

## COMPLEX FORMATION BETWEEN POLY(METHYLMETHACRYLATE) AND SOME TRANSITION METAL IONS

*A. N. Eboatu and S. M. Alhaji*

CHEMISTRY DEPARTMENT, USMANU DANFODIYO UNIVERSITY SOKOTO, NIGERIA

(Received December 4, 1989)

Differential scanning calorimetric and infrared spectroscopic studies revealed that poly(methylmethacrylate) interacts with  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cr}^{3+}$  both in solution and in suspension. The tendency for these metal ions to complex with the polymer follows the sequence  $\text{Fe}^{3+} < \text{Ni}^{2+} < \text{Cr}^{3+}$ . These observations are explained in terms of the radii of the ions and steric factors.

During the past decade, there has been a spate of interest in the phenomenon of polymer-metal ion interactions [1-3]. The reason for this lies undoubtedly in the enormous array of applications of these polymer-metal complexes.

These applications in turn arise from the dramatic changes in polymer properties consequent upon the introduction of strong intra- and inter-molecular coulombic interactions resulting from the presence of ions. The applications include detoxification [4], chemotherapy [5], ion-exchange resins, sheet formation aids in the paper industry, catalysis, soil release and antistatics in textiles, to mention just a few.

Polymer-metal complexes have been studied by techniques and tools as diverse as IR spectroscopy [2], potentiometry [6, 7], viscometry [2],  $^1\text{H}$  and  $^{13}\text{C}$  N.M.R spectroscopy [4] and equilibrium dialysis [8, 9]. Other possibilities include thermogravimetry, magnetic susceptibility measurements, electrical conductivity measurements and differential scanning calorimetry (DSC). The present article reports the results of studies of the interactions between PMMA and three common transition metal ions,  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cr}^{3+}$ .

*John Wiley & Sons, Limited, Chichester  
Akadémiai Kiadó, Budapest*

## Experimental

### *Materials*

PMMA was procured from Aldrich Chemical Company Inc., USA. Its inherent viscosity of 0.56 was determined in chloroform at 20° with an Ubbelohde viscometer. Analar grade iron(III) nitrate, nickel(II) nitrate and chromium(III) nitrate from BDH were used as obtained.

### *Methods*

#### a) Suspension technique

Exactly 0.50 g of polymer was placed in each of 8 conical flasks containing 150 cm<sup>3</sup> of aqueous metal ion solution at different concentrations. The mixtures in the flasks were thoroughly shaken at 38° for 18 h. The slightly swollen polymer mass was filtered, washed with deionized water and dried in a desiccator.

#### b) Solution technique

Standard solutions of the polymer and the metal salts were made in acetic acid. In the case of Cr<sup>3+</sup>, the salt was dissolved in acetone as it is only sparingly soluble in the acid. Equal volumes of the polymer solution were mixed with varying amounts of the metal ion solutions in 8 different flasks. The mixtures were also shaken for 18 h at the same temperature as in the suspension technique. Finally, the polymer-ion complex was recovered by using deionized water as non-solvent.

### *Thermal analysis*

A Mettler TA 3000 differential scanning calorimeter was employed. For each run, about 4.5 mg of sample was encapsulated in an aluminium pan, with an empty pan as reference. Samples were scanned at a rate of 10 deg·min<sup>-1</sup> (21.0 J·sec<sup>-1</sup>) from 80 to 430°. By means of a computer incorporated into the machine, the glass transition temperature ( $T_g$ ), the melting point (*m.p.*) and the overall enthalpic change ( $\Delta H$ ) of the treated and untreated samples were obtained.

### *Infrared studies*

The spectra of the "native" and the inoculated polymer were obtained with a Perkin-Elmer 710B IR spectrophotometer. Mulls of the sample in IR

grade liquid paraffin were scanned. Sodium chloride cells were used. The IR investigation was carried out only on the "solution" product.

## Results and discussion

Because of their low lattice energies, the nitrates of these three transition metals dissolve in the polyester and are expected to change a number of thermomechanical properties such as  $T_g$ ,  $m.p.$  and  $\Delta H$  as well as the IR absorbances of characteristic functional groups. This expectation is borne out by the results in Figs 1-3.

