Metal Salts Interaction with Acrylic Acid–Maleic Acid Copolymer: An Infrared Spectroscopic Study

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ABSTRACT: A study was carried out in which aqueous solutions of acrylic acid–maleic acid copolymer (mole ratio of monomers: 3:2) were diluted with solutions of various salts [NaCl, $MgCl_2$, $CaCl_2$, $SrCl_2$, $ZnCl_2$, $Al(NO_3)_3$ and $Fe(NO_3)_3$]. This copolymer was found to interact with all these salts to make solutions of enhanced acidity that infrared spectroscopy suggested was a result of charge stabilization of the polyanion by counterions occupying atmospheric or site-bound locations. The cations of the salts NaCl, $MgCl_2$, $CaCl_2$ and $SrCl_2$ appeared to occupy atmospheric positions only; in contrast, with poly(acrylic acid) they showed some site binding. Zinc ions, on the other hand, gave identical bridging bidentate interactions with both polymers. The cations from the trivalent salts $Al(NO_3)_3$ and $Fe(NO_3)_3$ were atmospheric and site bound (bridging bidentate), respectively, and these were also different from their interactions with poly(acrylic acid). The addition of $Fe(NO_3)_3$ to the copolymer caused gelation, as with poly(acrylic acid), but formation of the gel was slower and did not result in phase separation. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1680–1684, 2000

Key words: polyelectrolyte; copolymer; counterion binding; infrared spectroscopy

INTRODUCTION

The interaction of polyelectrolytes with ionic salts in an aqueous solution is of both theoretical and practical importance and has been studied extensively.[1] In an aqueous solution counterions have been shown to be capable of distributing themselves around an ionized polyelectrolyte molecule in one of three different states. These are (1) free, that is, not associated with any particular polyion; (2) atmospheric, that is, associated with an individual molecule but labile; or (3) site-bound, that is, associated with individual functional groups on the specific molecules.[2] The atmospheric ions occupy the potential well around each polyion, which is the three-dimensional space around each molecule created by its Coulombic charge. Bound ions, by contrast, often develop partial covalency via coordination to the hetero atoms of the functional groups, typically oxygen in carboxylic acid polyelectrolytes.

Ion binding has been studied using a variety of techniques and been shown to be influenced by the size and charge of the counterion, the charge and conformation of the polyanion, and the states of hydration of the species involved.[1] Binding to poly(acrylic acid) has been especially widely studied. For example, many years ago the phenomenon of gelation of this acid by calcium, magnesium, and barium ions was studied by Wall and Drennan,[3] who attributed gelation to ionic crosslinking. A few years later Gregor et al.[4,5] showed by titrimetry that complexation constants with divalent metal ions followed the order

Table I   Metal Salts Used in the Study

Salt	Grade	Supplier
NaCl	AnalaR reagent	BDH, Poole, Dorset, UK
MgCl$_2$	Laboratory reagent	BDH, Poole, Dorset, UK
CaCl$_2 \cdot$ 2H$_2$O	AnalaR reagent	BDH, Poole, Dorset, UK
SrCl$_2 \cdot$ 6H$_2$O	ACS reagent	Aldrich, Dorset, UK
ZnCl$_2$	Specified laboratory reagent	Fisons, Loughborough, UK
Al(NO$_3$)$_3 \cdot$ 9H$_2$O	ACS reagent	Aldrich, Dorset, UK
Fe(NO$_3$)$_3 \cdot$ 9H$_2$O	General-purpose reagent	Hopkin & Williams, Essex, UK

$$Mg < Ca < Co < Zn < Mn < Cu$$
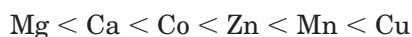
This order has been shown to be the same as the so-called Irving–Williams series,[6] a series based on stability constants for ions with a variety of complexing molecules.[7]

