) material flows at the lowest temperature, again owing to the less ionic, more coordinative character of its association. The penetration curve for the Ni(II) material is somewhat different from the others in that it is relatively linear, showing only a hint of a rubbery plateau. These data generally support the stress–strain, stress relaxation and creep results.

The instantaneous set and hysteresis behaviour of these materials is shown in *Figures 8* and *9*, respectively. The Na(I) and Mg(II) materials show the strongest network, i.e. low instantaneous permanent set and hysteresis, although they fracture at very low strains. Within groups IA and IIA both instantaneous permanent set and hysteresis increase with increasing cation size, again indicating that smaller cations result in stronger, more stable networks. Both the instantaneous permanent set and hysteresis of the Ni(II) material are much lower than for the Zn(II) material. This supports the other results, which indicate that Ni(II) is much more effective at crosslinking the carboxy-telechelic polyisoprene than Zn(II), most probably due to a higher coordination number and the formation of more stable complexes.

The neutralization of carboxy-telechelic polymers with group IVA cations was discussed to some extent in the 'Experimental' section. The metal alkoxide is added in sufficient quantities to cap as many chain ends as possible with carboxylato alkoxy metal groups. The non-substituted alkoxy groups are then hydrolysed to form metal–oxygen–metal intermolecular bridges. The partial hydrolysis of the excess metal alkoxide gives rise to metal–OH groups, which react with the as-yet unhydrolysed alkoxide groups to form the metal–oxygen–metal groupings and alcohol as a by-product. Broze *et al.*[41,43,44] have previously addressed the preparation of these materials as well as their viscoelastic behaviour in both bulk and solution.

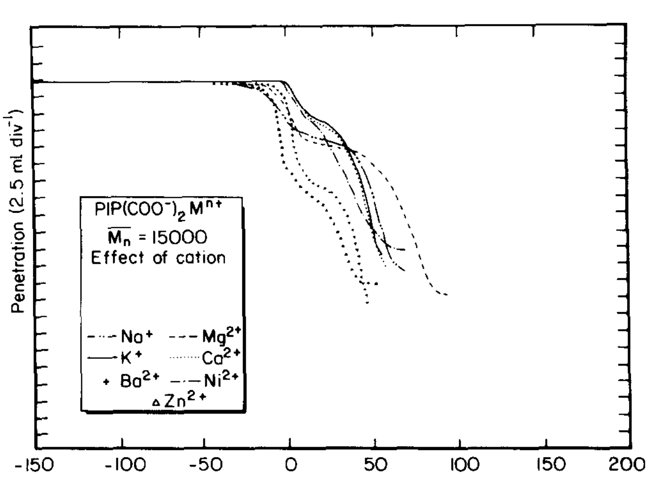

Figure 7 Thermomechanical behaviour of $\overline{M}_n = 15000$ carboxy-telechelic polyisoprene end point neutralized with various cations

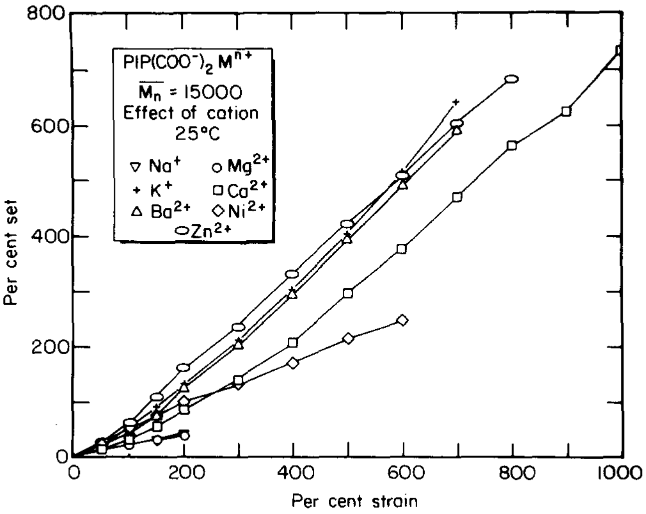

Figure 8 Instantaneous set of $\overline{M}_n = 15000$ carboxy-telechelic polyisoprene end point neutralized with various cations

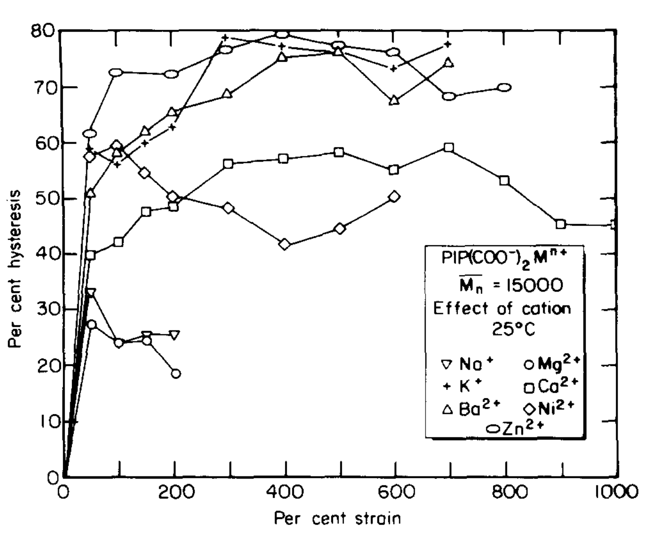

Figure 9 Hysteresis of $\overline{M}_n = 15000$ carboxy-telechelic polyisoprene end point neutralized with various cations

