Polymer Bulletin 12, 127-132 (1984)

Polymer Bulletin

Analysis

Microcalorimetric Investigation of the Association of Syndiotactic Poly(Methacrylic Acid) with some Divalent Metal Ions

Michel Morcellet

Laboratoire de Chimie Macromoleculaire, Laboratoire associé au C.N.R.S. n°351,
Université des Sciences et Techniques de Lille, 59655 VILLENEUVE D'ASCQ CEDEX, FRANCE

Summary

The interaction of syndiotactic poly(methacrylic acid) (PMA) with a series of divalent metal ions was studied by microcalorimetry. In all cases, the formation of the complex is endothermic with the following order for ΔH: Cu(II) > Zn(II) > Cd(II) > Ni(II) ~ Co(II) > Mn(II) > Ca(II) > Mg(II). This unfavorable enthalpy change is balanced by very large positive entropy changes which account for the high values of the formation constants.

Introduction

The equilibrium process in which a metal ion interacts with a polyelectrolyte has been widely studied by numerous methods (MORAWETZ, 1965). Among polycarboxylic acids, the most extensively investigated have been poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMA) as linear or cross-linked polymers (GREGOR et al., 1955a, 1955b, LOEBL et al., 1955, MANDEL and LEYTE, 1964, DAVID et al., 1968, ANSPACH and MARINSKY, 1975, MARINSKY and ANSPACH, 1975, MARINSKY, 1982). Maleic acid-ethylene, propylene and isobutene alternating copolymers were also studied (FELBER et al., 1968, 1971, CRESCENZI et al., 1974).

In most cases, measurements of free energy changes ΔG gave large values indicating very stable complexes, especially when compared with complexes of simple dicarboxylic acids (McAULEY et al., 1967). Nevertheless free energy measurements alone do not allow to conclude to the nature of the polycarboxylic acid -metal interaction and to distinguish between simple electrostatic interaction and site binding (FELBER and PURDIE, 1971).

Measurements of the enthalpy change ΔH which reflects the changes in the number and strength of bonds formed or/and broken during the process are then necessary (DEGISCHER and NANCOLLAS, 1970).

In early works (LOEBL et al., 1955) ΔH was deduced from the temperature dependence of the formation constant, but this method has revealed very restricting. In more recent works, direct calorimetric measurements of ΔH together with precise measurements of ΔG have allowed the calculation of the entropy change ΔS and a detailed explanation of the experimental results.

We report in this paper some data on the heat of interaction of syndiotactic poly(methacrylic acid) with divalent transition metal ions.

Experimental:

-Poly(methacrylic acid)(PMA):Syndiotactic PMA($\overline{M}_w$=75000) was prepared by free radical polymerization in water, initiated by $K_2S_2O_8$ at pH 10 and 50°C,according to the method of BOVEY (1963).PMA was converted in its sodium salt by neutralization with sodium hydroxyde,followed by a dialysis against water.The concentration was adjusted to about 0.01 eq. COOH per liter for calorimetric measurements.

-Salts:Copper,Nickel and Cobalt perchlorates(Fluka),Zinc and Manganese sufates,Calcium chloride,Cadmium and Magnesium nitrates(Merck)were used as metal ion sources.Solutions were prepared by accurately weighting and diluting.
In some cases,the exact concentration was checked by titration (for example iodometric titration for copper or complexometric titrations with EDTA for Zn,Cd,Ca,Mg).Good agreement was always found between the two values.

