Complexing of some transition metal ions with poly(heptyl itaconate) containing tetraethylenepentamine side chains

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Copolymers of poly(monoheptyl-co-diheptyl itaconate) were modified by inserting up to thirteen tetra ethylene pentamine units per hundred monomer units in the chain. These modified copolymers were reacted with cobale (II), and copper (II) chlorides. Polymer–metal complexes were formed by the interaction between the TETRAEN ligands and the transition metal ions which led to crosslinking in the samples. The formation of ion clusters was also detected, with the most common cluster dimension of 15 nm, although larger aggregates tended to form at higher metal concentrations. The thermal stability of the copolymer was also improved after complex formation.

(Keywords: ion complexing; polyitaconates; tetraethylene pentamine ligands; ion clustering)

INTRODUCTION

The monomer itaconic acid makes an ideal starting point for the synthesis of comb-branched polymers with two side chains attached to each monomer unit. A series of di-n-alkyl itaconates with side chain lengths ranging from C_1 to C_{20} have been prepared and studied[1,2], and copolymers based on these structures have also received some attention[3,4]. One group of copolymers which were found to exhibit particularly interesting behaviour included structures formed by the copolymerization of mono- and dialkyl itaconates. These could be prepared with varying quantities of carboxyl units attached to the chain and subsequent neutralization of these produced ionically crosslinked matrices[5].

The interaction of polymers with ions can lead to quite dramatic changes in properties and the nature of the interaction depends on the type of ionizable or chelating structure which is incorporated into the polymer. Predominantly non-polar polymers with low levels of acidic groups present in the chain can form so-called 'ionomers' in the solid state when neutralized with bases. The introduction of either Group I or Group II cations leads to a structure crosslinked by aggregation of the ions into clusters. These ionomers have been extensively studied and reviewed[6,7].

Transition metals can also be used to crosslink or complex polymers if suitable ligands can be introduced into the polymer chain. Polystyrene has been used as a starting material for the preparation of chelating structures. Copolymers made by grafting ethylene imine onto polystyrene have been reported by Saegusa *et al.*[8–10] Other workers have used the ethylenediaminetetraacetic acid moiety as the ligand[11] and have carried out ion absorption studies using these structures. Yeh *et al.*[12] have examined the crosslinking reaction between polymer chelates and transition metals, while Pineri and coworkers[13,14] detected ion clustering when iron(III) chloride and nickel(II) chloride were added to terpolymers of (butadiene–styrene–4-vinylpyridine). The formation and structure of poly(vinylpyridine)–metal complexes have been examined by Agnew and coworkers[15–17], who were also able to elucidate the structure of the complex in some cases.

This paper described preliminary work on the interaction of some transition metals with poly(itaconic acid esters) containing a limited number of side chains with the general structure $-NH(CH_2CH_2NH)_xH$ where $x=4$.

EXPERIMENTAL

Polymer ligand preparation

Polymer ligands were prepared by the reaction between poly(monoheptyl-co-di-heptyl itaconate) [poly(MHpI-co-DHpI)] and tetraethylenepentamine (TETRAEN), as described in a previous publication[18].

Visible spectroscopy

Confirmation that there was a reaction between the polymer ligand and transition metal halides was obtained from measurements on a Beckman model 24 visible spectrophotometer. Solutions of the polymer ligand were prepared in chloroform and added to a solution of either cobalt(II) chloride or copper(II) chloride in 1:1 chloroform–methanol mixtures. The spectra of each solution and the mixture were recorded in the wavelength range 450–900 nm.

Dynamic mechanical properties

The damping characteristics and the complex modulus of the copolymers and their metal complexes were measured as a function of temperature using a Rheovibron viscoelastometer model DDV-II-C. A frequency of 11 Hz was selected for the measurements.

Thermogravimetric analysis

Weight loss curves for a number of the systems were established using a Perkin-Elmer TGS-2 system linked to a DSC2 instrument. Well dried samples (90–95 mg) were

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placed in the weighing pan of the thermo balance and thermal degradation was carried out in an atmosphere of (oxygen free) nitrogen at a constant flow rate.