The coordination of ions to other carboxylic acid polyelectrolytes has also been studied. These include poly(maleic acid),[8] poly(itaconic acid),[9] poly(ethylene–maleic acid),[10] poly(methacrylic acid),[11,12] poly(vinyl methyl ether–maleic acid),[10] and poly(α-hydroxy acrylate).[13] The current article reports on a study of an additional copolymer of maleic acid: poly(acrylic acid–maleic acid) [3:2 mole ratio of monomers]. This polymer is of technical importance as a component of commercial dental cements,[6] and its similarities and differences from poly(acrylic acid), which is also used in dental cements,[6] are of interest. The experimental techniques used in the current study were infrared spectroscopy and pH determination. These techniques have been employed previously[14,15] to demonstrate that poly(acrylic acid) increases its ionization in the presence of di- and trivalent salts and that these salts form distinctly site-bound complexes, the detailed stereochemistry of which has been determined. The present study was carried out with the aim of examining how interactions of salts with poly(acrylic acid–maleic acid) compare with those that occur with an acrylic acid homopolymer.

EXPERIMENTAL

The details of the salts employed in this study are given in Table I. Solutions of these salts, each at a concentration of 1.0 mol dm^{-3}, were made in 100-cm^3 grade A volumetric flasks. To prepare samples, 1.0 cm^3 aliquots each of these solutions were added to 1.0 cm^3 aliquots of the copolymer solution, which had been previously diluted to 50% of its original (as supplied) concentration, also using grade A glassware. The copolymer (ESPE, Germany) consists of acrylic and maleic acid monomers in a mole ratio of 3:2 at 43% concentration in water.[16] The initial dilution therefore made a solution that was 21.5% copolymer, and subsequent dilutions created solutions of 10.75% concentration. By comparison, previous studies on poly(acrylic acid) used solutions made by a dilution of a stock solution that was 25% in poly(acrylic acid) to make a concentration of 12.5% for the experimental work. In addition to the salt-containing samples, a control solution, diluted with water alone, was prepared. Deionized water was used throughout.

The pH value for each of the solutions was measured using a digital pH meter (Type PHA, Whatman International, Maidstone, Kent, United Kingdom). This meter read to 0.01 pH units with an estimated uncertainty of 0.02 units.

Specimens for infrared spectroscopy were prepared by applying small amounts of solution by brush to calcium fluoride plates and allowing them to dry for about 20 min, until they had reached a tack-free state. Spectra in the region 1300–2000 cm^{-1} were obtained in transmission using a recording infrared spectrometer (Type 983G, Perkin-Elmer, Beaconsfield, Bucks, United Kingdom), and the precise positions of the bands were determined using the built-in program of the spectrometer.

RESULTS AND DISCUSSION

As can be seen from Table II, the pH measurement for the copolymer solution was 1.48, a value similar to the 1.5 obtained previously for poly-(acrylic acid) at a similar concentration. The results for the salts showed they reduced this value

Table II   Values of pH for Solutions of Copolymer (Concentration: 10.75%) in Presence of Salts

Salt	pH
None	1.48
NaCl	0.68
$MgCl_2$	0.54
$CaCl_2$	0.50
$SrCl_2$	0.53
$ZnCl_2$	0.42
$Al(NO_3)_3$	0.32
$Fe(NO_3)_3$	0.83

by varying amounts, depending on the nature of the cation. All salts were used at identical mole ratios, which means the overall charge varied between the solutions. This was done to allow comparison with previously published work and was considered valid because the prime interest of the present study was to determine qualitatively rather than quantitatively how the interaction of salts varies with the copolymer compared with the homopolymer.

Results for infrared spectroscopy are shown in Table III. Although relatively dry, these coatings are considered useful for indicating the type of interactions that occur in solution because such films are known to retain a proportion of bound water.[17] Examples of spectra for the copolymer only and for one copolymer–salt adduct are shown in Figure 1.