-Methods:The microcalorimetric measurements were performed at 27°C with a Tian-Calvet differential microcalorimeter (Setaram,France).The cells were divided into two parts so that mixing of the two solutions could be completly achieved by two or three rotations of the microcalorimeter,once the thermal equilibrium was reached.
In all experiments equal volumes of the two solutions were used(1:1 dilutions).
As the recorded heat effect also includes the dilution heat of the polymer solution and the dilution heat of the salt solution,separate measurements were carried out for correction of the sample dilution effect.
Some experiments were carried out by varying the ratio R (concentration of carboxylate groups/concentration of the metal ion).In most cases the metal ion was in excess compared to the ligand.
The microcalorimeter was calibrated by Joule effect and tested by measuring the heat of dilution of sodium chloride solutions (FORTIER et al.,1973) or the heat of formation of water(ΔH= 55.815 kJ/mole;OLOFSSON and HEPLER,1975).

Results and discussion:

The stability constants B_2 for the PMA:M^{2+} systems were previously determined by MANDEL and LEYTE(1964).The treatment of their experimental data to obtain the formation curves(according to BJERRUM,1941 and GREGOR et al.,1955a) show that in a wide pH range,a MA_2 complex is formed,corresponding to the following reactions:

$$2(R\text{-}COO^-,H^+) + M^{2+} \longrightarrow (R\text{-}COO)_2M + 2H^+ \qquad (1)$$

$$2\,AH + M^{2+} \longrightarrow MA_2 + 2H^+ \qquad B_2$$

and to the formation of an eight-membered chelate ring. No distinct step is observed for the intermediate formation of a MA^+ complex.
For our calorimetric data, the equilibrium to be considered is:

$$2\,A^- + M^{2+} \rightleftharpoons MA_2 \qquad K_2 \qquad (2)$$

The relation between K_2 and B_2 is $B_2 = K_2 . k_a^2$ where k_a is the apparent dissociation constant of the polyacid (GREGOR et al., 1955a). Thus, provided that the k_a value is known, K_2 may be calculated (see Table I) (k_a=2.5 10^{-7} for syndiotactic PMA).
For all the divalent ions under study, K_2 is very large, indicating that the formation of the MA_2 complex is nearly complete. (The K_2 value for the parent Cu-glutaric acid system is only $\sim 2\ 10^3$ as estimated from B_2 values of MARTELL and CALVIN, 1958). Thus, in the experimental conditions used, we can consider that our heat data refer to the complete formation of a MA_2 complex.

TABLE I
Stability constants for the PMA:M^{2+} complexes

	log B_{av} [a)]	B_2	K_2 [b)]
Cu	-1.8	2.5 10^{-4}	4.0 10^9
Cd	-2.2	4.0 10^{-5}	6.3 10^8
Zn	-2.6	6.3 10^{-6}	1.0 10^8
Ni	-2.8	2.5 10^{-6}	4.0 10^7
Co	-2.85	2.0 10^{-6}	3.2 10^7
Mg	-3.1	6.3 10^{-7}	1.0 10^7

a) Data of MANDEL and LEYTE (1964)
b) Calculated from B_2 values using k_a=2.5 10^{-7}

Table II gives the values of ΔG (calculated from $\Delta G = -RT \mathrm{Log}\, K_2$) the experimental values of ΔH, the heat of formation of one mole of complex MA_2, and the calculated entropy change ΔS. Each ΔH value is the average of many measurements made at various R values, ranging from 0.05 to 20. The ΔH value was found nearly insensitive to the R value, within experimental errors, in agreement with the high stability of the MA_2 complexes.

TABLE II

Thermodynamic data for the PMA:M^{2+} complexes

	-ΔG kcal/mole	ΔH kcal/mole	ΔS e.u.
Cu	13.2	5.1± 0.3	60.9±3.6
Zn	11.0	3.5± 0.15	44.9±1.9
Cd	12.1	2.6± 0.2	48.9±3.8
Ni	10.4	1.1± 0.1	38.6±3.5
Co	10.3	1.1± 0.1	37.9±3.5
Mn	-	0.5± 0.05	-
Ca	-	0.5± 0.03	-
Mg	9.6	0.14± 0.01	32.5±2.3