Electron microscopy

Polymer samples were prepared as thin films by compression moulding with a hot press. The samples (0.2–0.5 mm thick) were sectioned (100–150 μm) by an LKB ultratome III and mounted on copper grids. The instrument used was a Jeol JEM 100C transmission electron microscope with ×200000 magnification and 0.014 resolution.

RESULTS AND DISCUSSION

Most of the work reported here was carried out using a copolymer sample, poly(MHpI-co-DHpI) which contained 13 TETRAEN chains per 100 monomer units. This was selected as a reasonable compromise between samples with low ethyleneamine contents, which gave low ion binding, and the higher TETRAEN contents, which tended to produce rather hard, brittle, materials.

Spectral evidence

Polymer ligand–metal complexes were prepared by the addition of a colourless solution of modified copolymer in chloroform to a green solution of copper(II) chloride in 1:1 chloroform–methanol. This resulted in the formation of a blue solution of the polymer–copper complex. The visible spectra are shown in *Figure 1*. The copper(II) chloride solution has a broad absorption band with a maximum at 850 nm and this disappears on addition of the polymer ligand. A new absorption band at 650 nm was observed, which is consistent with the formation of a copper complex with nitrogen donors. The intensity of this absorption was proportional to the extent of complex formation, as one would expect, and this is illustrated in *Figure 2*, where the spectra are recorded for the stepwise addition of a 0.01 M copper(II) chloride solution to an equimolar polymer ligand solution to give 10, 25, 50 and 100 mol% reaction.

These reactions were all quite rapid at the low concentrations used. Addition of a violet solution of cobalt(II) chloride to the polymer ligand resulted in a red solution of polymer–cobalt complex and the spectra recorded after 1.5 and 3.0 h show virtually no intensity change in this time scale as can be seen in *Figure 3*.

Viscoelastic behaviour

Introduction of a transition metal into the matrix of the polyligand, poly(MHpI-co-DHpI)-(TETRAEN), resulted in property changes which can be explained by assuming that crosslinking has taken place. Films from the polymer–metal complexes had the characteristic colour of the metal after coordination and were much tougher than the uncomplexed copolymer. Comparison of the complex modulus behaviour for a copolymer sample with 5 mol% TETRAEN side chains, in the presence and absence of cobalt(II) chloride, indicated that there was an enhancement of the rubbery plateau region after the samples had passed through the glass transition. The modulus–temperature curves are shown in *Figure 4* and, apart from a small increase in the glass transition temperature, there is the formation of a plateau above 350 K resulting from the polymer–cobalt interactions.

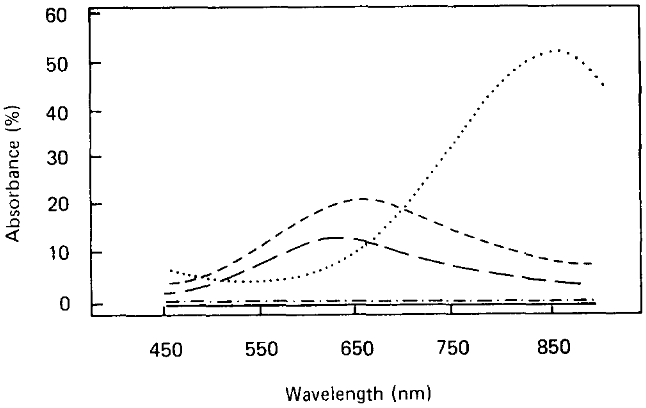

Figure 1 Visible spectra in $CHCl_3$ for poly(monoheptyl-co-diheptyl itaconate) (a) modified with TETRAEN (–·–·–); (b) after complexing with copper(II) chloride (50% of ligands) (– – –)); (c) after complexing with all ligands (-----); (d) copper(II) chloride solution only (·····)

