Adsorbed metal ions as stabilizers for the thermal degradation of polyacrylamide

Hugh D. Burrows, Henry A. Ellis and Stanley I. Utah
Chemistry Department, University of Ife, Ile–Ife, Nigeria
(*Received* 25 *February* 1981)

The thermal degradation of polyacrylamide has been studied in the presence of various metal ions using thermogravimetry. The thermal decomposition of the polymer in general occurs at higher temperatures in the presence of metal ions than with the pure polymer. Empirical measures of the stabilizing effect of the metal ions have been made by determining the temperatures of 12% and 50% decomposition, and the integral procedural decomposition temperature (IPDT). For main group metal ions, the stabilizing effect, as measured by the difference in ipdt between polymer–metal complex and copolymer, was inversely proportional to the radius of the metal ion, suggesting that the strength of the complex between the ion and polymer is important in determining stability. Transition metal ions, in contrast, showed no simple dependence of stabilizing effect on ionic radius, but showed, instead, a dependence upon the ligand field stabilization energy.

INTRODUCTION

Metal ions show considerable potential as stabilizers against thermal degradation[1–9]. Research in this area has fallen into two distinct lines. Much of the early work involved introduction of various metal additives[1–4]. For example, polymers such as PVC have been stabilized against dehydrochlorination by salts, usually of divalent metal ions[2–4]. The most successful of such stabilizers involve long chain alkylcarboxylates of cadmium(II), barium(II), and zinc(II)[3,4]. Though the mechanism of stabilization is not clear, it seems likely that the metal ion prevents loss of hydrogen chloride by functioning as a Lewis acid. In certain cases, formation of esters between the carboxylate grouping and polymer has been reported[3]. With other polymers, metal carboxylates are frequently introduced during processing, e.g. as mold release agents[2], and may adversely affect the thermal properties of the polymer. Thus, small amounts of zinc stearate may function as oxidation catalysts in the thermal degradation of certain polycarbonate polymers[10]. Other additives which have been used include metals themselves. For example, polymer–copper composites have been shown to be thermally more stable than pure polymer in the case of poly(methyl methacrylate)[9].

An alternative approach to the introduction of metals as stabilizers in polymer systems has involved the preparation of coordination polymers. Such coordination polymers can either be formed by treating an organic polymer containing a recurrent chelate group with suitable metal salts to form the metal derivative[5], or by reacting a polydentate ligand, such as bis(8-hydroxy-5-quinolyl)methane,[7] or bis-α-thiopicolinamide,[6] with metal ions, and polymerizing through metal ion coordination. In both cases it is possible to prepare polymers possessing high thermal stability. In addition, iron containing polyferrocenyl polymers are also found to possess high thermal stability[1]. However, the synthesis of this type of polymer is frequently complicated, making it expensive to prepare.

We have been interested in combining the advantages of polymers stabilized by coordinated metal ions with the simplicity of preparation of conventional polymers stabilized by introduction of metal additives. Polymers containing amide groups are known to adsorb metal ions strongly[11–13], with the metal ions probably coordinating with the amide group. It is interesting to see whether such adsorbed metal ions can stabilize the polymers against thermal degradation. We report a study of the effect of various adsorbed metal ions on the thermal degradation of polyacrylamide.

EXPERIMENTAL

Materials

All reagents were of the highest bgrade commercially available. Water soluble polyacrylamide was prepared from the monomer by reaction with potassium persulphate and isopropanol in aqueous solution under a nitrogen atmosphere[14]. The polymer was precipated by addition of further isopropanol, washed with the same solvent, and dried in a vacuum oven for two days at 50°C. The weight average molecular weight of the polymer was determined by viscometry in 1 mol dm^{-3} sodium nitrate solution at 30°C[15], and had a value 7.1×10^4, in reasonable agreement with literature values for polyacrylamide synthesized via this route[14].

