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Effect of the nature of crosslinking agents on the thermal decomposition of metal complexes of crosslinked polyacrylamide-supported dithiocarbamates

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Abstract

The thermal decomposition of metal complexes of dithiocarbamate functions supported on crosslinked polyacrylamides in different structural environments was investigated. The dithiocarbamate functions were incorporated into the polyacrylamide supports by a two-step polymer-analogous reaction. The phenomenological and kinetic parameters of the thermal decomposition of the metal complexes were observed to vary with the nature of the crosslinking agent in the polymer support. The thermal stabilities of the metal complexes are higher than the stability of the free dithiocarbamate resin. In the Cu(II) and Ni(II) complexes of *N,N*′-methylenebisacrylamide-crosslinked polyacrylamide-supported dithiocarbamates the Ni(II) complexes have the higher thermal stability. In the Cu(II) and Ni(II) complexes, the activation energy decreases with increasing crosslinking, reaches a minimum, then increases and again decreases. The energy values fit into the general equation for a cubic polynomial. The entropies of the metal complexes are more positive than the entropy of the uncomplexed resin.

INTRODUCTION

The complexation of metal ions by a polymer-supported ligand is governed by the microenvironments around the ligand functions [1–3]. Thus the thermal stabilities of the ligands and the derived complexes vary with the nature of the polymer matrix and the nature and extent of the crosslinking agent. Complexation with a metal ion which results in stable ring structures usually enhances the thermal stability of the systems [4,5]. Dithiocarbamates usually form ring-structured complexes because of the characteristic bidentate coordination structure [6].

This paper describes thermogravimetric studies of the metal complexes of dithiocarbamate functions supported on polyacrylamides in different structural environments. In this study attempts have been made to evaluate

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the effects of the nature and extent of the crosslinking agent on the thermal stabilities of the metal complexes of the dithiocarbamate functions supported on crosslinked polyacrylamides. Polyacrylamides with 2–20 mol.% of divinylbenzene (DVB), *N,N'*-methylenebisacrylamide (NNMBA) and tetraethylene glycol diacrylate (TTEGDA) crosslinks were used. These crosslinking agents differ in their relative rigidity and polarity. The effects of the extent of the NNMBA crosslinking on the thermal stabilities of the Cu(II) and Ni(II) complexes were investigated. The thermal stabilities of Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) complexes of 4 mol.% DVB- and 2 mol.% TTEGDA-crosslinked systems were also investigated.

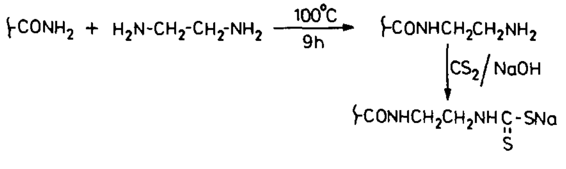
EXPERIMENTAL

The preparation of different crosslinked polyacrylamides, functionalization with ethylenediamine to afford the amino resins, dithiocarbamylation and preparation of the metal complexes were carried out as reported earlier [7]. The TG curves were recorded on a Delta Series TGA-7 thermal analyser at a heating rate of 20°C min^{-1} under a nitrogen atmosphere.