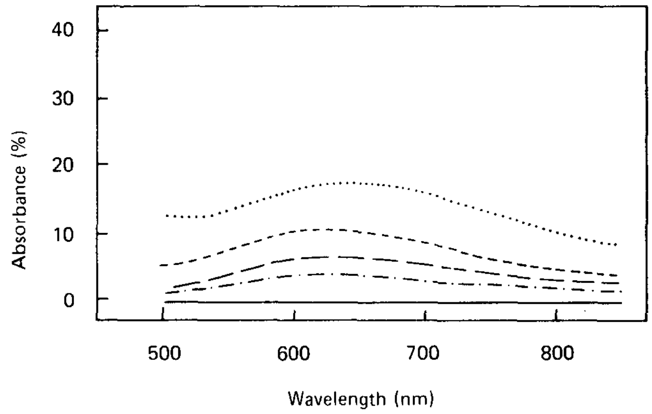

Figure 2 Visible spectra of chloroform solutions of poly(monoheptyl-co-diheptyl itaconate) modified with TETRAEN (———); after reaction of copper(II) chloride solution with (a) 10 mol% of ligand (–·–·–); (b) 25 mol% of ligand (– – –); (c) 50 mol% og ligand (-----); (d) 100 mol% of ligand (·····)

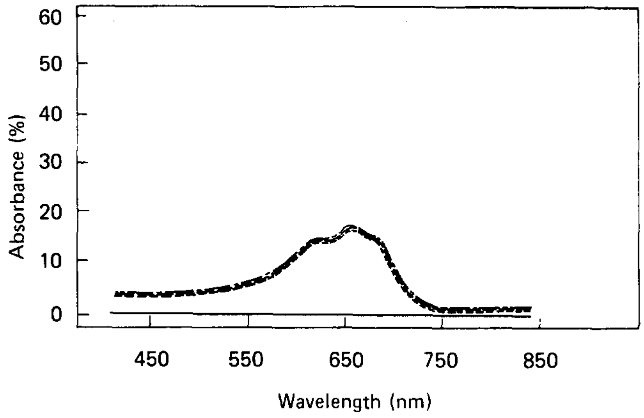

Figure 3 Visible spectra for poly(monoheptyl-co-diheptyl itaconate) containing 13 mol% monoheptyl itaconate modified with TETRAEN (———), and after reaction with cobalt(II) chloride solution: (a) at zero time (·····); (b) after 90 min (– – –); (c) after 180 min (–·–·–)

As the concentration of the TETRAEN side chain increased, the amount of bound metal increased and the level of crosslinking was raised. Polymer–metal complexes then became more rigid and glassy over a wider

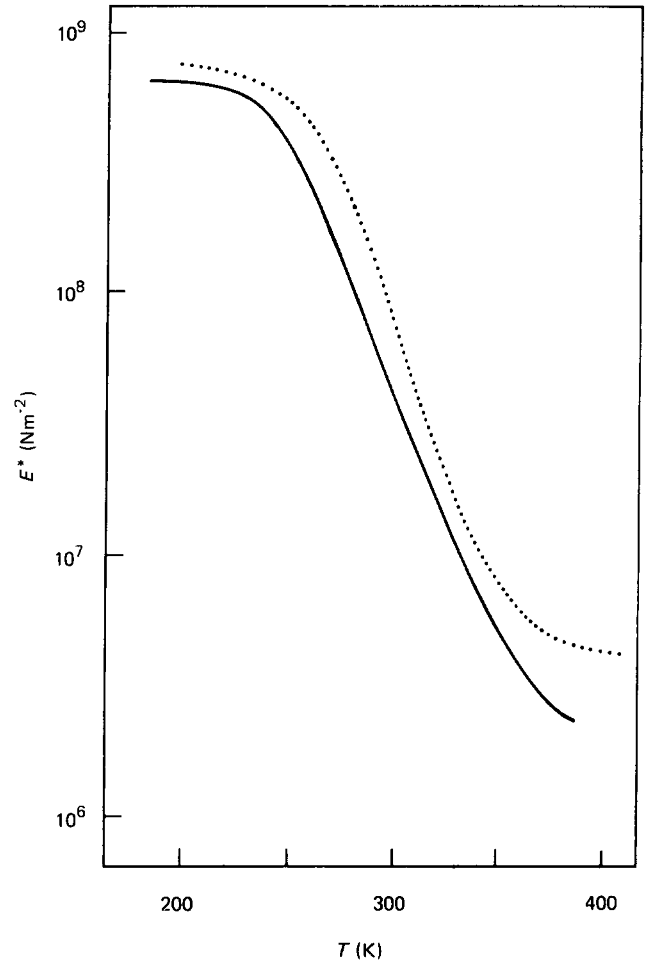

Figure 4 Temperature dependence of the complex modulus E^* for poly(mono heptyl-co-diheptyl itaconate) containing 5 mol% monoheptyl units and modified with TETRAEN. (a) (——) without added cobalt(II) chloride; (b) (·····) with cobalt(II) chloride added