All spectra showed a band at about 1408 cm^{-1}, with a shoulder at approximately 1440 cm^{-1}. This region is characteristic of symmetric carbonyl stretching, but that it was identical in all spectra means it has no value in determining structure. By comparison with previously published spectra, the shoulder at 1440 cm^{-1} can be assigned to acrylic acid carboxylic groups[17] and the band at 1408 cm^{-1} to the maleic acid carboxylic groups.[18]

The spectrum of the salt-free copolymer shows a main band at 1724 cm^{-1}, which is characteristic of free carboxylic acid groups in polyelectrolytes.[19] There is a broad band at 1636 cm^{-1}, which is characteristic of water, together with a very slight shoulder at 1627 cm^{-1}, a position generally characteristic of carboxylate groups.[20] This presumably arises because of the small degree of ionization of some of the acid groups in the presence of water. This band becomes enhanced with NaCl, $MgCl_2$, $CaCl_2$ and $SrCl_2$, a finding consistent with the reduced pH caused by these salts.

That this band is hardly altered in frequency by these salts suggests there is no chelation to the polymer, merely enhancement of ionization. This, in turn, suggests these salts occupy atmospheric rather than site-bound locations.

Previous studies have suggested that a band in the infrared spectrum at 1634 cm^{-1} indicates unidentate bonding,[21] and on this basis such a geometry was assigned to one of the interactions of $MgCl_2$, $CaCl_2$ and $SrCl_2$ with poly(acrylic acid).[14] However, this band was so close to that of water
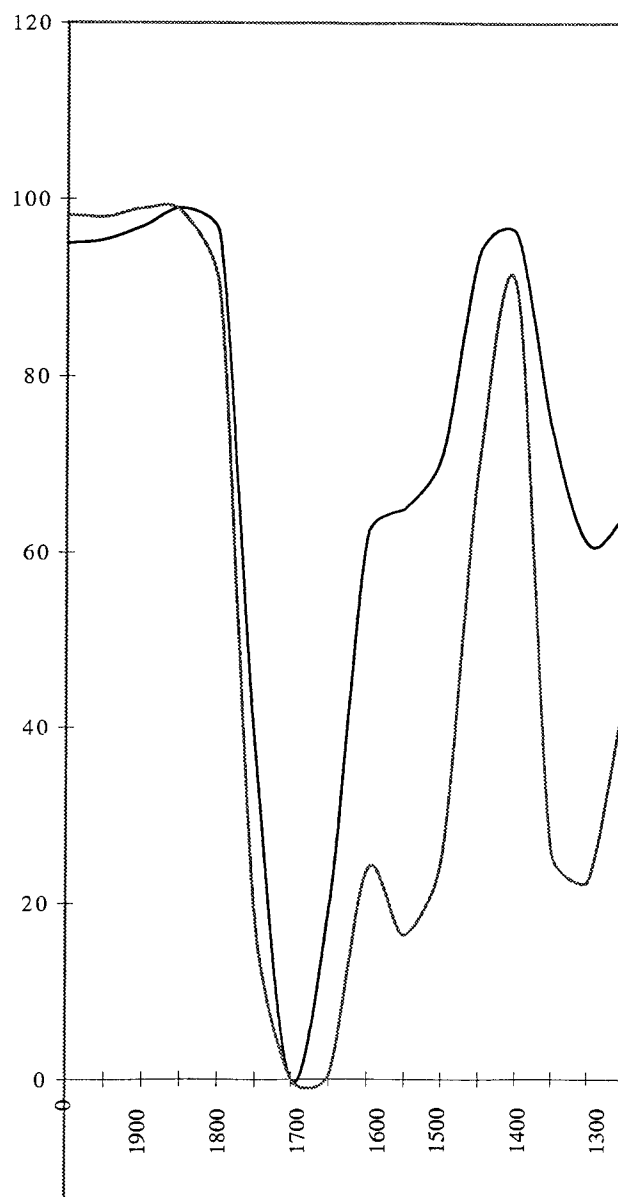

Figure 1   Examples of infrared spectra. Key: Bold = copolymer only; Grey = copolymer plus calcium chloride.