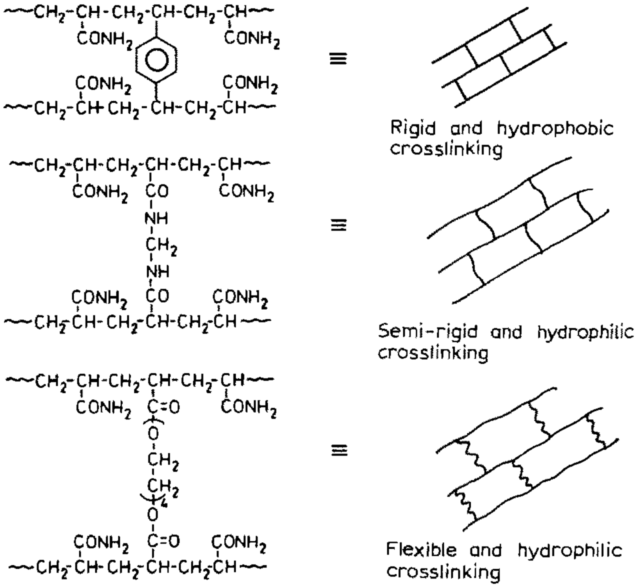
RESULTS AND DISCUSSION

Dithiocarbamate functions were incorporated into DVB-, NNMBA- and TTEGDA-crosslinked polyacrylamides by amination and subsequent dithiocarbamylation reactions (Scheme 1). DVB is extremely rigid and hydrophobic, TTEGDA is hydrophilic and flexible while NNMBA is intermediate between these two. The nature and relative amounts of the crosslinking agents would affect the strain energies at the crosslinking points, resulting in the variation of thermal stabilities. The relative rigidity/flexibility of the three crosslinked systems is represented in Scheme 2.

The change in thermal stability with different metal ions was carried out in the case of Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) complexes of 4 mol.% DVB- and 2 mol.% TTEGDA-crosslinked systems. The effect of the extent of NNMBA crosslinking on the thermal stabilities of the metal complexes was investigated. The decompositions were completed in most cases by 1073 K and the residues in all cases were found to be the corresponding metallic sulphides.



Scheme 1. Preparation of DVB-, NNMBA- and TTEGDA-crosslinked polyacrylamide-supported dithiocarbamates.



Scheme 2. Relative rigidities of the DVB-, NNMBA- and TTEGDA-crosslinked polyacrylamides.

Evaluation of kinetic parameters

The kinetic parameters are calculated by the least-squares method using the reported integral (eqn. (1)) [8] and approximation (eqn. (2)) [9] methods. The integral equation is used in the form

$$\log g(\alpha)/T^2 = \log[AR/\phi E(1 - 2RT/E)] - E/2.303RT \tag{1}$$

and the approximation equation in the form

$$\log g(\alpha)/T^{1.921503} = \log AE/\phi R + 8.68703 - 1.921503 \log E - 0.120394(E/T) \tag{2}$$

A plot of the left-hand side of eqn. (1) against $1/T$ gives a straight line with slope $-E/2.303R$. The pre-exponential factor A is calculated using the equation $\log AR/\phi E$. In eqn. (2) also the left-hand side is plotted against $1/T$; the slope obtained is $0.120394E$ and the intercept is $\log AE/\phi R + 0.68703 - 1.921503 \log E$. From this ΔS is calculated using

$$A = \bar{k}T_s/h \exp(\Delta S/R) \tag{3}$$

where A is the pre-exponential factor, $\bar{k}$ the Boltzmann constant, S the entropy of activation, R the universal gas constant, h Planck's constant, T the temperature in kelvins and T_s is the peak temperature in the DTG curve.

Metal complexes of DVB-crosslinked polyacrylamide-supported dithiocarbamates

The thermogravimetric curves of the 4 mol.% DVB-crosslinked polyacrylamide-supported dithiocarbamate and its various metal complexes are given in Fig. 1. The metal complexes are obviously more stable than the diothiocarbamate resin. All the thermogravimetric curves showed three stages of decomposition. The first-stage decompositions were in the temperature range 307–486 K with mass losses in the range 8–16%. This mass loss can be considered as the removal of coordinated or adsorbed water molecules present in the complexes as is evident from the IR spectra. The second-stage decompositions of the uncomplexed dithiocarbamate resin occurred in two steps in the temperature ranges 465–511 K and 512–583 K with mass losses of 7% and 12% respectively. The first step is the decomposition of the amide groups and the second step is the decomposition of free ligands. In metal complexes, these two steps are observed but not as distinctly as in the case of the uncomplexed resin. In various complexes, the second-state decompositions were in the temperature range 440–617 K with mass losses in the range 13–21%.

The third stage is the major decomposition and it is shifted by the incorporation of various metal ions. The temperature ranges of the decomposition of the dithiocarbamate resin and its various metal complexes for this stage are given in Table 1.