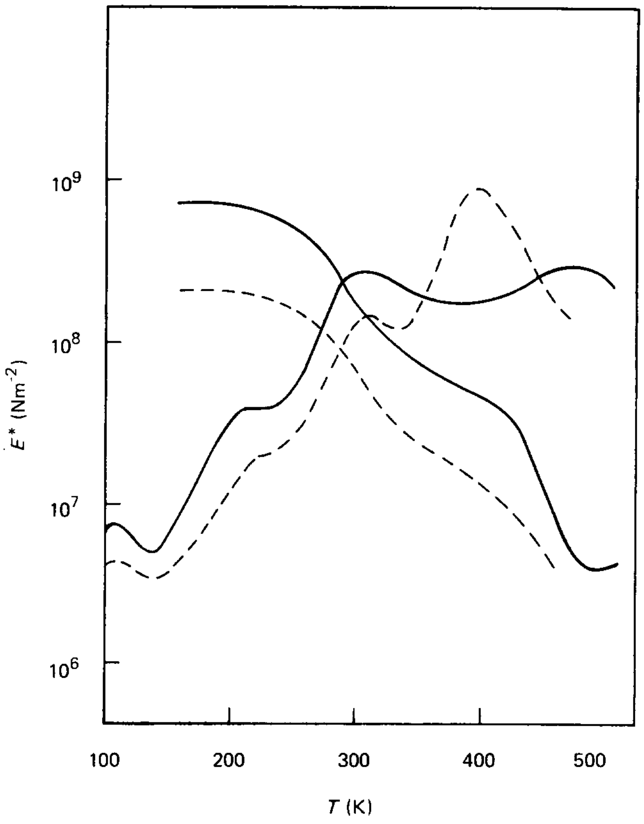

Figure 5 Temperature dependence of the complex modulus E^* and the damping tan δ for poly(monoheptyl-co-diheptyl itaconate) with 13 mol% monoheptyl units, modified with TETRAEN. (a) (– – –) in the absence of cobalt(II) chloride; (b) (———) in the presence of cobalt(II) chloride

temperature range. This is illustrated in *Figure 5* for a copolymer with 13 mol% TETRAEN with and without added cobalt(II) chloride. The glassy modulus of the polymer–metal complex is significantly higher than that of the uncomplexed copolymer. The modulus drop for the glass transition is quite small for both samples compared with that of the 5% TETRAEN polymer, indicating that the additional hydrogen bonding in the side chains is also raising the overall modulus in the sample. There is also a much more pronounced plateau region between 300 K and 400 K in the metal-complexed system, reflecting strong crosslinking interactions.

The interaction between cobalt and the TETRAEN side chains also suppresses the degradation reaction which causes the damping maximum at 400 K. This has been shown to be a reaction resulting in both intra- and interchain imide formation involving the pendant ethyleneamine units[18]. It may only postpone it, however, as there is evidence of another damping maximum at 500 K, which is accompanied by a drop in the modulus curve, and this could be interpreted as the onset of a new degradation reaction. As will be seen in the next section, the temperature at which the modulus drop occurs does not coincide with the onset of weight loss in the polymer, which begins at 550 K, and an alternative explanation for the decrease in modulus is that this is due to a breakdown of the metal–polymer coordination, i.e. a type of 'melting' of the crosslinks.

Thermogravimetric analysis

The increase in the thermal stability of the polymer–metal complexes can be verified by examining the weight loss curves shown in *Figure 6(a)*. The onset of the decrease in polymer weight moves to higher temperatures when the metals are present and the rate of weight loss is slower than for the uncomplexed polymer. A thermal volatilization thermogram was measured for the polymer–cobalt complex in Glasgow University under the direction of Dr I. C. McNeill, which substantiates the weight loss pattern (see *Figure 6(b)*). The maximum degradation occurred at 670 K, which was interpreted as representing the breakdown of the complex with the evolution of ammonia as a major degradation product.