### Thermal studies

#### a) Polymer in suspension

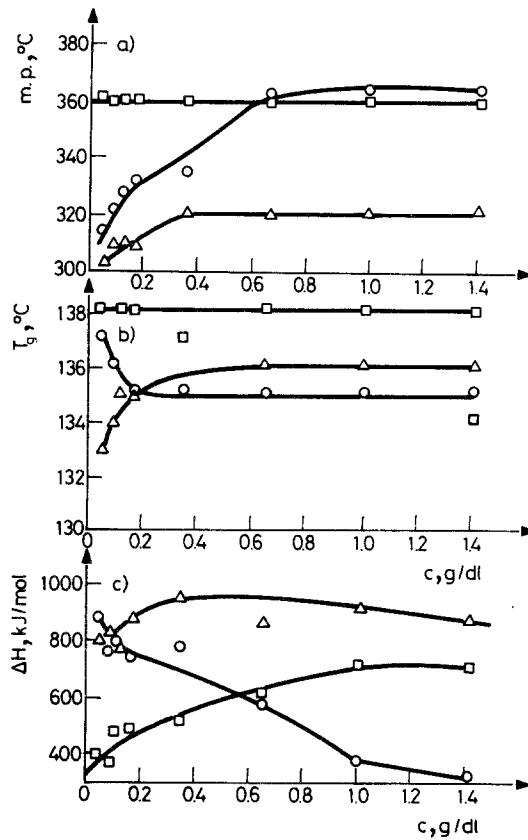
Although PMMA is insoluble in water, it does swell somewhat, thereby enabling polymer-metal ion interaction to occur. As can be seen in Fig. 1a, doping with metal ions reduces the  $m.p.$  of the polymer; this effect is manifested most strongly in the presence of  $Cr^{3+}$  and least strongly with  $Fe^{3+}$ . Variations in the  $Fe^{3+}$  concentration make hardly any difference in the initial  $m.p.$  value. In the cases of  $Ni^{2+}$  and  $Cr^{3+}$ , the  $m.p.$  first drops, but later rises as the ion concentration increases. In all three cases, a limiting  $m.p.$  value is recognizable.

It is clear in Fig. 1b that, at all concentrations, the  $T_g$  of PMMA is little affected by the incorporation of  $Fe^{3+}$ . On the other hand, the  $T_g$ 's for the samples treated with either  $Ni^{2+}$  or  $Cr^{3+}$  are lower than that of the untreated sample. The saturation phenomenon is also evident. In all cases (Fig. 1c), the introduction of metal ions leads to higher  $\Delta H$  values as compared to that of the pure polymer. This effect is most pronounced in the presence of  $Cr^{3+}$ .

#### b) Polymer in solution

It is observed in Fig. 2a that as in the "suspension" studies, the presence of metal ions lowers the  $m.p.$  values. In fact, the extent of the depression is greater here than in the former case. This no doubt implies a more facile interaction between the polymer and the metal ion in solution than in suspension. The trend  $Fe^{3+} < Ni^{2+} < Cr^{3+}$  still persists. The DSC curves of the "solution" products are observed to be split into three overlapping peaks at the  $m.p.$  Accordingly, the  $m.p.$  and  $\Delta H$  values used (Figs 2a and 2b) are averages. Figure 2b shows the variation in  $T_g$  with metal ion concentration.

This Figure indicates some departure from the pattern exhibited by the "suspension" product. However, in all cases, the  $T_g$  of the complex is lower than that of the pure sample.