The primary goals of the present study of Ti(IV) carboxylato-telechelic polyisoprene were (1) to compare the mechanical properties of these materials with those of the materials neutralized with monovalent and divalent cations and (2) to determine the effect of the amount of Ti(IV) used (the terminology 'degree of neutralization' is not considered appropriate for this case) on the mechanical and dynamic mechanical properties. A series of materials for study was prepared by reacting $\overline{M}_n$ = 15000 carboxy-telechelic polyisoprene with various amounts of Ti(IV) isopropoxide. This series of materials had titanium/polymer molar ratios of 0.5, 1, 2 and 3. The molar ratio of 0.5 corresponds to stoichiometric neutralization of the classical type, i.e. assuming that each tetravalent cation associates ionically with four carboxy end-groups.

Figure 10 shows the stress–strain behaviour of this series of materials at a strain rate of 100% min^{-1}, the same strain rate used for other comparisons. Clearly, the amount of excess titanium has a very strong effect upon the stress–strain behaviour. The material with the titanium/polymer ratio of 0.5 sustains only a very low stress and flows to an extension of more than 900%. Doubling the amount of Ti(IV) to a molar ratio (Ti/PIP) of 1 more than doubles the maximum stress developed but also reduces the maximum strain to about 400%. Doubling the amount of Ti(IV) again (Ti/PIP = 2) more than doubles the maximum stress again and reduces the ultimate strain to less than 300%. Increasing the Ti/PIP ratio of 3 further increases the maximum stress but reduces the ultimate strain only slightly. It is clear that the modulus increases dramatically upon increasing the Ti/PIP ratio from 1 to 2. This is an indication of an increase in the crosslink density or crosslink functionality. *Table 3* gives the ultimate stress, ultimate strain and modulus as a function of Ti/PIP ratio.

The effect of strain rate on the stress–strain behaviour gives further evidence that the network improves as the Ti/PIP ratio increases. These data are given in *Figure 11* for Ti/PIP ratios of 1 and 2. As the ratio increases from 0.5 to 1 to 2 the strain-rate dependence decreases markedly, particularly between 1 and 2. This result suggests that it is in the Ti/PIP range of 1 to 2 that network formation occurs. Increasing the ratio from 2 to 3 has no obvious effect on the strain-rate dependence. This supports the modulus data, which show the largest change when Ti/PIP is increased from 1 to 2.

Figures 12 and *13* show the stress relaxation and creep behaviour, respectively, of these materials. Clearly, both the strength and stability of the network improve as the Ti/PIP ratio is increased. The material with a Ti/PIP ratio of 0.5 creeps so rapidly that it cannot be measured. Increasing the Ti/PIP ratio to 1 markedly stabilizes the material, but it is not until the ratio reaches 2 that a reasonably stable network is formed. Increasing the ratio to 3 has little effect upon the stress relaxation behaviour except at long times. This, as well as the creep data, suggests that the network is indeed further stabilized by increasing the Ti/PIP ratio from 2 to 3.

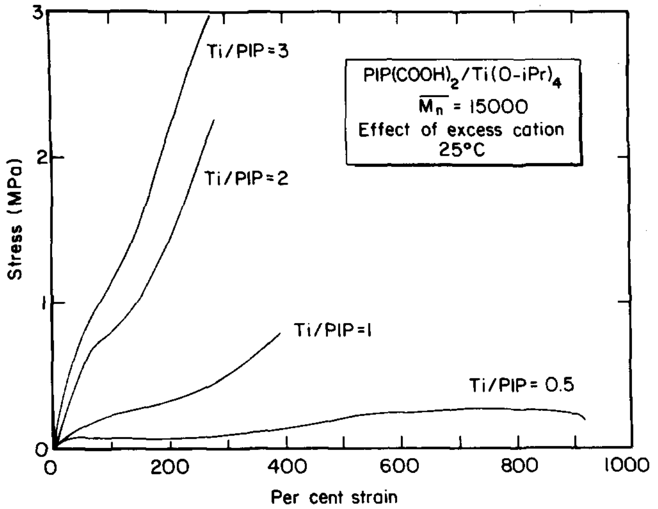

Figure 10 Stress–strain behaviour of $\bar{M}_n$ = 15000 carboxy-telechelic polyisoprene neutralized with various amounts of titanium(IV)

Table 3 Ultimate stress, ultimate strain and modulus of $\bar{M}_n$ = 15000 PIP neutralized with various amounts of titanium

Ti/PIP	Ultimate stress (MPa)	Ultimate strain (%)	Modulus (MPa)
0.5	0.19	920	0.31
1	0.80	390	0.31
2	2.27	280	1.10
3	2.97	280	2.30