Ion clustering

In ionomeric structures, crosslinking is effected by the clustering of metal ions in the polymer matrix; as the associated anions are bonded to the main polymer chain, the aggregate can form a crosslinking site for several polymer chains. In the case of polymer ligands to which a metal salt is added, the co-ordinated system formed may be more complex; nevertheless there is good reason to believe that ion clustering can still take place. The most convincing evidence comes from electron microscopy. The micrographs shown in *Figures 7(a)–(d)* are representative of polymer samples containing 0, 10, 25 and 100 mol% of cobalt(II) chloride. The irregular dark areas

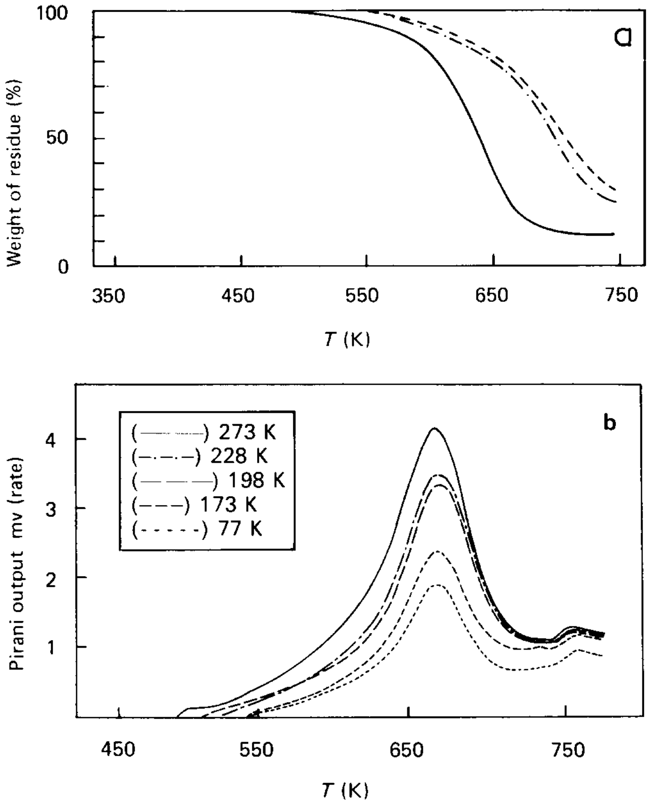

Figure 6 (a) Weight loss thermograms for poly(monoheptyl-co-diheptyl itaconate) containing 13 mol% monoheptyl units modified with TETRAEN: (———) no metal present; (–·–·–) with added cobalt(II) chloride; (– – –) with added copper(II) chloride. (b) TVA thermogram for modified copolymer complexed with cobalt(II) chloride. The temperatures represent those of the traps used to collect the volatile degradation products

generally increase in size and number as the metal content goes up; these are thought to be due to the clustering of the ions in the predominantly non-polar matrix. The aggregates vary in size from 15 to 60 nm, although there is a suggestion that the smaller 15 nm aggregates are also present in the high metal concentration complexes. The large units may then be aggregates of the smaller. These results were reproducible and it is unlikely that they are merely optical artefacts.

The presence of transition metal ion clusters and their crosslinking effect has been reported by Pineri and coworkers[13,14] for the terpolymer poly(butadiene–styrene–4-vinylpyridine) which had been reacted with iron(III) chloride and nickel(II) chloride. Their electron-micrographs for the iron(III)-crosslinked terpolymers showed regular dark areas, which were identified as the metal aggregates. These had a wide range of particle size distribution, with the largest 150–200 nm in diameter, but the vast majority were 10 nm ir less. The general similarity between their micrographs and those in *Figure 7* is quite pronounced and suggests the systems behave in much the same fashion. Perhaps what is not clearly established is whether the large aggregates contain metal chloride which is not chelated to the polymer but which continues to exist as the 'free' salt. This point may be clarified in future studies.