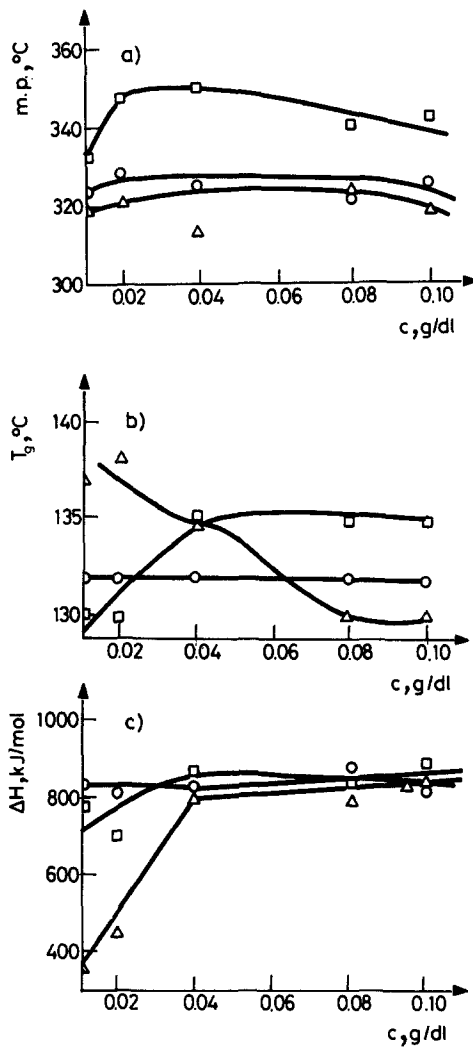


**Fig. 1** Influence of metal ion on some physical properties of PMMA (in suspension); □ - Fe<sup>3+</sup>; Δ - Cr<sup>3+</sup>; ○ - Ni<sup>2+</sup>

It is seen in Fig. 2c that, as in Fig. 1c, the  $\Delta H$  values are elevated vis-à-vis that of the uncomplexed material. As in the "suspension" studies,  $\Delta H$  increases in the presence of Fe<sup>3+</sup> and Cr<sup>3+</sup>. Unlike the former case, however, even that of the Ni<sup>2+</sup> treated sample increases with the ion concentration here. Again, all cases exhibit a saturation effect.

*IR studies*

The results depicted in Fig. 3a indicate clearly that complex formation results in a downward shift of the characteristic IR absorption frequency of the carbonyl group. It is observed that the magnitudes of the shifts are dif-



**Fig. 2** Influence of metal ion on some physical properties of PMMA (in solution); □ - Fe<sup>3+</sup>; Δ - Cr<sup>3+</sup>; ○ - Ni<sup>2+</sup>

ferent for the three metal ions. The trend is  $\text{Fe}^{3+} < \text{Ni}^{2+} < \text{Cr}^{3+}$ , like that in the thermal studies. From this work (Fig. 3b), it is evident that there is hardly any change in the methoxy frequency on the introduction of  $\text{Fe}^{3+}$ . Even in the presence of  $\text{Cr}^{3+}$  and  $\text{Ni}^{2+}$ , not much departure from the frequency for the pure sample is discernible. A similar shift in carbonyl absorption frequency has been reported by Mehbinnie *et al.* [10].

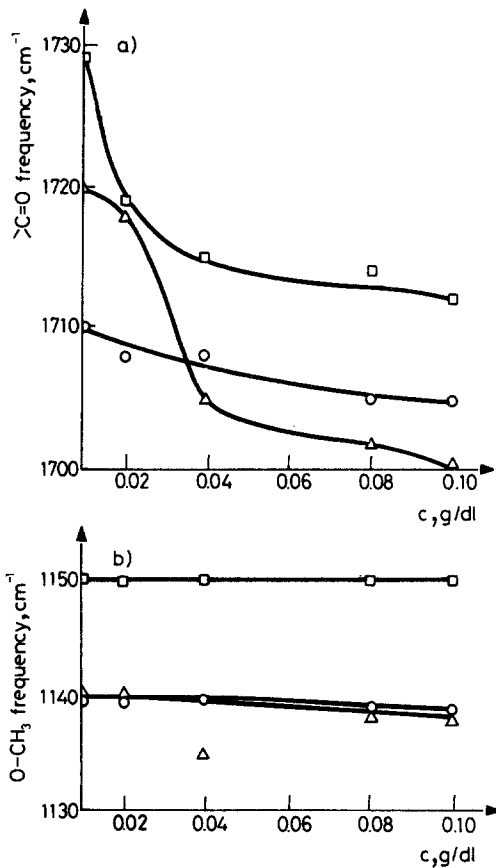
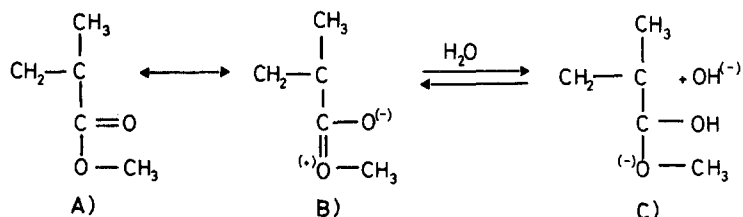


