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Metal Ion Effects in Ionic Copolymers

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Abstract

This paper presents a discussion of four areas in which the interaction between organic polymers and metal species is of importance. The first section discusses the effect of metal ions in random ionomers in bulk, where the presence of ions strongly influence the mechanical properties. The next topic covers the influence of metal ions on aqueous solutions of block copolymers, and describes the morphogenic effects seen in such systems. The third section deals with the use of metal ions in non-aqueous solutions of block copolymers leading to the formation of microreactors with a high degree of size control. Finally, the attachment of organometallic species to the corona of block copolymer micelles in non-aqueous solution is discussed in terms of the effect of the metal on the micelle dimensions.

Introduction

The presence of metal atoms or ions in polymers can lead to major changes in both the physical and chemical properties. The physical effects can include drastic changes in the bulk mechanical properties such as the modulus or the viscosity, and changes in solution morphologies of block copolymers, to pick two examples from very different areas. Useful chemical effects include the possibility of designing small microreactors for the formation of protected nanoparticles. Also, the incorporation of organometallic species into block-copolymers results in changes to the physical characteristics of the micelles, such as changes in the coil dimension of the modified block, as well as chemical changes, such as modification of the reactivity of the styrene ring by $Cr(CO)_3$ groups, as has also been observed in classical reactions with this group. These three areas represent only a small sampling of the many ways in which metal complexation can influence the properties of polymers; they form the basis of this presentation.

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Part 1: Metal Ions and Random Ionomers

It has been known for a long time that interactions of metal ions with pendant anionic groups on a polymer chain can affect many properties of random copolymers. For example, the modulus of a poly(styrene-co-sodium methacrylate) copolymer can increase by three orders of magnitude at low (ca. 5-10 mol%) metal carboxylate content, viscosities can increase by orders of magnitude, glass transition temperatures (T_g) can increase by hundreds of degrees, all strictly as a result of the presence of small metal cations. The detailed elucidation of some of these effects has spanned a period of more than thirty years and is worth describing because it involves several unexpected features. This part of the presentation, therefore, will be devoted to a brief presentation of the morphology of random ionomers, especially those based on styrene and sodium methacrylate, and the underlying reason for the effect that this type of metal macromolecule complexing exerts of the mechanical properties of polymers.

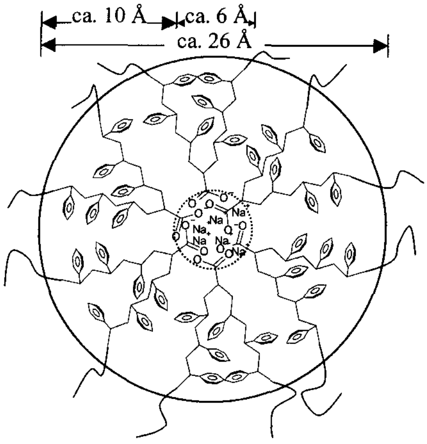

Figure 1: Schematic of a sodium methacrylate multiplet showing the region of restricted mobility of the polystyrene.

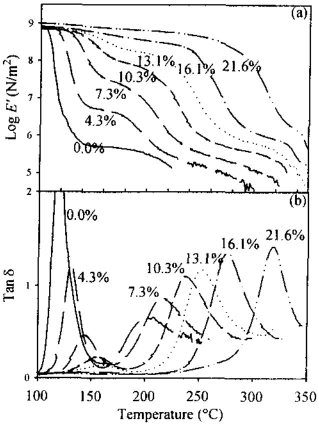

Figure 2: Plots of modulus vs. temperature (a) and loss tangent vs. temperature (b) at different ion contents.

Figure 1 shows a schematic illustration of a multiplet of sodium carboxylate groups in polystyrene. The sodium carboxylate groups are distributed statistically along the backbone, the copolymer having been prepared by free radical copolymerization of styrene and methacrylic acid followed by neutralisation of the methacrylic acid with sodium hydroxide or sodium methoxide. In the absence of highly polar solvents, e.g. in the bulk, the ions will tend to aggregate. However, the aggregation is limited by the fact that each carboxylate group is attached to a polymer chain in its immediate vicinity. Because of the relative sizes of the sodium carboxylate group and the part of that polymer chain to which this group is attached, the total number of such groups which can come together is quite limited. Estimates based on the distance between the aggregates, as obtained from small angle x-ray scattering, suggest that the number of ion pairs is of the order of five.