Examination of Table II shows that the heats of formation of the metal-dicarboxylate complexes are predominantly endothermic.In spite of this unfavourable enthalpy change,all the complexes are stabilized by a large and positive entropy change. This reflects the liberation of coordinated water molecules from the ions interacting to form the complexes.
The heat of formation of the complexes decreases in the following order:Cu>Zn>Cd>Ni≂Co>Mn>Ca>Mg.Except for Mn this order is the same as that found for ethylene-maleic acid (EMA) copolymers:Cu>Zn>Mn>Co=Ni (FELBER and PURDIE,1971).ΔH values for the copper complexes are also similar(5.1 and 3.6 kcal/mole respectively) and close to the values reported by CRESCENZI et al. (1974)for maleic acid-ethylene,propylene and isobutene alternating copolymers(4.4,4.0 and 4.0 kcal/mole respectively)
For the poly(acrylic acid):Cu system,a much smaller value ΔH= 1.6 kcal/mole was reported(LOEBL et al.,1955).Since it was obtained from a temperature dependence of the formation constant it is subject to the limitation that the van't Hoff relation is linear over the entire range of temperature.

As said above,the entropy changes are large and especially much larger than those reported for simple dicarboxylic acid-metal complexes:ΔS=20-35 e.u.(McAULEY et al.,1967).This could reflect a long range perturbation of the solvation layer of the polymer upon complexation.

It is interesting to examine the order in which ΔH decreases for metal complexes of different size.For oxalate complexes (five membered chelate ring)the order is Mn>Ni>Co>Cu;for malonate complexes(six membered ring):Mn>Zn>Cu=Co>Ni;for succinate

complexes(seven membered ring):Cu=Zn>Co=Mn>Ni(McAULEY et al., 1967).For EMA and PMA complexes(see above) the larger values are also for Cu and Zn complexes(seven and eight membered ring respectively).Thus,the formation of the Cu complex becomes progressively the more endothermic as the chelate size increases,resulting from an increase of the absolute value of ΔH (from -0.05 to +5.1 kcal/mole).
According to McAULEY et al.(1967) the formation of the copper complexes is accompanied by a tetragonal distortion of the octahedral symetry with a shortening of the bonds in the x y plane and a lengthening of the bonds in the z direction.
The resulting closer contact of the metal ion with the carboxylate groups has two effects:i)the change of the coordination number from six to four gives a more positive entropy of formation ii)an increased endothermicity is also expected due to the breaking of metal-water bonds.Our results for Cu(and perhaps also for Zn and Cd) are in agreement with this interpretation.
The variation of ΔH with the size of the chelate ring probably reflects the increased strain introduced in the ligand upon coordination.From that point of view,the study of the isotactic PMA-metal systems would probably lead to different results. It has been shown by O'NEILL et al.(1965) that the binding constant K_B(and therefore the free enthalpy ΔG)of Cu to PMA is three times greater for the isotactic than for the syndiotactic sample(this support the hypothesis that two neighbouring side chains are involved in the formation of the complex).

Influence of added salt:

Some measurements were also made in the presence of added salt (0.1M $NaClO_4$).
For Cu,ΔH was +4.8± 0.4 kcal/mole.As the formation constant B_2 is also quite insensitive to the presence of added salt(MANDEL and LEYTE,1964) it is concluded that the thermodynamics of the PMA:Cu complex is unchanged.

Appendix 1:

The use of the sodium salt of PMA may be questionned and it could be considered better to use a tetraalkylammonium salt of PMA in which ionic interactions are weaker.Thus additional measurements in which the sodium salt of PMA was mixed with a large excess of tetraethylammonium chloride were carried out. The enthalpy of the reaction:

$$\mathrm{PMA,Na} \; + \; (\mathrm{Et})_4\mathrm{N}^+,\mathrm{Cl}^- \longrightarrow \mathrm{PMA},(\mathrm{Et})_4\mathrm{N} \; + \; \mathrm{Na}^+ + \mathrm{Cl}^-$$