The metal salts used in the present study were the nitrates of barium(II), cobalt(II), copper(II), iron(II), manganese(II), mercury(I), nickel(II), strontium(II), thallium(I), thorium (IV) and zinc(II), and the chloride of tin(II). As expected from absorption isotherms, the amount of metal ion adsorbed by the polymer increased initially on increasing metal ion concentration, but became constant at higher metal ion concentrations[16]. Polymer–metal ion complexes were prepared by mixing

0032–3861/81/121740–05$02.00

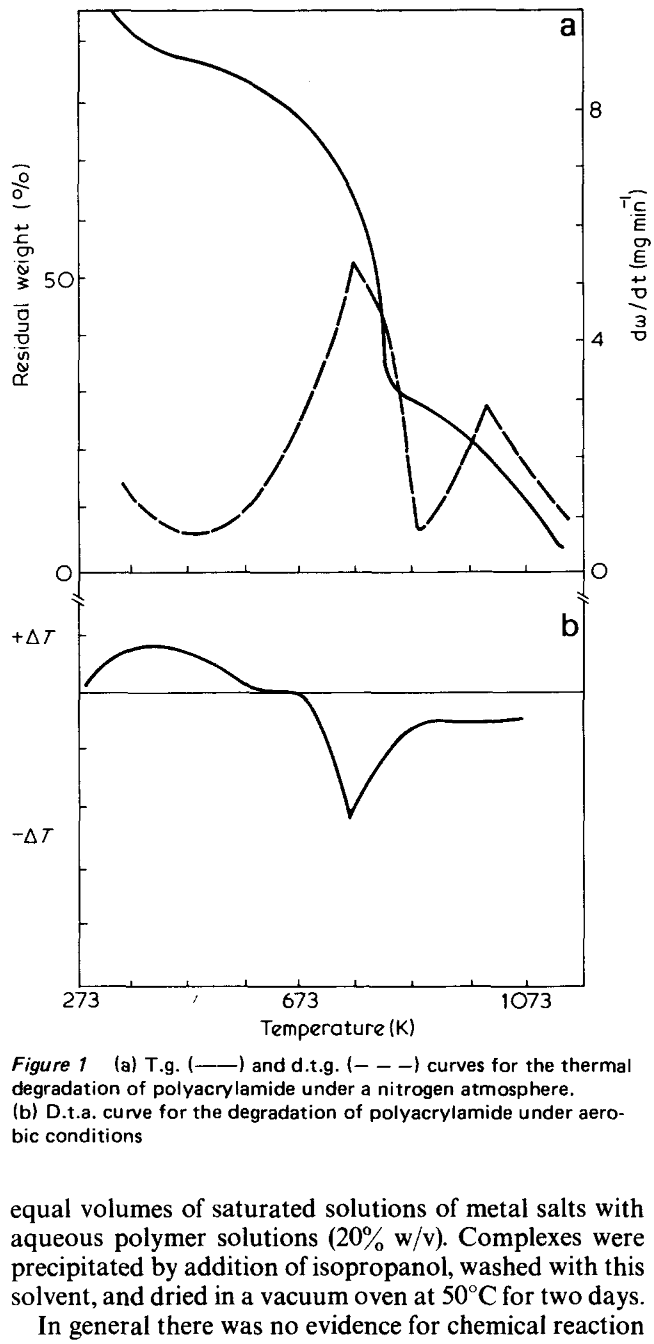


Figure 1 (a) T.g. (——) and d.t.g. (– – –) curves for the thermal degradation of polyacrylamide under a nitrogen atmosphere.
(b) D.t.a. curve for the degradation of polyacrylamide under aerobic conditions

equal volumes of saturated solutions of metal salts with aqueous polymer solutions (20% w/v). Complexes were precipitated by addition of isopropanol, washed with this solvent, and dried in a vacuum oven at 50°C for two days.

In general there was no evidence for chemical reaction between polymerand metal ions. However, on addition of mercury(I) nitrate, the polymer solution became more viscous, and developed a greyish colour, possibly as a result of partial disproportionation of the metal ion.[17] With the other polymer–metal ion mixtures, clear evidence for adsorption or metal ions came from the residual weights on thermal degradation of the polymer,[16] and the fact that the polymers were coloured when coloured metal ions had been used. In addition, with zinc(II) and manganese(II), the amount of metal ion adsorbed under these conditions (13.3% and 3.6% respectively) was determined by EDTA titration using Eriochrome Black T as indicator.