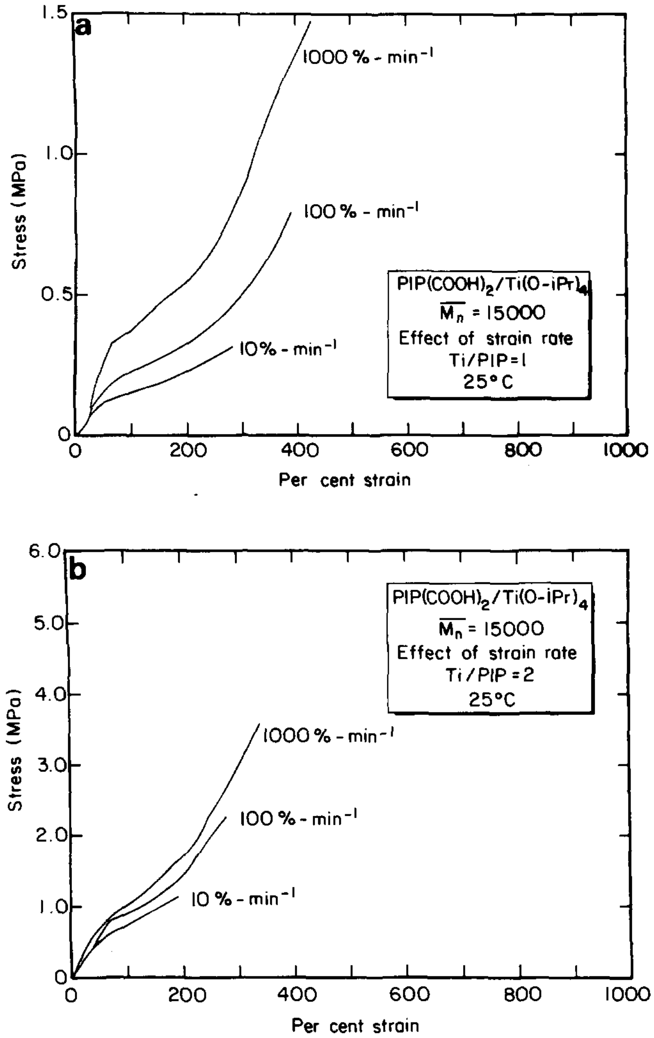

Figure 11 Effect of strain rate on stress–strain behaviour of $\bar{M}_n$ = 15000 materials neutralized with Ti/PIP ratios of (a) 1 and (b) 2. Note scale change for the stress values in (a) and (b)

The thermomechanical behaviour of these materials is illustrated in *Figure 14*. The material with a Ti/PIP ratio of 0.5 displays no evidence of a rubbery plateau. Increasing the ratio of 1 results in a very weak plateau, while both of the materials with a higher ratio exhibit significant and very similar plateaux. This is a further indication that network formation really occurs between the ratios of 1 and 2. The dynamic mechanical data shown in *Figure 15* suggest similar conclusions. Although the material with a Ti/PIP ratio of 1 shows a reasonable plateau, the plateau modulus is significantly higher for the materials with ratios of 2 and 3. It was observed that both instantaneous set and hysteresis of these materials decrease greatly with increasing Ti/PIP ratio. For the materials with ratios of 2 and 3, the instantaneous sets are very similar.

It is interesting to note that compression moulding of the materials at elevated temperatures was quite

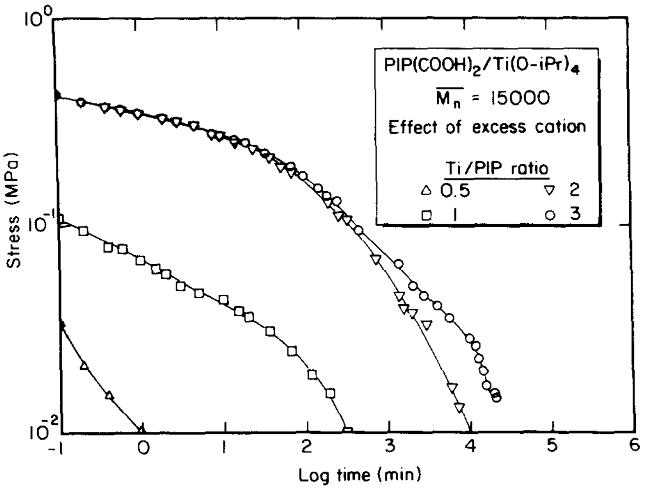

Figure 12 Stress relaxation curves for $\bar{M}_n = 15\,000$ carboxy-telechelic polyisoprene neutralized with various amounts of titanium(IV)