An isolated multiplet of the type shown in Figure 1 would be expected to act like a thermo-reversible crosslink because the backbone segments in the immediate vicinity of these ionic groups are held by the ion pairs to the multiplet. This hold-down by the ion pair decreases the mobility of the chain in the vicinity of the multiplet. This mobility reduction decreases as a function of distance from the multiplet. Thus, crosslink like behaviour would be expected, and has indeed been observed, as shown in Figure 2. It should noted that the modulus in the "plateau" region between ca. 150 and ca. 250 °C (depending on the ion content) increases with increasing ion content, reflecting an increasing degree of ionic crosslinking with increasing ionic concentration.

The loss tangent curves presented just below the modulus curves in Figure 2 are most interesting. The very high peak seen for polystyrene is a reflection of the glass transition. With increasing ion content, the peak height decreases and the position of the peak moves to higher temperature. This behaviour is generally associated with the low temperature side of the inflection point in the modulus curve. What is of particular interest, however, is that another peak appears at the high temperature end of the plateau region, in the temperature range above about 200 °C; this represents another glass transition. From the areas under the loss tangent curves, it has been suggested that at ca. 5 mol% of ions, the relative volumes of the low glass transition material and of the high glass transition material are comparable; this brings up a very interesting question. How can ca. 5 mol% of an ionic material (sodium methacrylate), with a total volume fraction of the ion pairs (sodium carboxylate) of less than ca. 2 vol%, endow ca. 50 vol% of the polymer with a very much higher glass transition temperature? It should be stressed that the material behaves like a two-phase system, with the volume fraction of the high glass transition component being approximately 50%.

The explanation lies in an understanding of the multiplet nature of the aggregation, and is based on the mobility effect which was alluded to before. The chain segments which are very close to the multiplet move more slowly at any given temperature than the chain segments which are far from the multiplet, because of the rigid attachment of the chain segments to the multiplet. This reduction in mobility decays with increasing distance from the multiplet. A single multiplet, as was pointed out above, behaves as a crosslink. However, we need to ask what happens when the ion concentration increases, and multiplets occur in progressively greater proximity to each other? Regions of restricted mobility begin to overlap. Thus, while a single multiplet, which even with its region of restricted mobility is still smaller than 30 Å; does not have an independent glass transition temperature, when the region of restricted mobility exceeds the range 50 to 100 Å, a new glass transition temperature becomes evident, specifically associated with the region of restricted mobility. Since the band of restricted mobility is of the order of 10 Å around each multiplet, (estimated from the persistence length of the polymer chain), the total volume of material of restricted mobility in the overlapping regions far exceeds the volume fraction of ionic co-monomer alone. The overlapping regions of restricted mobility reach percolation at approximately 5.4 mol% of ionic and material, and because the mobility is so much lower in the regions of restricted mobility than in the unaffected regions, the modulus is very much higher. Thus, the regions of restricted mobility act as a filler, again with a volume fraction very much higher than that of the ionic component. We see, therefore, that metal ion interactions in random ionomers can exert a profound effect on the properties, vastly in excess of their volume fraction in the material.

Part 2: Metal Ions and Diblock Copolymers in Solution

The second example to be discussed involves the effect of metal ions on the morphology of diblock copolymers in solution. It has recently been observed that highly asymmetric, amphiphilic diblock copolymers can aggregate to for assemblies of a range of morphologies including nanosized spheres, rods, and vesicles. Several factors can influence the morphology. These factors can be as subtle as changing the dimension of the polymer coil at constant molecular weight, which can induce a transition from one morphology to another, e.g. spheres to rods. Morphological changes can be accomplished by changing various parameters, including the presence of metal ions, but other factors such as the nature of the solvent, relative block lengths, temperature, and even changes in preparation method can also be employed. Some of the observed trends in the formation of various morphologies will be outlined before the details of the effects of metals ions on the morphologies is presented.