Apparatus and Methods

Dynamic thermogravimetry (t.g.)[18] was performed on a Stanton Redcroft TG 750 apparatus on 35–45 mg samples over a temperature range of ambient to 1173 K (900°C). Samples were heated at a rate of 20° min^{-1} under an atmosphere of dry nitrogen. Derivative thermogravimetric curves (d.t.g.) were obtained by manual differentiation. Three empirical parameters were used for estimating the thermal stability of the polymer systems. The 12% and 50% decomposition temperatures were measured directly from the t.g. curves[19]. In addition, the integral procedural decomposition temperatures (ipdt) over the range from room temperature to 1175 K were determined, as described by Doyls[20]. Semiquantitative data from d.r.g. curves yielded similar measures of stabilizing ability.

In a few cases, polymer degradation was also studied by differential thermal analysis (d.t.a.) using a Digital Negler L70/120 instrument with aluminium oxide being used as reference. Samples were heated between room temperature and 1225 K at a heating rate of 10°C per minute. However, with this system it was not possible to study the degradation under an inert atmosphere. The results of these studies are included for comparison.

RESULTS

Thermal degradation of polyacrylamide

Thermogravimetry (t.g.) revealed a curve possessing at least two distinct stages. The d.t.g. curve showed maxima at 765 K and 1005 K (*Figure 1a*). Complete chemical analysis of the degradation products proved difficult. However, qualitative tests showed that on heating the polymer to 525 K, ammonia was liberated, and the polymer changed from colourless to yellow. Analysis of the t.g. curve showed a weight loss corresponding to loss of one ammonia molecule per two amide groups. When the degradation was studied by d.t.a. in the presence of air, an initial exothermic step was observed over a similar temperature range to the initial loss of ammonia. This was followed by one or more endothermic steps (*Figure 1b*). The initial exothermic step suggests cyclization, whilst the subsequent endothermic peaks are consistent with breakdown of the polymer backbone.

Thermal degradation of polyacrylamide in the presence of adsorbed metal ions

Studies by t.g. and d.t.g. on the degradation of the polymer in the presence of adsorbed metal ions showed broad similarities to the behaviour of pure polyacrylamide. However, with the exceptions of mercury(I) and thallium(I), the decomposition of the polymer in the presence of adsorbed ions occurs at higher temperatures than with the pure polymer. In addition, the initial slopes of the t.g. curves were shallower in the majority of cases, indicating reduced rates of breakdown compared with the pure polymer. Typical t.g. curves are shown in *Figure 2.* In the d.t.g. curves, the peak observed at 765 K with the polymer was seen to be absent in the case of the polymer with iron(II), nickel(II), or cobalt(II), and was shifted to higher temperatures in the presence of copper(II), manganese(II), zinc(II), and tin(II). With thallium(I) and mercury(II), however, this peak was virtually identical to that in the pure polymer. With the nickel(II), cobalt(II), zinc(II) and mercury(I) polymer systems, new peaks were observed in the d.t.g. curves at temperatures below 765 K, suggesting the involvement of some new thermal degradation step.

As with the pure polymer, complete product identification for the decomposition of the polymer–metal ion complexes proved difficult. However, qualitative tests indicated that on heating to 525 K in the presence of nitrogen, ammonia was liberated, and the polymer system became coloured, or more coloured. As with the pure polymer, d.t.a. studies on the degradation of polymer in the presence of copper(II), zinc(II) or manganese(II) under aerobic conditions indicated an initial exothermic stage, followed, at temperatures above 650 K, by an exothermic change.

To obtain information on the effects of adsorbed metal ions on the polyacrylamide degradation, various empirical parameters have been measured, including the temperatures of 12% and 50% decomposition, and the ipdt. These, together with the final percentage weight of the residue following heating to 1175 K, are presented in *Table 1*.

DISCUSSION

From thermal analysis studies, the complete thermal degradation of polyacrylamide occurs in at least two stages. At temperatures up to 525 K, ammonia is liberated, and t.g. studies suggest one molecule is evolved for every two amide groups. The results strongly suggest imide formation, similar to that observed on either intermolecular[21], or intramolecular[22] deamination in the pyrolysis of other amides. In support of this, the DTA results, although carried out under aerobic conditions, indicate an exothermic peak in the same temperature range, typical of cyclization reactions[23] such as the imide formation.