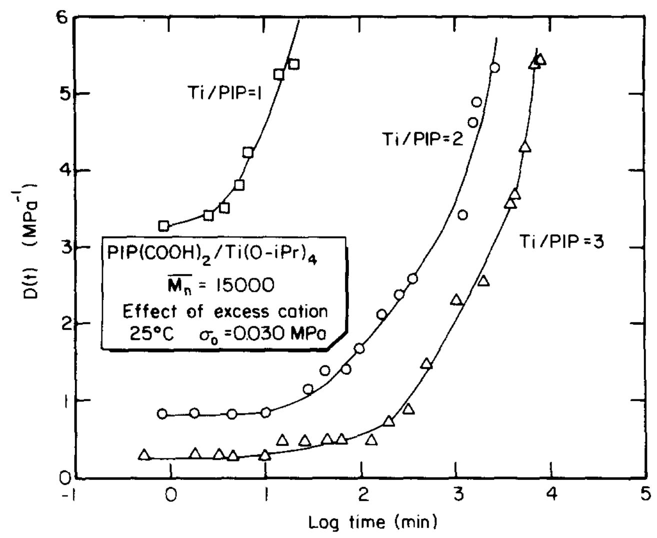

Figure 13 Creep curves for $\bar{M}_n = 15\,000$ carboxy-telechelic polyisoprene neutralized with various amounts of titanium(IV)

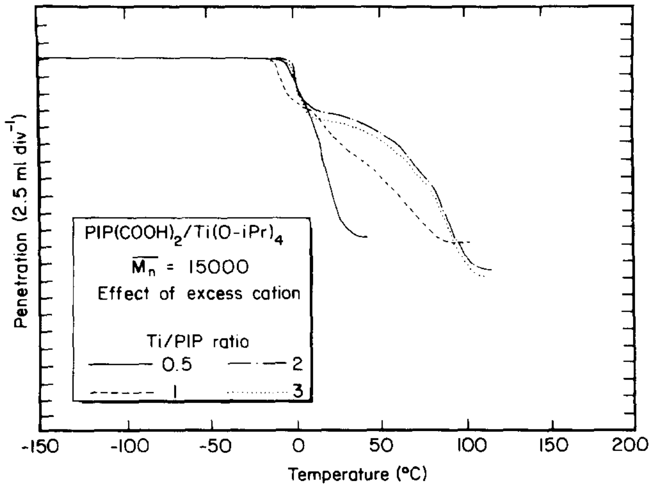

Figure 14 Thermomechanical behaviour of $\bar{M}_n = 15\,000$ carboxy-telechelic polyisoprene neutralized with various amounts of titanium(IV)

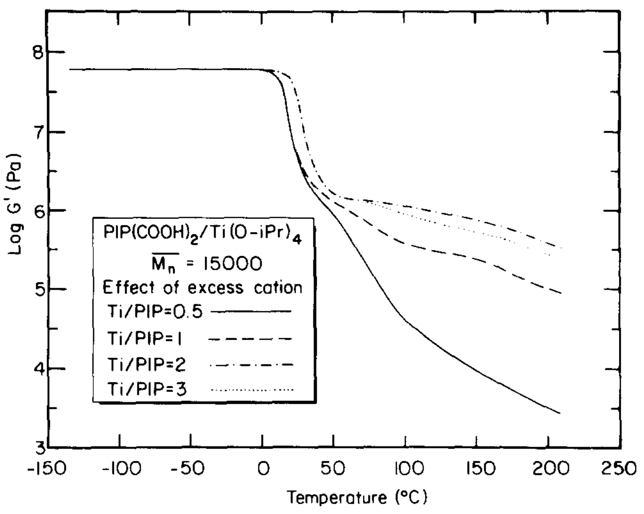

Figure 15 Storage modulus (G') curves for $\bar{M}_n = 15\,000$ carboxy-telechelic polyisoprene neutralized with various amounts of titanium(IV)

successful. This is most probably due to the thermal scrambling of the titanium carboxylate bonds linking the polyisoprene chain extremities to the metal oxo alkoxide groupings responsible for the crosslinking[43,44]. It is worth noting that the neutralization process based on an excess of tetravalent Ti(IV) alkoxide followed by hydrolysis of the unreacted alkoxide groups is quite similar to the sol–gel reactions reported for making inorganic glasses by hydrolysis of metal alkoxides. Wilkes and coworkers[64,65] have incorporated organic-based oligomeric species that have appropriate functional groups to undergo a co-condensation reaction with inorganic-based alkoxides. Proceeding in this way, these workers have successfully created organic/inorganic hybrid materials. The data reported in the present work suggest that the materials resulting from the neutralization of carboxy-telechelic polyisoprene by an excess of Ti(IV) alkoxide display mechanical properties that are superior to those of materials produced by neutralization with a stoichiometric amount of group IA or IIA metal alkoxides. The higher functionality of the crosslinks formed by the Ti(IV)-based materials, as well as a possible filler effect, might explain the advantages of these materials over the traditional ionomeric materials.

Mechanical properties of $\bar{M}_n = 33\,000$ materials

Figure 16 shows the stress–strain behaviour of the carboxy-telechelic polyisoprene ionomers having a number-average molecular weight of 33 000 and neutralized to different extents with Na(I), Mg(II), Al(III) and Ti(IV). The ultimate stress and ultimate strain are given in *Table 4*. The first observation to make is that the $\bar{M}_n = 33\,000$ ionomers display much higher stresses than the $\bar{M}_n = 15\,000$ ionomers neutralized with the same cations. This is due to the more extensive entanglement network that results from the higher molecular weight.