CONCLUSIONS

There is clear evidence of complexing between the pendant TETRAEN ligand bound to the polymer chain and the ions, Cu(II) and Co(II). This leads to some crosslinking of the samples, which also results in the formation of ion clusters in the polymer matrix. The polymer–metal

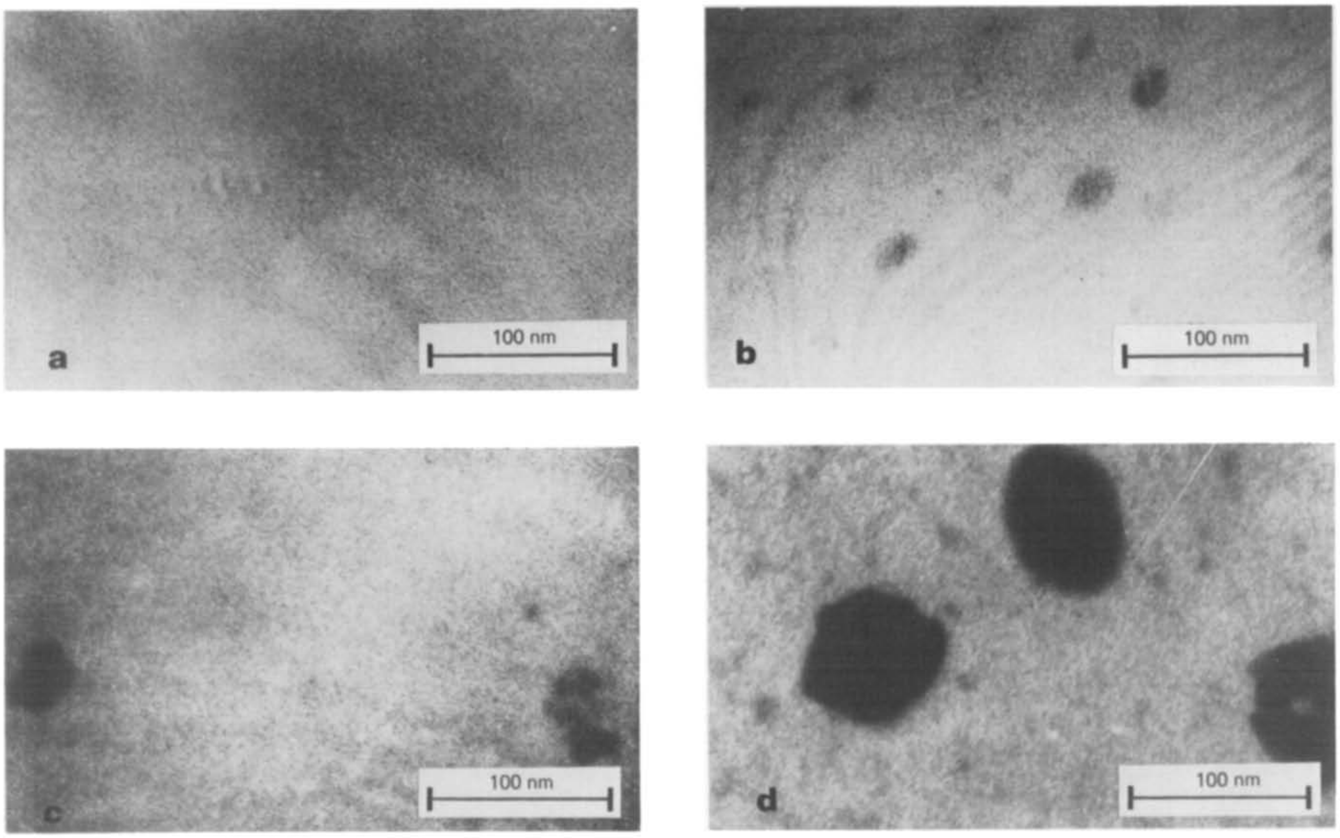

Figure 7 Electron micrographs of films of poly(monoheptyl-co-diheptyl itaconate) containing 13 mol% of monoester and modified with TETRAEN. (a) No added cobalt(II); (b) 10 mol% cobalt(II); (c) 25 mol% cobalt(II); (d) 100 mol% cobalt(II)

interaction also enhances the thermal stability of the copolymer by suppressing the tendency for imide formation.

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