Table III   Infrared Bands in the Spectra of Copolymers with Salts (Numbers in Parentheses Indicate Position of Shoulders on Main Peaks)

Salt	Asymmetric O=C—O⁻ Stretch (cm⁻¹)	Symmetric O=C—O Stretch (cm⁻¹)
None	(1627[a])	1408 (1440)
NaCl	1632 (1640)	1408 (1443)
$MgCl_2$	1629 (1638)	1409 (1440)
$CaCl_2$	1622 (1638)	1408 (1435)
$SrCl_2$	1628 (1638)	1408 (1441)
$ZnCl_2$	1616 (1635)	1407 (1438)
$Al(NO_3)_3$	1629 (1636)	1411
$Fe(NO_3)_3$	1611 (1635)	1419

[a] Shoulder on broad band at 1636 cm⁻¹ assigned to water in specimen.

and to the band that seems to stem from general ionization of the acid groups only, it may have arisen from either of these features in the specimen. This assignment should therefore be reconsidered. By contrast, the second band exhibited by poly(acrylic acid) with NaCl, $MgCl_2$, $CaCl_2$ and $SrCl_2$ can still be safely assigned to site-binding with chelating bidentate geometry. Its absence from the spectra of these salts with the acrylic acid–maleic acid copolymer shows there is no such site binding between the copolymer and these salts. The reason for this difference from the acrylic acid homopolymer is not clear.

The interaction of $ZnCl_2$ with the copolymer was different from the other divalent metal chlorides in that its band at 1616 cm⁻¹ was a clear indication of site binding. This band occurred at a similar position to the band in the spectrum of the $ZnCl_2$–poly(acrylic acid) adduct and has previously been attributed to site binding with bridging bidentate geometry.[14] It also showed a slight shoulder at 1635 cm⁻¹, a band which may be assigned to water within the specimen.

The interactions of the cations of the metal nitrates with the poly(acrylic acid–maleic acid) were also different from those previously observed with an acrylic acid homopolymer. In the spectrum of the $Al(NO_3)_3$–poly(acrylic acid) adduct there was a single band at 1616 cm⁻¹, which, like the $ZnCl_2$–poly(acrylic acid) adduct, was assigned to site binding with bridging bidentate geometry. In the case of the $Al(NO_3)_3$–copolymer system, there was a single band at 1629 cm⁻¹, which suggests atmospheric rather than site-

bound counterions. In this specimen, too, there was a shoulder from 1638 to 1640 cm⁻¹, which may be assigned to water.

For $Fe(NO_3)_3$ the converse is the case.[15] In association with poly(acrylic acid) it shows a band at 1526 cm⁻¹, corresponding to chelate bidentate geometry, and a band at 1632 cm⁻¹, assigned tentatively to unidentate coordination, but possibly arising instead from either atmospheric location or retained water. With the acrylic acid–maleic acid copolymer, $Fe(NO_3)_3$ showed a single band at 1611 cm⁻¹, which is consistent with coordination via a bridging bidentate structure. Gelation of the copolymer with $Fe(NO_3)_3$ was also notably different from gelation of poly(acrylic acid). It was slower, taking 2–3 min for the entire solution to be converted from a relatively mobile liquid to a soft gel. Poly(acrylic acid), on the other hand, underwent a much more rapid reaction and formed two phases,[15] with the precipitated phase a fairly stiff gel. Poly(acrylic acid) with $FeCl_3$ is known for similar behavior.[22]

In addition to differences in the region of the asymmetric carbonyl stretch, all metal salts showed bands in the region below 1400 cm⁻¹. A variety of bands have been reported previously in this region for various monomeric metal carboxylates,[23] and they have been shown to be associated with an array of structures. Consequently, this region cannot be used to make structural assignments,[21] and no conclusions can be drawn from the positions of these bands in the present study.