Figure 16a illustrates that the stress–strain behaviour of the ionomers neutralized stoichiometrically with Na(I) and Mg(II) is quite similar up to an elongation of about 200%, while at higher strains the Mg(II) material displays a higher stress level at a given strain. The similarity of the initial response is due to the fact that both materials have similar entanglement networks, while the deviation

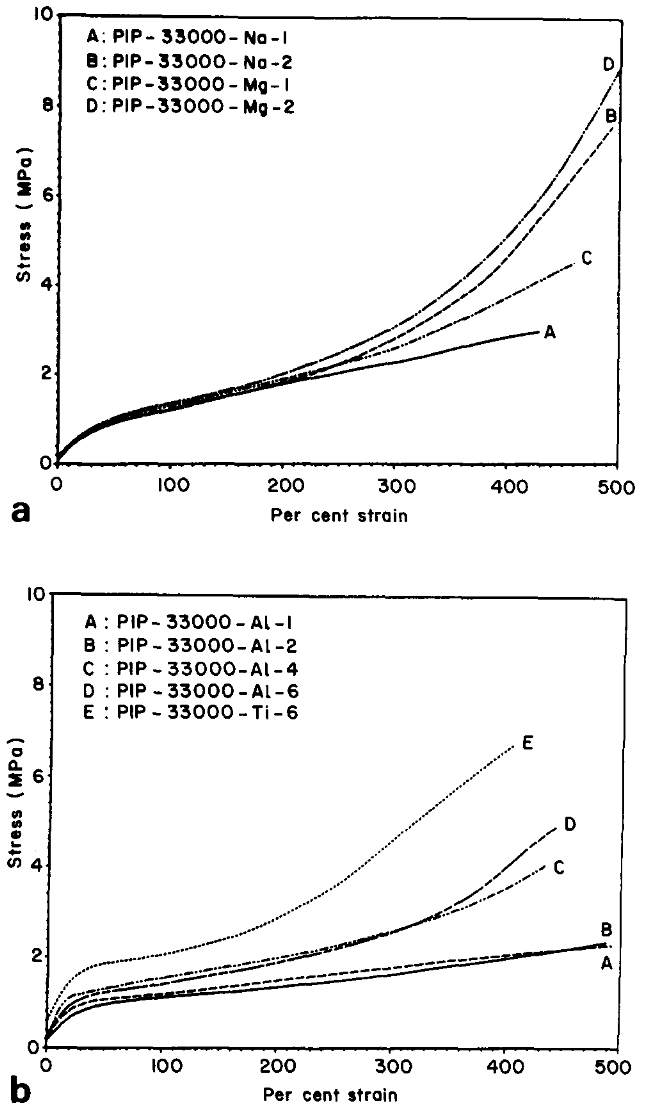

Figure 16 Stress–strain curves for $\bar{M}_n = 33\,000$ ionomers neutralized with (a) Na(I) and Mg(II) and (b) Al(III) and Ti(IV)

Table 4 Ultimate stress and ultimate strain of $\bar{M}_n = 33\,000$ PIP neutralized with various cations

Cation	Ultimate stress (MPa)	Ultimate strain (%)
Na-1	3.0	430
Na-2	7.6	490
Mg-1	4.5	450
Mg-2	9.0	500
Al-1	2.2	490
Al-2	2.2	490
Al-4	4.0	430
Al-6	4.8	440
Ti-6	6.7	400

at higher strains results from the two different cations. The higher stress displayed by the Mg(II) material results from the stronger attractive force resulting from both its smaller radius and its higher charge, as predicted by equation (2). However, the stoichiometrically neutralized Al(III) material displays a much lower stress at high elongations, as illustrated by curve A of *Figure 16b*. This is believed to be due to the fact that Al(III) is not highly ionic.

With the addition of twice the stoichiometric amount of either Na(I) or Mg(II), the materials exhibit higher stresses, particularly at high elongations. Similar behaviour has been observed for sulphonated polyisobutylene telechelic ionomers. There are two possible reasons for this behaviour. First, it is likely that more than the stoichiometric amount of neutralizing agent needs to be added to neutralize all of the acid groups. Unneutralized acid groups would not be as strongly associated and the network would therefore not be as strong. Secondly, the excess neutralizing ions, owing to their ionic character, would be expected on a purely thermodynamic basis to locate near to or within the ionic regions, thus reinforcing the ionic aggregates and reducing the extent of ion hopping that occurs in the ionomers.

There is little change in the stress–strain behaviour of the Al(III) materials with the addition of twice the stoichiometric amount of neutralizing agent. However, observed stresses are considerably higher when either four or six times the stoichiometric amount of Al(III) is added. Jérôme *et al.*[41,43,48,49] have reported that neutralization of carboxy-telechelic polymers with transition-metal (e.g. titanium and zirconium) alkoxides is limited by steric hindrance, and that much greater than the stoichiometric amount must be added to ensure complete neutralization (about one Ti(IV) or Zr(IV) alkoxide per chain end). A similar argument should apply to the Al(III) alkoxides. On complete neutralization, not only do the crosslink density and crosslink functionality increase, but dangling chain ends due to unassociated acid groups are eliminated. Finally, the Ti(IV) ionomer displays a much higher stress at a given strain than the Al(III) ionomer for the case in which six times the stoichiometric amount of neutralizing agent was used (curves D and E of *Figure 16b*).