For the uncomplexed resin this stage occurs in two steps whereas for the various metal complexes, this stage is a single step. The kinetic parameters are given in Table 2. The activation energy for the decomposition decreased in the order Co(III) > Zn(II) > Ni(II) > Cu(II) > Hg(III) > uncomplexed resin. The greater stability of the metal complexes compared

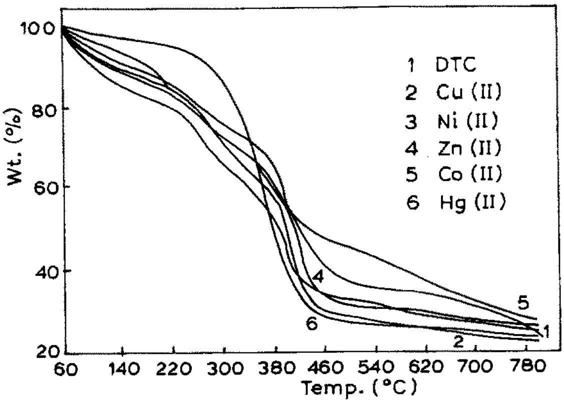


Fig. 1. TG curves of 4 mol.% DVB-crosslinked polyacrylamide-supported dithiocarbamate and metal complexes.

TABLE 1

Phenomenological data of the thermal decomposition of 4 mol.% DVB-crosslinked polyacrylamide-supported dithiocarbamate and metal complexes

Resin/complex	Decomposition temp. range in TG (K)		Peak temp. in DTG (K)	Mass loss (%)
	T_i	T_f	T_s	
DTC	589	841	694	37
Co(II)	617	756	676	21
Ni(II)	603	817	692	27
Cu(II)	632	1073	687	36
Zn(II)	600	916	692	44
Hg(II)	585	1073	646	66

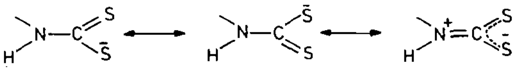
TABLE 2

Kinetic parameters of the thermal decomposition of 4 mol.% DVB-crosslinked polyacrylamide-supported dithiocarbamate and metal complexes

Resin/complex	Eqn. (1)				Eqn (2)			
	E (kJ mol^{-1})	A (s^{-1})	ΔS (J)	r	E (kJ mol^{-1})	A (s^{-1})	ΔS (J)	r
DTC	67.7	1.1×10	−232.2	0.9989	68.2	5.9	−237.2	0.9989
Co(II)	125.8	4.4×10^4	−162.8	0.9967	125.5	7.1×10^4	−158.9	0.9945
Ni(II)	112.0	6.1×10^3	−179.4	0.9992	112.5	1.1×10^4	−174.6	0.9992
Cu(II)	110.1	1.3×10^3	−192.0	0.9870	110.5	2.4×10^3	−157.3	0.9869
Zn(II)	125.1	2.6×10^4	−167.5	0.9983	125.5	4.7×10^4	−162.5	0.9983
Hg(II)	97.5	4.2×10^2	−201.1	0.9934	97.9	7.6×10^2	−196.2	0.9935

to that of the uncoordinated resin may be due to the formation of stable ring structures of the metal complexes. With dithiocarbamates, the formation of ring structures of the complexes is possible because of the bidentate coordination of the ligand function by resonance (Scheme 3). For the uncomplexes resin and its Zn(II) complex the decompositions were incomplete even at 1073 K.

The entropies of the complexes are higher than that of the uncomplexed resin. This points to the distortion of the ordered polymer chains for complexation with metal ions, resulting in an increase in entropy.



Scheme 3. Resonance in dithiocarbamates.

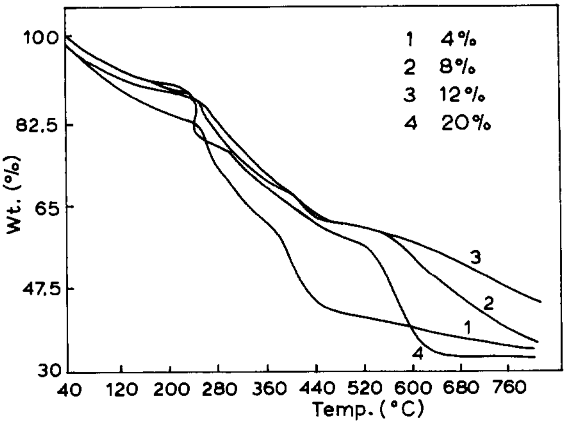


Fig. 2. TG curves of the Cu(II) complexes of polyacrylamide-supported dithiocarbamates with varying extents of NNMBA crosslinks.