In aqueous solutions of highly asymmetric block copolymers of polystyrene-*b*-poly(acrylic acid), PS-*b*-PAA, in which the insoluble (PS) block comprises at least 80 wt.%, a range of morphologies can be achieved by varying the relative block lengths of the two blocks. The polymers will self assemble to form crew-cut micelle like aggregates. Experimentally the aggregates are formed by dissolving the polymer in *N,N*-dimethyl formamide (DMF), adding water until the polymers begin to self assemble, and then dialysing against distilled water. Thus, the morphologies form under near

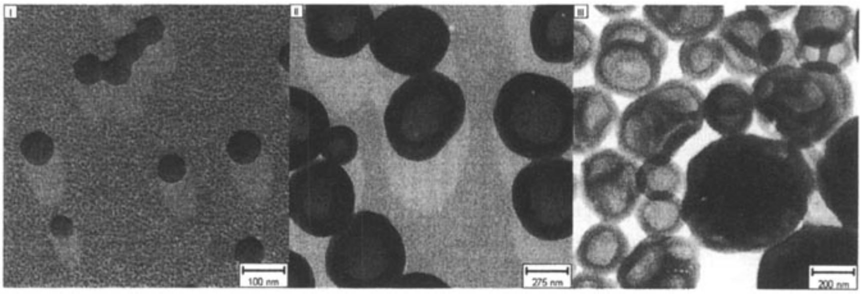

Figure 3: Several different morphologies result from varying the $CaCl_2$ concentration in the solution. I) Spheres at 71 μM, II) Vesicles at 115 μM, and III) LCV's at 130 μM

equilibrium conditions, and are then "frozen in", so that investigation is possible by transmission electron microscopy, TEM. By this technique, spherical, rod-like, bilayer (vesicles and lamellae) and compound micelle morphologies have all been found. The series just mentioned is found as one progressively increases the fraction of the insoluble block in the copolymer.

The effect of metals (introduced as salts or hydroxides) on the morphologies is major. The addition of either $CaCl_2$, or NaOH in micromolar amounts, or NaCl in millimolar amounts produces very different morpologies from those of pure polymer solutions. For example, a 2 wt.% solution PS(410)-*b*-PAA(13) in DMF yields a vesicular morphology without any added NaOH if the previously described method is employed. As the concentration of NaOH is increased, the vesicles are changed to spheres whose diameter decreases with increasing NaOH. The addition of 28 μM NaOH to the DMF solution results in a combination of spheres with an average diameter of 38 nm and some vesicles. The trend continues until the diameter has decreased to 33 nm at 115 μM NaOH.

An even more interesting result is seen upon the addition of $CaCl_2$. This salt results in drastic changes in the observed morphologies of the aggregates. Figure 3 shows a series of TEM micrographs illustrating the effects of added $CaCl_2$ on PS(410)-*b*-PAA(13). The morphology of this polymer from a 1 wt.% solution in DMF is a spherical aggregate with a diameter of 31 nm. A $CaCl_2$ concentration of 71 μM results in an increase of the diameter to 39 μM in diameter. At 85 μM vesicles begin to form. Higher concentrations of 90 and 115 μM results in ever larger vesicles. At 130 μM $CaCl_2$ the vesicles appear to become unstable and a new morphology begins to evolve, which culminates in the final TEM image shown which illustrates the large compound vesicle (LCV) morphology.