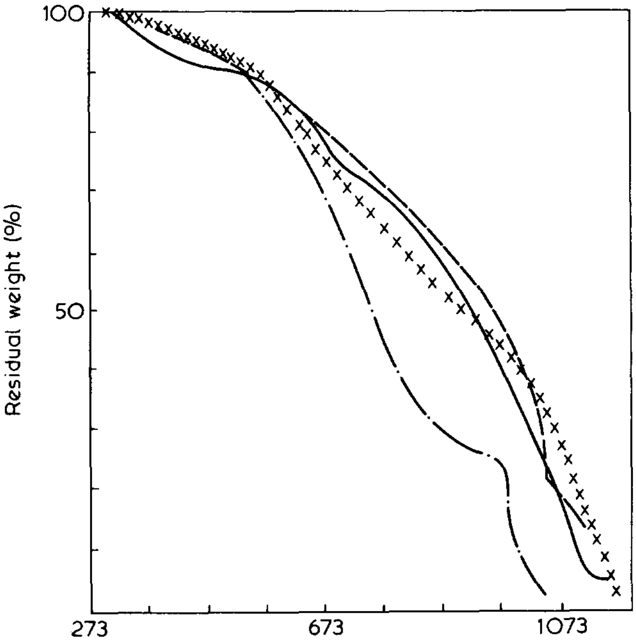
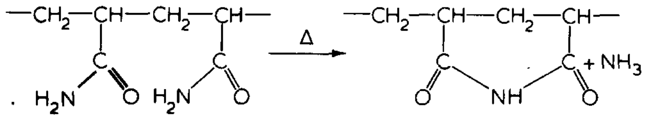


Figure 2 T.g. curves for the thermal degradation under nitrogen of polyacrylamide in the presence of: manganese (II) (——); tin (II) (— — —); zinc (II) (xxx); thallium (I) (— · — · —)



In their attempts to polymerize acrylamide thermally, Staudinger and Urech[24] saw similar amide loss, and formation of an insoluble product, which was suggested to be a crosslinked imide. It was subsequently suggested[25] that pyrolysis of polyacrylamide yields imides involving both crosslinking, and deamination of amide groups on the same chain.

In this study, twelve metal ions were found to be readily adsorbed without chemically modifying polyacrylamide. In the case of mercury(I) however, there may have been some disproportionation of the metal ion. These results are in agreement with the known tendency of polyacrylamide[11,12], and polyamides[13] to adsorb metal ions strongly. The metal ion is probably bound fairly weakly to the oxygen of the amide group[26]. Whilst metal–amide complexes are not normally observed in aqueous solutions[27], they can be prepared in non-aqueous solvents[26]. As with the case of the pure polymer, initial thermal degradation of the polymer–metal ion systems also involves deamination, presumably via imide formation. However, with all of the metal ions studied, ammonia loss is inhibited. This shows up most clearly in the temperatures for 12% weight loss (corresponding roughly to loss of a single ammonia for every two amide groups). The temperatures for this are all higher in the presence of adsorbed metal ions than with pure polymer.

Assignment of the subsequent degradation steps is more difficult. It is likely that breaking of the polymer backbone is occurring, and analogy with the thermal degradation of simple amides and imides[21] suggests that formation of nitriles and acids may be involved. It should be noted that the high temperature degradation is

Table 1 Thermal analysis data for degradation of polyacrylamide–metal ion systems

Metal ion	Temperature of 12% decomposition (K)	Temperature of 50% decomposition (K)	ipdt	Final percentage weight of residue	Ionic radius (A)*
None	430	780	686	3	–
Ba(II)	531	825	750	8	1.34
Co(II)	510	808	711	20	0.72
Cu(II)	578	879	749	3	0.72
Fe(II)	510	931	731	22	0.74
Hg(I)	604	794	624	2	1.27†
Mn(II)	563	930	763	5	0.80
Ni(II)	552	799	693	17	0.69
Sn(II)	604	980	810	12	0.93
Sr(II)	583	870	768	8	1.12
Th(IV)	614	875	781	17	1.02
Tl(I)	531	757	690	2	1.47
Zn(II)	583	905	767	4	0.74