Metal complexes of polyacrylamide-supported dithiocarbamates with varying extents of NNMBA crosslinks

The TG curves of the Cu(II) complexes of dithiocarbamates with 4, 8, 12, and 20 mol.% of NNMBA crosslinks are given in Fig. 2. The thermogravimetric curves of the 4 mol.% and 20 mol.% NNMBA-crosslinked systems have three stages of decomposition whereas the 8 mol.% and 12 mol.% crosslinked systems have four stages. In all cases, the first stage can be considered as the decomposition of the adsorbed and/or coordinated water molecules present in the complexes. This stage occurs in the temperature range 303–477 K with mass losses of between 8 and 11%. The second-stage decompositions were in the temperature range 448–506 K with mass losses in the range 12–25%. This stage may be the decomposition of the unfunctionalized amide groups and free ligands in the complexes. The third stage in all cases was used for the kinetic analysis of the complexes. The thermal decomposition data are given in Table 3.

TABLE 3

Phenomenological data of the thermal decomposition of Cu(II) complexes of polyacrylamide-supported dithiocarbamates with varying extents of NNMBA crosslinks

NNMBA (mol.%)	Decomposition temp. range in TG (K)		Peak temp. in DTG (K)	Mass loss (%)
	T_i	T_f	T_s	
4	622	770	683	26
8	650	744	697	16
12	648	750	656	18
20	634	751	704	27

TABLE 4

Kinetic parameters of the thermal decomposition of Cu(II) complexes of polyacrylamide-supported dithiocarbamates with varying extents of NNMBA crosslinks

NNMBA (mol.%)	Eqn. (1)				Eqn. (2)			
	E (kJ mol^{-1})	A (s^{-1})	ΔS (J)	r	E (kJ mol^{-1})	A (s^{-1})	ΔS (J)	r
4	169.1	9.4×10^{10}	−41.7	0.9842	169.5	1.7×10^{11}	−36.9	0.9838
8	134.3	2.7×10^{3}	−187.5	0.9971	134.9	4.9×10^{4}	−182.5	0.9971
12	132.7	1.6×10^{3}	−190.6	0.9937	133.7	3.2×10^{3}	−184.9	0.9976
20	153.8	2.5×10^{9}	−72.1	0.9941	154.6	7.5×10^{9}	−63.0	0.9951

The kinetic data are given in Table 4. The activation energy decreases with increasing crosslinking up to 12 mol.% and then increases further. The activation energy E and the extent of crosslinking C fit into the general equation for a cubic polynomial of the type

$$E = a + bC + cC^3 + dC^3$$

the specific equation being $E = 261.915 - 31.960C + 2.432C^2 - 0.055C^3$.

A plot of the activation energy E of the Cu(II) complexes against the extent of NNMBA crosslinking (C) is given in Fig. 3. The activation energy decreases with increasing crosslinking, reaches a minimum at 11 mol.% and then increases up to the chosen limits of the experiment. This indicates a lower thermal stability for the 11 mol.% crosslinked system.

The decompositions of the Cu(II) complexes of 4 and 12 mol.% crosslinked resins were incomplete even at 1073 K, but in the 8 and 12 mol.% crosslinked systems the decompositions were completed with a

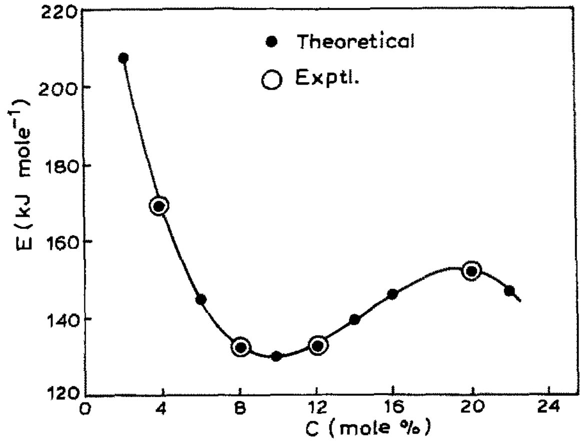


Fig. 3. Activation energy vs. extent of NNMBA crosslinking in Cu(II) complexes of polyacrylamide-supported dithiocarbamates.