A range of different interactions is operative in these different systems. The underlying principle behind the effect of the salt is that it modifies the balance of forces which effect the aggregate during its formation. The balance involves stretching of the core (PS) block, interfacial tension between the core and solvent, and repulsion between the corona chains. In the case of NaOH, a strong base, the corona (PAA) chains are ionised to a greater extent than in neutral solution, therefore there is greater interchain repulsion, and so the aggregate will tend to decrease in size to reduce the extent of interaction within a single aggregate. On the other hand, calcium salts appear to bind to the acrylic acid units of the corona in such a way that the Ca^{2+} ions bridge the corona chains, thereby greatly reducing the interchain repulsion. This decrease of interchain repulsion allows the aggregate to compensate for other forces which now become important. Specifically, the aggregate will now attempt to minimise the total surface by forming larger aggregates, thus reducing the amount of interfacial energy per chain in the aggregate. However, in order for this to happen, the core chains must stretch, which results in an entropic penalty. The balance of these two forces results in the change from spheres to vesicles to LCV's.

Part 3: Reverse Micelles and Microreactors

The same type of block copolymers (PS-*b*-PAA) can be used to form a very different type of system in organic solvents. Once again, highly asymmetric blocks are used; however, in this case the two blocks consist of a long soluble block, styrene, and a short block of the acrylic acid. Both blocks can be dissolved in a 1:10 mixture of methanol and benzene, in which they are present as free chains. The AA block can then be neutralised by adding various metal hydroxides or metal acetates; specifically, $Cs(OH)$, $Ba(OH)_2$, $Cd(Ac)_2$, $Pb(Ac)_2$, $Ni(Ac)_2$, and $Co(Ac)_2$ were used in the study being discussed. During neutralisation the polymers aggregate to form reverse, star-like micelles.

These micelles can have interesting applications. For example, Cd neutralized micelles can be exposed to H_2S to form CdS nanoparticles with a high degree of size control, as shown in Figure 4. Such particles are also very stable, because they are protected by the micelle in which they were formed, and can be isolated from solution and redisolved at a later time with very little change in properties. The size control is due to the thermodynamics of the micelle formation. As the metal acetate or hydroxide is added to the solution, the unimer chains become unstable and the insoluble blocks begin to self assemble. In the early stages of this process, the core chains are held together only weakly, and exchange between the aggregate and the solution is still possible. As more of the acrylic acid is neutralised by metal ions, a point is reached where such exchange is no longer possible, and the morphology is "frozen-in". Thus, aggregates with very uniform aggregation numbers are achieved. This leads to a high degree of size control.

Through a combination of size exclusion chromatography (SEC), TEM, static light scattering (SLS), and dynamic light scattering (DLS) studies, it was possible to determine scaling relationships for the aggregation numbers (Z) and core radii (R_{core}) in terms of the degree of polymerisation (N_B) of the insoluble block. The results were

$$R_{core} = K_{R,ave} N_B^{0.58\pm0.03} \quad (1)$$

$$Z = K_{Z,ave} N_B^{0.74\pm0.08} \quad (2)$$

where $K_{Z,ave}$ and $K_{R,ave}$ depend on the specific metal used.

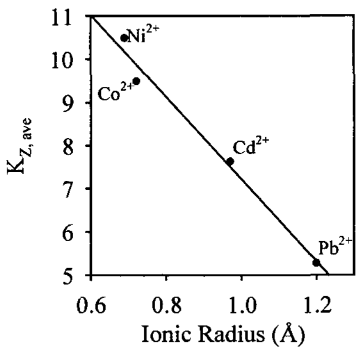

Figure 4: Plot of $K_{Z\ ave}$ relative to the ionic radius of the transition metals which were investigated.

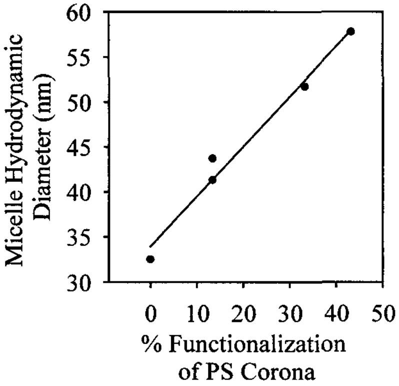

Figure 5: DLS results showing the increase in hydrodynamic radius of the micelles as a function of $Cr(CO)_3$.