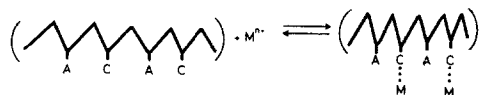
Fig. 3 Influence of metal ions on characteristic IR frequencies  $\square$  -  $\text{Fe}^{3+}$ ;  $\Delta$  -  $\text{Cr}^{3+}$ ;  $\circ$  -  $\text{Ni}^{2+}$

Binding is a mutual interaction phenomenon which depends upon the structures of the components. Though PMMA may undergo both electrostatic and hydrophobic interactions with metal ions, it is envisaged that only

dipole - coulombic interactions are possible. To explain this, we take into account the binding sites of the polymer (Scheme I):



For the formation of anionic units (which would interact with metal ions), the equilibrium  $\text{B} \rightleftharpoons \text{C}$  is a favourable one. However, our preliminary viscometric studies did not reveal the polyelectrolyte behaviour of PMMA. It is therefore reasonable to assume that the main interaction mode between the metal ion and the polymer segments is dipole - electrostatic in nature. If a small segment of the polymer molecule is considered, complex formation with a metal ion,  $\text{M}^{n+}$ , would be represented symbolically by the equilibrium shown in Scheme II:



The simplest formula that can be used to determine the binding of a substrate onto polymers, viz. that of the Klotz method [11], has the following form:  $\frac{1}{r} = \frac{1}{n} + \frac{1}{nkCo}$  where  $r$  is the number of moles of bound ions per base mole of polymer, while  $n$ ,  $k$  and  $Co$  are the number of binding sites, the intrinsic binding constant and the equilibrium concentration of the substrate, respectively. This equation implies that the strength of binding will depend, among other things, upon the metal ion concentration. This is true of the observations carried out in this study.

From calculations, it is known that the crystal field stabilization energies of  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{Ni}^{2+}$  are  $-1.2$ ,  $0.0$  and  $-1.2$ , respectively. In other words,  $\text{Fe}^{3+}$  is the most stable of the three, and hence should exhibit the least tendency to form a complex with a given ligand. This theoretical consideration

is supported by our investigation. We now attempt to explain these observations in some detail.

The fact that the introduction of the metal ion lowers the *m.p.* of the polymer is attributable to the well-known effect of "impurities" on this property of solvents. Here, PMMA is merely acting as a solid solvent. Thus the observations are hardly surprising. As concerns  $T_g$ , it may be worth recalling the reports of Moacanin *et al.* [12] and Hannon *et al.* [13]. These authors maintain that ionic species either raise or lower the  $T_g$  of a polymer, depending upon the size of the ions. In general, the addition of a low molecular weight species is expected to depress  $T_g$ , as a result of the well-explored plasticization effect, which is due, among other things, to an increased free volume. The metal ions under discussion should lower the value of  $T_g$  because of their large ionic radii. This is again supported by the results of our investigation.

The greater effects of the metal ions on these thermomechanical properties in the "solution" than in the "suspension" experiments is a clear manifestation of the stronger interactions in the former than in the latter. The fact that the splitting in the DSC curve is observed only in the "solution" product lends further credence to this. It is felt that the splitting emanates from the separation or differentiation of isomeric "mixtures" due to adduct formation. In a recent article, Kozuka *et al.* [14] demonstrated that the binding of small molecules to polymers causes conformational changes.