* From ref. 33, unless otherwise stated
† Ref. 34

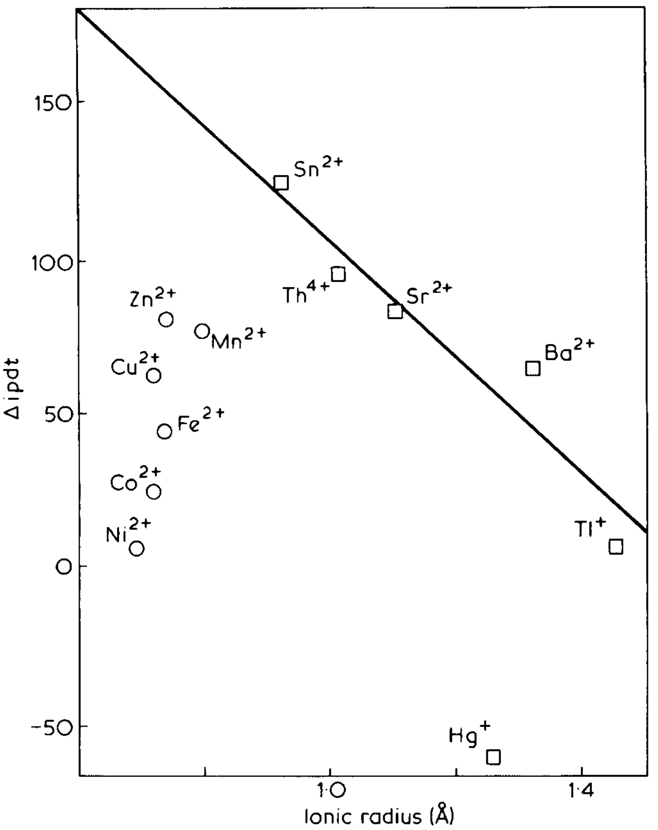


Figure 3 Plot of difference between ipdt for polymer–metal ion system and pure polyacrylamide against ionic radius for transition metal (○) and main group (□) metal ions. The line (slope -190 Å^{-1}) is obtained by least squares for the main group ions

endothermic, as would be expected for a depolymerization process.

To get some measure of the overall stabilizing effect of the metal ions, two empirical quantities were employed, the temperature of 50% decomposition[19], and the ipdt[20]. In both cases, it can be seen that the majority of ions show a stabilizing effect. The results for the 50% decomposition temperature roughly parallel those for the ipdt. The biggest stabilization is observed with iorn(II), manganese(II), tin(II) and zinc(II), whilst no significant overall stabilization is observed in the cases of mercury(I), nickel(II), and thallium(I). Studies on the thermal decomposition of various coordination polymers[6,7] have shown that the highest thermal stability is observed with polymers containing manganese(II) and zinc(II). If, as has been suggested[12], the binding of metal ions to polyacrylamide is largely electrostatic, it may be anticipated that the stabilization will be governed, at least in part, by the strength of binding, and hence by the radius of the metal ions. The difference between the ipdt of the polymer–metal ion systems and that of pure polymer was plotted against ionic radius (*Figure 3*). With the main group metal ions, a reasonable linear correlation was observed, with the stabilizing effect decreasing with increasing ionic radius. For a predominantly electrostatic interaction, the strength of a complex will be inversely proportional to the radius of the metal ion[28], and it is reasonable to conclude that the stabilizing effect of the main group metal ions results from their complexing with the polymer, and increases with increasing binding between the metal ion and amide group(s). This may impart an increased rigidity to the binding environment, and so inhibit the conformational changes necessary for deamination and depolymerization.