The room-temperature creep curves for these $\bar{M}_n = 33\,000$ materials are shown in *Figure 17*. The creep behaviour of these materials confirms that neutralization with Mg(II) results in a material having a more stable network than that resulting from neutralization with Na(I). Stress relaxation results, which are not shown, support this conclusion. In addition, excess neutralizing agent further stabilizes the network and shifts the relaxation and creep curves to longer times. A similar trend occurs with increasing excess of Al(III). The creep behaviour suggests that the Al(III) ionomer forms a more stable network than the Ti(IV) ionomer when both have six times the stoichiometric amount of the neutralizing cation. Finally, the shifting of the stress relaxation and creep curves to longer times suggests that the network formed by the $\bar{M}_n = 33\,000$ ionomers is more stable than that formed by the $\bar{M}_n = 15\,000$ ionomers. This improved stability is believed to result from the more extensive entanglement network formed with higher-molecular-weight polymers.

CONCLUSIONS

Further evidence has been obtained that the mechanical properties of halato-telechelic polyisoprene are highly dependent upon both the neutralizing cation and the neutralization pathway. It is quite clear that, for neutralization with elements of groups IA and IIA, which form highly ionic complexes with the carboxylate ion, the strength of association increases with decreasing cation size and increasing cation charge according to

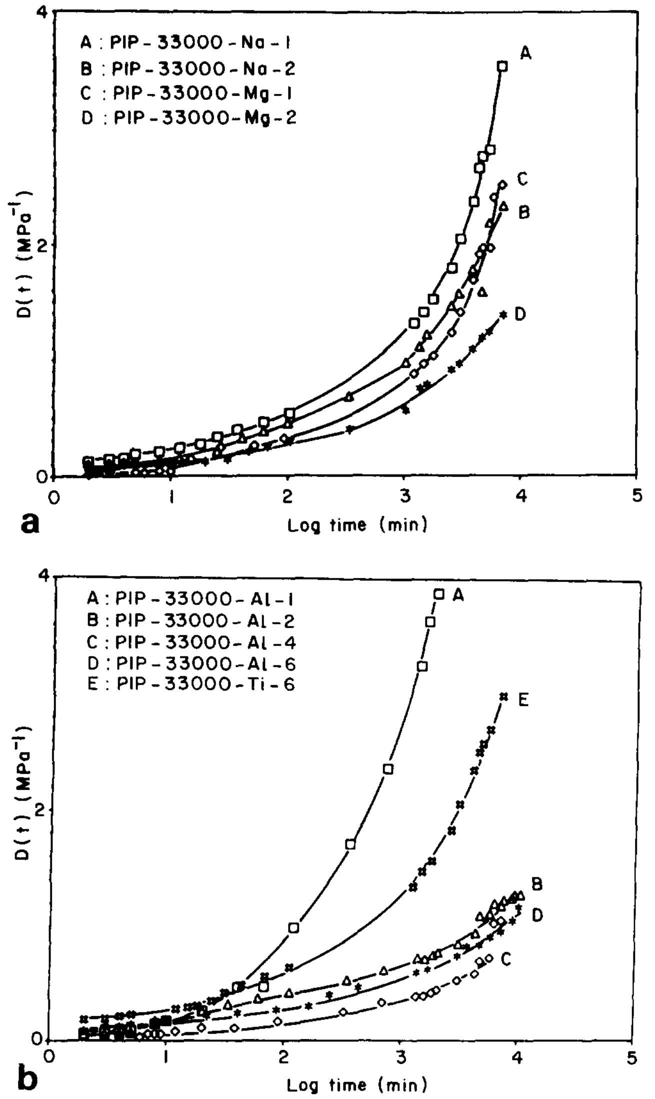

Figure 17 Creep curves for $\bar{M}_n = 33\,000$ ionomers neutralized with (a) Na(I) and Mg(II) and (b) Al(III) and Ti(IV)

electrostatics. This increasing strength of association results in the material being more stiff and elastic, except when the cation size is decreased to a point where the number of coordinating carboxylate ions might be reduced due to steric hindrance. This possible reduction in the number of coordinating carboxylate ions would result in a decrease in the functionality of the ionic crosslinks and thus a corresponding decrease in the mechanical properties of the material. We emphasize here that no direct evidence of structure was obtained to validate this conclusion experimentally.

Neutralization with zinc(II) and nickel(II) of the first transition series leads to materials with quite unusual properties. The zinc(II)-neutralized material displays rather poor properties—a very high ultimate strain but a stress that remains low and diminishes to zero at break. The nickel(II)-neutralized material displays much higher stresses as well as a high ultimate strain, suggesting strong ionic interactions and a well developed coordinative network. The stress–strain behaviour also suggests that nickel(II) may more rapidly reassociate with carboxylate ions during deformation.