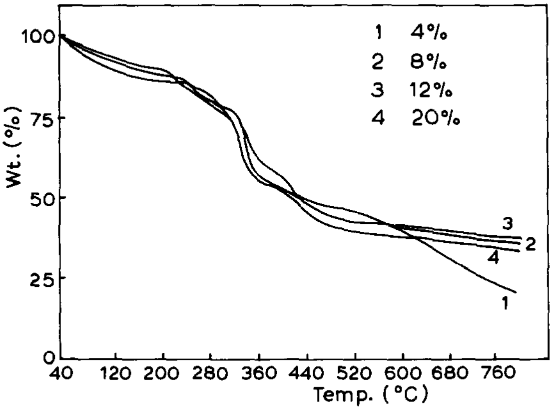


Fig. 4. TG curves of the Ni(II) complexes of polyacrylamide-supported dithiocarbamates with varying extents of NNMBA crosslinks.

fourth stage. In these cases the fourth-stage decompositions were observed in the temperature ranges 744–911 K and 750–919 K with 33% and 34% mass loss respectively.

Similarly the thermogravimetric curves of the Ni(II) complexes containing varying extents of NNMBA crosslinks are given in Fig. 4. In this case the TG curves of the 4, 8 and 12 mol.% crosslinked systems have four stages of decomposition but the 20 mol.% crosslinked system has only three stages. The first-stage decompositions were in the temperature range 303–477 K with mass losses in the range 8–12%. This is the removal of the adsorbed and/or coordinated water molecules in the complexes. The second-stage decompositions occur in the temperature range 448–650 K with mass losses of between 8 and 12%. This is the decomposition of amide groups and free dithiocarbamate ligands present in the complexes. The third-stage decompositions were used here for the kinetic analysis of the complexes. The procedural, final and peak temperatures of decompositions in the TG and DTG curves are given in Table 5.

TABLE 5

Phenomenological data of the thermal decomposition of Ni(II) complexes of polyacrylamide-supported dithiocarbamates with varying extents of NNMBA crosslinks

NNMBA (mol.%)	Decomposition temp. range in TG (K)		Peak temp. in DTG (K)	mass loss (%)
	T_i	T_f	T_s	
4	622	764	680	20
8	622	745	686	14
12	645	763	683	14
20	644	751	690	19

TABLE 6

Kinetic parameters of the thermal decomposition of Ni(II) complexes of polyacrylamide-supported dithiocarbamates with varying extents of DVB crosslinks

NNMBA (mol.%)	Eqn. (1)				Eqn. (2)			
	E (kJ mol^{-1})	A (s^{-1})	ΔS (J)	r	E (kJ mol^{-1})	A (s^{-1})	ΔS (J)	r
4	154.9	7.2×10^6	−120.5	0.9979	154.2	1.0×10^7	−117.5	0.9982
8	138.0	3.5×10^5	−145.7	0.9995	138.5	6.4×10^5	−140.7	0.9995
12	179.6	4.5×10^8	−86.2	0.9900	180.0	8.1×10^8	−81.3	0.9901
20	170.7	9.3×10^7	−99.3	0.9942	170.9	9.7×10^7	−99.0	0.9942

The activation energies of decomposition, the Arrhenius parameter, entropy of activation and the correlation coefficients are given in Table 6. The activation energy decreases with increasing crosslinking up to 12 mol.% and decreases thereafter. In this case also the values of the activation energy E and the extent of crosslinking C can be related by a cubic polynomial with the specific equation

$$E = 308.614 - 61.067C + 6.438C^2 - 0.187C^3$$

A plot of activation energy against the extent of NNMBA crosslinking is given in Fig. 5. The activation energy decreases with increasing crosslinking, reaches a minimum at 7 mol.% crosslinking, then increases with crosslinking and reaches a maximum at 17 mol.% crosslinking. Thus the Ni(II) complex of 7 mol.% crosslinked resin has the minimum thermal stability within the experimental limits.