As is evident in Figs 1c and 2c, complex formation raises the  $\Delta H$  values, especially at higher ionic concentrations. This observation is in line with those of Ogura and his collaborators. This is difficult to explain. It may perhaps mean that at high ionic concentrations interchain crosslinks begin to be significant. The saturation effect recorded in this study can only mean that for each metal ion, at a specific concentration (the charge on the ion being taken into account), the "active" ligand sites become fully occupied.

In Fig. 3, it is clear that only the C=O absorption frequency is appreciably altered by the introduction of the metal ions, i.e. the metal ions hardly complex with the polymer via the methoxy oxygen atom. From the empirical consideration (Scheme I), it is not surprising why this is so. Further, it is likely that steric factors are also significant here, the ester oxygen being too sterically hindered for easy approach by metal ions.



## Conclusions

The following conclusions are drawn from this work:

- I. The three transition metal ions interact with PMMA in suspension and also when the polymer is in solution.
- II. A more facile interaction is recorded if both the polymer and the ions are in solution.
- III. The ions co-ordinate with the polymer through the carbonyl ligand.
- IV. The ions tend to complex to the polymer in the sequence  $\text{Fe}^{3+} < \text{Ni}^{2+} < \text{Cr}^{3+}$ .
- V. Complex formation is enhanced by increase of the ionic concentration, though a saturation phenomenon is observed in all cases.

## References

- 1 E. Tsuchida and H. Nishide, *Adv. Polym. Sci.* 34 (1977) 125.
- 2 S. L. Davidora and N. A. Plate, *Co-ord. Chem. Rev.*, 16 (1975) 195.
- 3 H. G. Biederman and W. Graf, *Makromol. Chem.*, B 177 (1976) 631.
- 4 E. A. Bekturov, S. E. Kudaibergenov, G. S. Kanapyarova and A. A. Kurmanbaeva, *Polym. Chem.*, 25 (1984) 220.
- 5 N. N. Hughes, *Inorg. Chem. Biol. Processes*, Wiley, N. Y., (1981) 414.
- 6 H. Nishide, N. Oki and E. Tsuchida, *Eur. Polym. J.*, 18 (1982) 799.
- 7 E. G. Kolawole and S. M. Matheison, *J. Polym. Sci., Polym. Phys. Edn.*, 15 (1977) 2291.
- 8 H. Shojishima, *J. Polym. Sci., Polym. Lett. Edn.*, 23 (1985) 245.
- 9 A. N. Gent and W. R. Rodgers, *J. Polym. Sci., Polym. Chem. Edn.* 23 (1985) 829.
- 10 W. R. Mehbinnie and J. D. Miller, *Adv. Inorg. Chem. Radiochem.*, 12 (1969) 135.
- 11 D. Gary, R. Jaycoose and J. Smid, *J. Polym. Sci.*, 20 (1982) 1629.
- 12 J. Morcanin and E. F. Cuddihy, *J. Polym. Sci., Part C14* (1966) 313.
- 13 M. J. Hannon and K. F. Wissburn, *J. Polym. Sci., Polym. Phys.*, 13 (1975) 113.
- 14 H. Kozuka, T. Takagishi and N. Kuroki, *J. Polym. Sci., Polym. Lett. Ed.*, (1984) 363.
- 15 K. Ogura, H. Sobne and S. Nakamura, *J. Polym. Sci., Polym. Phys.*, 11 (1973) 2079.

**Zusammenfassung** — DSC- und IR-Untersuchungen zeigen, daß Polymethylmethacrylat mit  $\text{Fe}^{3+}$ -,  $\text{Ni}^{2+}$ - und  $\text{Cr}^{3+}$ -Ionen sowohl in Lösungen als auch in Suspensionen Wechselwirkungen eingeht. Die Tendenz dieser Metallionen, mit dem Polymer einen Komplex zu bilden steigt in der Reihenfolge  $\text{Fe}^{3+} < \text{Ni}^{2+} < \text{Cr}^{3+}$ . Die Beobachtungen wurden anhand der Ionenradien und sterischer Faktoren erklärt.