It was found that four to six times the stoichiometric amount of aluminium(III) and titanium(IV) is necessary to crosslink carboxylato-telechelic polyisoprene effectively owing to the reaction pathway followed and the resulting network structure. These materials display relatively high ultimate properties, which compare favourably with those of materials neutralized with other cations.

Increasing molecular weight from $\bar{M}_n = 15\,000$ to 33 000 results in the formation of a more extensive, and thus more stable, entanglement network as assessed by stress relaxation and creep experiments. This entanglement network also leads to higher stresses and elongations in stress–strain experiments.

Small-angle X-ray scattering experiments indicate that the $\bar{M}_n = 15\,000$ halato-telechelic polyisoprene ionomers display the characteristic ionic peak while the $\bar{M}_n = 33\,000$ ionomers do not. While this does suggest that the lower-molecular-weight materials do form ionic aggregates, the lack of a peak for the higher-molecular-weight materials does not preclude their presence in these ionomers. In fact, mechanical properties do verify that ionic association does occur. The absence of an ionic peak for the $\bar{M}_n = 33\,000$ ionomers is probably due to the lower concentration of ionic groups as well as possibly less long-range order.

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REFERENCES

1 Lundberg, R. D. and Makowski, H. S. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **18**, 1821
2 Lundberg, R. D. and Phillips, R. R. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 1143
3 Lundberg, R. D. *J. Appl. Polym. Sci.* 1982, **27**, 4623
4 Peiffer, D. G. and Lundberg, R. D. *Polymer* 1983, **24**, 300
5 Makowski, H. S., Lundberg, R. D., Westerman, L. and Bock, J. in 'Ions in Polymers' (Ed. A. Eisenberg), Adv. Chem. Ser. 187, American Chemical Society, Washington, DC, 1980, Ch. 1
6 Agarwal, P. K., Makowski, H. S. and Lundberg, R. D. *Macromolecules* 1980, **13**, 1679
7 Agarwal, P. K. and Lundberg, R. D. *Macromolecules* 1984, **17**, 1918
8 Agarwal, P. K. and Lundberg, R. D. *Macromolecules* 1984, **17**, 1928
9 Agarwal, P. K., Garner, R. T. and Lundberg, R. D. *Macromolecules* 1984, **17**, 2794
10 Sanui, K. and MacKnight, W. J. *J. Polym. Sci., Polym. Phys. Edn.* 1974, **12**, 1965
11 Azuma, C. and MacKnight, W. J. *J. Polym. Sci., Polym. Chem. Edn.* 1978, **15**, 547
12 Rahrig, D., Azuma, C. and MacKnight, W. J. *J. Polym. Sci., Polym. Phys. Edn.* 1978, **16**, 59
13 Rahrig, D., MacKnight, W. J. and Lenz, R. W. *Macromolecules* 1979, **12**, 195
14 Rahrig, D. and MacKnight, W. J. in 'Ions in Polymers' (Ed. A. Eisenberg), Adv. Chem. Ser. 187, American Chemical Society, Washington, DC, 1980
15 Dietrich, D., Keberle, W. and Witt, H. *Angew. Chem., Int. Edn.* 1970, **9**, 40
16 Hwang, K. K. S., Yang, C. Z. and Cooper, S. L. *Polym. Eng. Sci.* 1981, **21**, 1027

17 Hwang, K. K. S., Yang, C. Z. and Cooper, S. L. IUPAC 28th Macromol. Symp., 1982, p. 900

18 Miller, J. A., Hwang, K. K. S. and Cooper, S. L. *J. Macromol. Sci.-Phys.* (*B*) 1983, **22**, 321

19 Spechard, T. A., Hwang, K. K. S., Yang, C. Z., Laupan, W. R. and Cooper, S. L. *J. Macromol. Sci.-Phys.* (*B*) 1984, **23**, 175