is ΔH=0.12 kcal/mole.This reaction is endothermic as expected for this kind of process.
The values of ΔH for the reaction:

$$\mathrm{PMA},(\mathrm{Et})_4\mathrm{N} \; + \; \mathrm{M}^{2+} \longrightarrow \mathrm{PMA,M} \; + \; (\mathrm{Et})_4\mathrm{N}^+$$

are then only slightly lower than those reported in Table II. ΔS values are not significantly changed(for example,ΔH=4.9

kcal/mole and $\Delta S=60.3$ e.u. for the copper complex).

Appendix 2:

The following values were found for the heats of dilution of PMA and of the metal salts. These values correspond to 1:1 dilutions.

PMA: $\Delta H_d = -7$ cal/mole (literature data of CRESCENZI et al., 1972: $\Delta H_d = -10$ cal/mole)

Salts: initial concentration: 0.2M

$Cu(ClO_4)_2$: -50.7 cal/mole
$Co(ClO_4)_2$: -56.9 cal/mole
$MnSO_4$: -170.3 cal/mole
$Mg(NO_3)_2$: -81.3 cal/mole
$(Et)_4NCl$: +60 cal/mole
$Ni(ClO_4)_2$: -56.2 cal/mole
$ZnSO_4$: -114.1 cal/mole
$Cd(NO_3)_2$: -90.7 cal/mole
$CaCl_2$: -95.7 cal/mole

References:

ANSPACH,W.M. and MARINSKY,J.A.,J.Phys.Chem. 79,433(1975)
BOVEY,F.A.,J.Polym.Sci.A1,843(1963)
CRESCENZI,V.,DELBEN,F.,PAOLETTI,S. and SKERJANC,J.,J.Phys. Chem. 78,607(1974)
CRESCENZI,V.,QUADRIFOGLIO,F.and DELBEN,F.,J.Polym.Sci. A2 10, 357(1972)
DAVID,C.,DE PAUW,A. and GEUSKENS,G.,J.Polym.Sci.C22,319(1968)
DEGISCHER,G. and NANCOLLAS,G.H.,J.Chem.Soc.A,1125(1970)
FELBER,B.J. and PURDIE,N.,J.Phys.Chem.,75,1136(1971)
FELBER,B.J.,HODNETT,E.M. and PURDIE,N.,J.Phys.Chem.,72,2496 (1968)
FORTIER,J.L.,LEDUC,P.A.,PICKER,P. and DESNOYERS,J.E.,J.Solution Chem.,2,467(1973)
GREGOR,H.P.,LUTTINGER,L.B. and LOEBL,E.M.,J.Phys.Chem.,59,34 (1955a)
GREGOR,H.P.,LUTTINGER,L.B. and LOEBL,E.M.,J.Phys.Chem.,59,366 (1955b)
LOEBL,E.M.,LUTTINGER,L.B. and GREGOR ,H.P.,J.Phys.Chem.,59, 559(1955)
McAULEY,A.,NANCOLLAS,G.H. and TORRANCE,K.,Inorg.Chem.,6,136 (1967)
MANDEL,M. and LEYTE,J.C.,J.Polym.Sci.A 2,2883(1964)
MARINSKY,J.A. and ANSPACH,W.M.,J.Phys.Chem.79,439(1975)
MARINSKY,J.A.,J.Phys.Chem.,86,3318(1982)
MARTELL,A.E. and CALVIN,M."Die Chemie der Metalchelateverbindungen"Verlag Chemie,Weinheim(1958)
MORAWETZ,H.,High Polymers 21,369(1965)
OLOFSSON,G. and HEPLER L.G.,J.Solution Chem.,4,127(1975)
O'NEILL,J.J.,LOEBL,E.M.,KANDANIAN,A.Y. and MORAWETZ,H.,J.Polym. Sci. A3,4201(1965)

Accepted July 3, 1984