CONCLUSIONS

This study has shown that poly(acrylic acid–maleic acid) interacts with various salts in aqueous solution to give enhanced ionization, resulting in reduced pH. This is attributed to stabilization of charge-separated forms of the polymer by the cations from the salt, with the ions occupying atmospheric or site-bound locations. These interactions were generally different from those that occur in similar solutions of acrylic acid homopolymer. In general, mono- and divalent ions were found to give a single band in the infrared spectrum, at about 1630 cm⁻¹, which is the same position as the shoulder on the main acid band in the salt-free copolymer. This band is assigned to ionized carboxylic acid groups, and its occurrence in the presence of certain salts suggests that these salts do not coordinate to the carboxylate but occupy

atmospheric positions. Similar bands occurred with these salts in the presence of poly(acrylic acid), though there was an additional band in each case corresponding to a chelating bidentate structure; such bands were absent from all spectra of the acrylic acid–maleic acid copolymer. The behavior of zinc chloride with the copolymer was different from that of the other divalent metal salts, since it showed a band at 1616 cm^{-1}. This indicates site-binding in the form of a bridging bidentate interaction and is similar to that occurring with poly(acrylic acid).

Both Al(NO$_3$)$_3$ and Fe(NO$_3$)$_3$ showed single bands, at 1629 and 1611 cm^{-1}, respectively, suggesting (1) atmospheric location and (2) site binding via bridging bidentate structures. Both of these interactions are different from those observed in poly(acrylic acid). In the case of Fe(NO$_3$)$_3$, there was complete gelation of the copolymer–metal salt solution. However, the formation of the gel was slower than the corresponding reaction with poly(acrylic acid) and did not result in precipitation of the polymer phase.

REFERENCES

1. Mandel, M. In Polyelectrolytes; Hara, M., Ed.; Marcel Dekker: New York, 1993.
2. Oosawa, F. Polyelectrolytes; Marcel Dekker: New York, 1970.
3. Wall, F. T.; Drennan, J. W. J Polym Sci 1951, 7, 83.
4. Gregor, H. P.; Frederick, M. J Polym Sci 1957, 23, 451.
5. Gregor, H. P.; Gold, D. H.; Frederick, M. J Polym Sci 1957, 23, 467.
6. Wilson, A. D.; Nicholson J. W. Acid Base Cements; The University Press: Cambridge, 1993.
7. Irving, H. M. N. N.; Williams, R. J. P. J Chem Soc 1953, 3192.
8. Muto, N.; Komatsu, T.; Nakagawa, T. Bull Chem Soc. Jpn 1973, 46, 2711.
9. Muto, N. Bull Chem Soc. Jpn 1974, 47, 1122.
10. Begala, A. J.; Strauss, U. P. J Phys Chem 1972, 76, 254.
11. Mandel, M.; Leyte, J. C. J Polym Sci, Part A 1964, 2, 3771.
12. Heitz, C.; François, J. Polymer 1999, 40, 3331,.
13. Ogawara, K.; Kawazoe, S.; Tamura, T.; Kawauchi, S.; Satoh, M.; Komiyama, J. Polymer 1998, 39, 437.
14. Nicholson, J. W. J Mater Sci; Mater Med 1998, 9, 273.
15. Nicholson, J. W. J Appl Polym Sci 1999, 70, 2353.
16. Schmitt, W.; Purrmann, R.; Jochum, P.; Gasser, O. European Patent App 1981, 24, 056.
17. Raju, K. S.; Myers, R. R. J Coatings Technol 1981, 53(676), 31.
18. Nicholson, J. W.; Wasson, E. A. Br Polym J 1989, 21, 513.
19. Allan, J. R.; Bonner, J. G.; Gerrard, D. L.; Birnie, J. Thermochimica Acta 1991, 185, 295.
20. Bellamy, L. J. The Infrared Spectra of Complex Molecules; Chapman and Hall: London, 1975.
21. Mesubi, M. A. J Mol Struct 1982, 81, 61.
22. Linden, L.-A.; Rabek, J. F. J Appl Polym Sci 1993, 50, 1331.
23. Deacon, G. B.; Phillips, R. Coord Chem Rev 1980, 33, 227.