20 Bagrodia, S., Pisipati, R., Wilkes, G. L., Storey, R. F. and Kennedy, J. P. *J. Appl. Polym. Sci.* 1984, **29**, 3065

21 Bagrodia, S., Wilkes, G. L. and Kennedy, J. P. *Polym. Eng. Sci.* 1986, **26**, 662

22 Tant, M. R. and Wilkes, G. L. *J. Macromol. Sci.-Rev.* (*C*) 1988, **28**, 1

23 Otocka, E. P., Hellman, M. Y. and Blyler, L. L. *J. Appl. Phys.* 1969, **40**, 4221

24 Mohajer, Y., Tyagi, D., Wilkes, G. L., Storey, R. F. and Kennedy, J. P. *Polym. Bull.* 1982, **8**, 47

25 Bagrodia, S., Mohajer, Y., Wilkes, G. L., Storey, R. F. and Kennedy, J. P. *Polym. Bull.* 1982, **8**, 281

26 Bagrodia, S., Mohajer, Y., Wilkes, G. L., Storey, R. F. and Kennedy, J. P. *Polym. Bull.* 1983, **9**, 174

27 Mohajer, Y., Bagrodia, S., Wilkes, G. L., Storey, R. F. and Kennedy, J. P. *J. Appl. Polym. Sci.* 1984, **29**, 1943

28 Bagrodia, S., Wilkes, G. L. and Kennedy, J. P. *J. Appl. Polym. Sci.* 1985, **30**, 2179

29 Bagrodia, S., Tant, M. R., Wilkes, G. L. and Kennedy, J. P. *Polymer* 1987, **28**, 2207

30 Tant, M. R., Wilkes, G. L., Storey, R. F. and Kennedy, J. P. *Polym. Bull.* 1985, **13**, 541

31 Tant, M. R., Wilkes, G. L., Read, M. D. and Kennedy, J. P. *J. Polym. Sci., Polym. Lett. Edn.* 1986, **24**, 619

32 Tant, M. R., Wilkes, G. L. and Kennedy, J. P. *J. Appl. Polym. Sci.* 1989, **37**, 2873

33 Broze, G., Jérôme, R. and Teyssié, Ph. *Macromolecules* 1981, **14**, 225

34 Broze, G., Jérôme, R., Teyssié, Ph. and Marco, C. *Polym. Bull.* 1981, **4**, 241

35 Broze, G., Jérôme, R. and Teyssié, Ph. *J. Polym. Sci., Polym. Lett. Edn.* 1981, **19**, 415

36 Broze, G., Jérôme, R. and Teyssié, Ph. *Macromolecules* 1982, **15**, 920

37 Broze, G., Jérôme, R. and Teyssié, Ph. *Macromolecules* 1982, **15**, 1300

38 Broze, G., Jérôme, R., Teyssié, Ph. and Marco, C. *Macromolecules* 1983, **16**, 996

39 Broze, G., Jérôme, R., Teyssié, Ph. and Marco, C. *J. Polym. Sci., Polym. Phys. Edn.* 1983, **21**, 2205

40 Broze, G., Jérôme, R., Teyssié, Ph. and Marco, C. *Macromolecules* 1983, **16**, 1771

41 Broze, G., Jérôme, R. and Teyssié, Ph. *J. Polym. Sci., Polym. Lett. Edn.* 1983, **21**, 237

42 Jérôme, R., Horrion, J., Fayt, R. and Teyssié, Ph. *Macromolecules* 1984, **17**, 2447

43 Broze, G., Jérôme, R., Teyssié, Ph. and Marco, C. *Macromolecules* 1985, **18**, 1376

44 Jérôme, R. and Broze, G. *Rubber Chem. Technol.* 1985, **58**, 223

45 Jérôme, R., Broze, G. and Teyssié, Ph. in 'Microdomains in Polymer Solutions' (Ed. P. Dubin), *Polym. Sci. Technol.* 1985, **30**, 243

46 Tant, M. R., Song, J. H., Wilkes, G. L., Horrion, J. and Jérôme, R. *Polymer* 1986, **27**, 1815

47 Horrion, J., Jérôme, R., Teyssié, Ph. and Williams, C. E. *Polymer* 1988, **29**, 1203

48 Vlaic, G., Williams, C. E. and Jérôme, R. *Polymer* 1987, **28**, 1566

49 Jérôme, R., Teyssié, Ph., Pireaux, J. J. and Verbist, J. J. *Appl. Surf. Sci.* 1986, **27**, 93

50 Register, R. A., Foucart, M., Jérôme, R., Ding, Y. S. and Cooper, S. L. *Macromolecules* 1988, **21**, 1009

51 Horrion, J., Jérôme, R. and Teyssié, Ph. to be published

52 Guinier, A. and Fornet, G. 'Small Angle Scattering of X-Rays', Wiley, New York, 1955

53 Kratky, O. *Progr. Biophys.* 1963, **13**, 105

54 Koberstein, J. T., Morra, B. and Stein, R. S. *J. Appl. Crystallogr.* 1980, **13**, 34

55 Tyagi, D., McGrath, J. E. and Wilkes, G. L. *Polym. Eng. Sci.* 1986, **26**, 1371

56 Longworth, R. and Vaughan, D. J. *Polym. Prepr.* 1968, **9**, 525

57 Register, R. A. and Cooper, S. L. *Macromolecules* 1990, **23**, 310

58 Vonk, C. G. *J. Appl. Crystallogr.* 1971, **4**, 340

59 Bonart, R. and Muller, E. H. *J. Macromol. Sci.-Phys.* (*B*) 1974, **10**, 177

60 Bonart, R. and Muller, E. H. *J. Macromol. Sci.-Phys.* (*B*) 1974, **10**, 345

61 Koberstein, J. T. and Stein, R. S. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **21**, 2181

62 Williams, C. E., Russell, T. P., Jérôme, R. and Horrion, J. *Macromolecules* 1986, **19**, 2877

63 Mahan, B. H. 'University Chemistry', Addison-Wesley, New York, 1967, p. 348

64 Huang, H., Orler, B. and Wilkes, G. L. *Polym. Bull.* 1985, **14**, 557

65 Huang, H., Orler, B. and Wilkes, G. L. *Macromolecules* 1987, **20**, 1322