The transition metal ions do not show such a simple dependence of their stabilizing ability on the ionic radius. As has been noted with various coordination polymers[6,7], the biggest stabilizing effect is observed with zinc(II) and manganese(II). Martins[6] has suggested that the strong stabilizing effect of the zinc(II) ion results from it only having a single stable oxidation state. However, this explanation is unsatisfactory in the present case as manganese(II) has a similar effect but has a large number of oxidation states, whereas nickel(II), which is the only common state of this metal, gives the lowest stabilization of the transition metal ions studied. An alternative explanation[7] is that the effect for manganese(II) and zinc(II) results from the special stability of the d^5 and d^{10} electronic configurations. Such special stability for these configurations of transition metals may suggest that ligand field effects are important. An important thermodynamic term with transition metal ions is the ligand field stabilization energy (LFSE)[29]. If the differences in ipdt for polymer–transition metal ion and for pure polymer are plotted against the relative LFSE, assuming octahedral geometry for metal ion complexes, it is seen that, with the exception of copper(II), a reasonable linear relationship is obtained (*Figure 4*), supporting the idea that this term is involved in the stabilization. The poor fit with copper(II) is not completely surprizing, as complexes of this ion commonly show large deviations from octahedral geometry due to extensive Jahn–Teller distortion[30]. Quantitative interpretation of the role of LFSE in the stabilization is difficult in the absence of knowledge of the binding around the metal ion. However, if metal ions are complexed by polyacrylamide according to the equation:

$$[M(H_2O)_6]^{n+} + (\text{–CONH}_2)_x \rightleftharpoons [M(H_2O)_{6-x}(\text{–CONH}_2)_x]^{n+} + xH$$

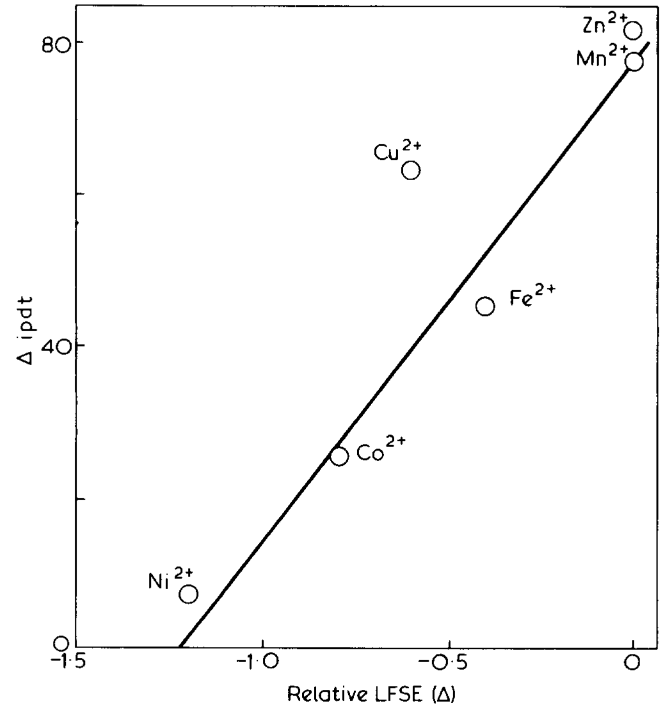


Figure 4 Plot of difference between ipdt for polymer–transition metal systems and pure polyacrylamide against relative ligand field stabilization energy

the position of equilibrium will be governed, at least in part, by the ligand field stabilizing effects of the water and amide ligands. Whilst it has not been possible to find the ligand field splitting for amide groups[31], it is known that urea, which should be similar to amides, lies lower in the spectrochemical series than water[32], and so has a smaller splitting. Formation of polymer–metal ion complex will thus be less favourable for ions possessing high LFSE than for those with low or zero values. Hence, the decrease in stabilizing effect with increasing LFSE probably reflects a decrease in the stability of the polymer–metal ion complex in these systems.