As shown in Figure 4, the pre-factor in equation 2 for polymers neutralised with transition metals show an almost linear relationship to the ionic radius of the metal. The effect of the metal species is assumed to be limited to the prefactor ($K_{Z,ave}$ or $K_{R,ave}$) only, and is seen to result in aggregation numbers and core radii which decrease from nickel to lead in the order of $Ni^{2+} > Cs^{+} > Co^{2+} > Ba^{2+} > Cd^{2+} > Pb^{2+}$. This same trend is also followed by the ionic radius of the neutralising metal acetate. Trends of this type are likely to be useful in the preparation of metal and semiconductor particles of controlled sizes. It should be pointed out, however, that other techniques have also been utilised in the production of such nanosized particles.

Part 4: Organometallics and Diblock Copolymers

One final system which has recently been under study in this group[9] is that of η^6-styrene chromium tricarbonyl (η^6-$SCr(CO)_3$) incorporated into reverse micelles. Star micelles with a sodium acrylate core and a polystyrene corona (PS(200)-*b*-PANa(58)) were treated with $Cr(CO)_6$. This results in the functionalization of some styrene groups with $Cr(CO)_3$. These micelles are being used as a prototype for organometallic systems which will hopefully lead to new catalyst supports.

The potential advantages of this type of system are based on the fact that the catalyst centres would be distributed throughout the coronae of a starlike micelle. Thus, the polymer chain, particularly on the outer edge of the corona, would be similar to a free polymer in solution with respect to degree of stretching and steric crowding; at the same time, however, every corona chain is effectively anchored to a coloidal particle, namely the glassy core of the micelle. This would allow reactivities similar to those of the pure homogeneous catalyst while still providing a useful means of recovery by several methods such as centrifugation or cooling the solution below the theta temperature of the corona. In this manner, it may be possible to achieve a catalyst which has almost the same reactivity of the free catalyst with the recoverability of the more common gel supported catalysts. One additional possibility is that of applying a very high loading of catalyst to the corona so that the local concentration of catalyst can be increased to the range of 0.1 M to 1.0 M within the corona while maintaining the total concentration (and cost) to levels of the order of 1 mM, thus allowing the kinetics of new concentration ranges to be investigated.

Preliminary studies have been conducted using the $Cr(CO)_3$ based system to investigate the physical changes seen in the polymer micelles at different loading levels. The micelles are synthesised by first making the reverse micelles from PS-b-PAA by neutralisation from a 1:10 benzene:methanol mixture with NaOH. These micelles can then be reacted with chromium hexacarbonyl ($Cr(CO)_6$), producing a yellow powder. The final product is best characterised by IR or solid state NMR.

It has been found that the process does not work in THF, which allows the $Cr(CO)_3$ fragment to migrate from one phenyl ring to the next all the way into the core. In addition, there is an apparent limit of ca. 45% functionalisation of the monomer units in the corona chain. Attempts at higher functionalisation result in only a slight increase in the level of substitution, and increasing amounts of chromium as a decompostion product of the metal carbonyl.

The effect of organometallic incorporation on the corona was studied by DLS and SLS experiments carried out in dioxane. The result of DLS (Figure 6) show an increase in the hydrodynamic radius of the micelle such that at 45% functionalisation, the micelle size has increased by a factor of approximately two. This is thought to be caused by two effects which may or may not be cooperative, depending on the solvent being used. The first effect is that of the extra steric crowding of the polymer chain due to the large $Cr(CO)_3$ fragment attached to the benzene ring of the styrene. This effect will always lead to an increase in the micelle size. The effect of the organometallic group in general is to enhance the solubility of the polymer in organic solvents, although for some polymer-solvent systems, the trend may be opposite. In this system, the expansion is obviously the dominant effect, although the relative roles of solubility and steric crowding are still unclear.

Conclusion

This paper has presented several systems which involve the association of metals with polymers. The types of association vary from ionic interactions, to ion binding and to covalently bonded organometallic complexes. The systems investigated have also spanned a large range of polymer structures, from random ionomers in bulk to block copolymers in solution. While this is only a small sampling of the systems in which metal ions interact with polymers, it should be evident that the use of metals to modify polymers can result in many profound changes in their properties. These changes can be used to develop new applications for a range of polymer systems.

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