REFERENCES

1 Loan, L. D. and Winslow, F. M. 'Polymer Stabilization', (Ed. W. L. Hawkins), Wiley–Interscience, New York, 1972, pp. 132–137
2 Nass, L. I. 'Encyclopedia of Polymer Science and Technology, vol. 12', (Eds. H. F. Mark, N. G. Gaylord and N. M. Bikales), Interscience, New York, 1970, pp. 725–768
3 Frye, A. H. and Hont, R. W. *J. Polym. Sci.* 1959, **40**, 419; *ibid* 1960, **45**, 1
4 Nagatomi, R. and Saeki, Y. *J. Polym. Sci.* 1962, **61**, S60
5 Lions, F. and Martins, K. V. *J. Am. Chem. Soc.* 1957, **79**, 2733
6 Martins, K. V. *J. Am. Chem. Soc.* 1958, **80**, 233
7 Horowitz, E. and Perros, T. P. *J. Inorg. Nucl. Chem.* 1964, **26**, 139
8 For a general discussion of the effect of coordination of metal ions on the thermal stability of organic polymers see Economy, J. and Mason, J. H. 'Thermal Stability of Polymers, vol. 1', (Ed. R. T. Conley), Marcel Dekker, New York, 1970, p 607 *et. seq.*
9 Nag, N. K., Mukhopadhyaz, R., De, S. K. and Bas, S. *J. Therm. Anal.* 1976, **9**, 395
10 Lee, L. H. *J. Polym. Sci.* 1964, **A2**, 2859
11 Saunders, D. and Pecsok, R. L. *Anal. Chem.* 1968, **40**, 44
12 Schmuckler, G. and Limoni, B. *J. Inorg. Nucl. Chem.* 1977, **39**, 137
13 Lederer, M. and Rinalduzzi, B. *J. Chromatogr.* 1972, **68**, 237
14 Sorenson, W. R. and Campbell, T. W. 'Preparative Methods in Polymer Chemistry', Interscience, New York, 2nd edn., 1968, p 248
15 Thomas, W. M. 'Encyclopedia of Polymer Science and Technology, vol. 1', (Ed. H. F. Mark, N. G. Gaylord and N. M. Bikales), Interscience, New York, 1964, p 187
16 Utah, S. I. *MSc Thesis* University of Ife, 1980
17 Cotton, F. A. and Wilkinson, G. 'Advanced Inorganic Chemistry', Wiley Eastern, New Delhi, 2nd edn., 1966, p 613
18 See Mackenzie, R. C. *Talanta* 1969, **16**, 1227 for nomenclature of thermal analysis
19 Conley, R. T. 'Thermal Stability of Polymers, vol. 1', (Ed. R. T. Conley), Marcel Dekker, New York, 1970, Ch 2
20 Doyle, C. D. *Anal. Chem.* 1961, **33**, 77
21 Davidson, D. and Karten, M. *J. Am. Chem. Soc.* 1956, **78**, 1066
22 Polya, J. B., Lindsay, T. M. and Bourus, A. N. *Can. J. Chem.* 1952, **30**, 135
23 See, for example, Smothers, W. J. and Chiang, Y. 'Handbook of Differential Thermal Analysis', Chemical Publishing Co., New York, 1966, p 185
24 Staudinger, H. and Urech, E. *Helv. Chim. Acta* 1929, **12**, 1107
25 Jones, G. D., Zomlefer, J. and Hawkins, K. *J. Org. Chem.* 1944, **9**, 500
26 Madan, S. K. 'Coordination Chemistry', (Ed. S. Kirschner), Plenum, New York, 1969, p 139
27 Certain amide ligands such as dipeptides may form chelate complexes with metal ions in aqueous solution. The bonding here, however, is partly through amine and partly through amide, Datta, S. P., Leberman, R. and Rabin, B. R. *Trans. Faraday Soc.* 1959, **55**, 2141
28 Phillips, C. S. G. and Williams, R. J. P. 'Inorganic Chemistry', Clarendon, Oxford, 1965, p 163
29 Ref. 17, p 688
30 Durrant, P. J. and Durrant, B. 'Introduction to Advanced Inorganic Chemistry', Longman, London, 2nd edn., 1972, p 1114
31 The values in fref. 26 for various cyclic amide complexes of nickel(II) are in the range 7950 ± 350 cm^{-1}. In contrast, $Ni(H_2O)_6^{2+}$ has $\Delta = 8500$ cm^{-1}, ref. 32, p 111
32 Jørgensen, C. K. 'Adsorption Spectra and Chemical Bonding in Complexes', Pergamon, Oxford, 1962, p 109
33 Ahrens, L. H. *Geochim. Coxmochim. Acta* 1952, **2**, 155
34 Stockar, K. *Helv. Chim. Acta* 1950, **33**, 1409