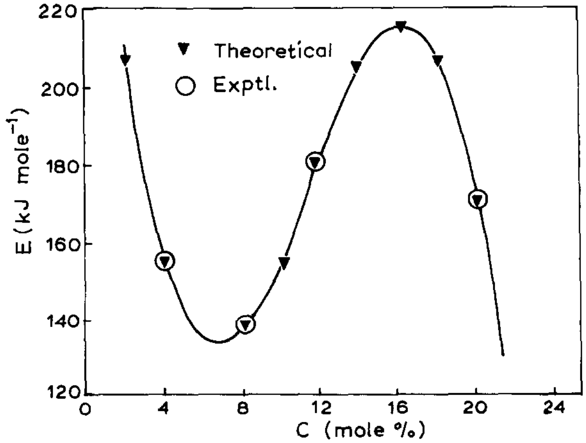


Fig. 5. Activation energy vs. extent of NNMBA crosslinking in Ni(II) complexes of polyacrylamide-supported dithiocarbamates.

The decompositions of the Ni(II) complexes of the 4 and 12 mol.% crosslinked resins were incomplete even at 1073 K, but for the 8 mol.% and 20 mol.% crosslinked resins, a fourth-stage decomposition occurs in the temperature ranges 780–1059 K and 766–951 K respectively with 34% mass loss. Only the thermal analysis of the metal complexes of dithiocarbamates was carried out in the present study. Usually the thermal stabilities of dithiocarbamates are increased by complexation with metal ions.

The entropies of the Cu(II) and Ni(II) complexes vary with the extent of NNMBA crosslinking. A general feature observed in this case is that a decrease in activation energy leads to a decrease in entropy. In the case of Cu(II) complexes, the entropy decreases with crosslinking, reaches a minimum at 12 mol.% and increases further. However, in the case of Ni(II) complexes, the entropy decreases at 8 mol.% crosslinking, increases at 12 mol.% and again decreases. These two observations are similar to the variation of the activation energy with the extent of NNMBA crosslinking in the complexes.

Metal complexes of TTEGDA-crosslinked polyacrylamide-supported dithiocarbamates

Thermogravimetric curves of the 2 mol.% TTEGDA-crosslinked polyacrylamide-supported dithiocarbamate and its metal complexes are given in Fig. 6. The curves show three stages of decomposition. The first-stage decomposition occurs in the temperature range 307–465 K with mass losses in the range 3–16%. This is the liberation of adsorbed or coordinated water molecules present as in the previous cases. The second-stage decomposition is a slow process which occurs in two steps corresponding to the decompositions of the unfunctionalized amide groups and free ligands. This is in the temperature range 413–561 K with mass losses of between 14

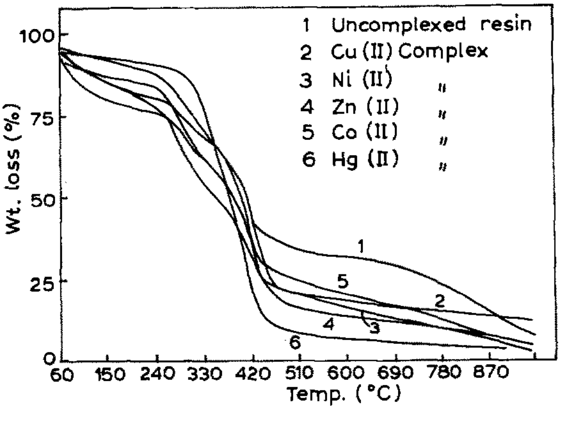


Fig. 6. TG curves of 2 mol.% TTEGDA-crosslinked polyacrylamide-supported dithiocarbamates.

TABLE 7

Phenomenological data of the thermal decomposition of 2 mol.% TTEGDA-crosslinked polyacrylamide-supported dithiocarbamate and metal complexes

Resin/complex	Decomposition temp. range in TG (K)		Peak temp. in DTG (K)	Mass loss (%)
	T_i	T_f	T_s	
DTC	529	753	665	29
Co(II)	561	745	667	24
Ni(II)	545	737	665	23
Cu(II)	569	753	679	34
Zn(II)	525	789	667	50
Hg(II)	541	773	649	61

and 18%. The third stage is used for the kinetic analysis. The temperature of initiation (T_i) and of termination (T_f) in TG and the peak temperature (T_s) in DTG are given in Table 7.

The kinetic data of the various systems are given in Table 8. The activation energies of decomposition of the metal complexes are higher than that of the uncomplexed resin and decrease in the order Co(II) > Cu(II) > Ni(II) > Hg(II) > Zn(II) > dithiocarbamate resin. The higher stabilities of the metal complexes compared with the uncomplexed resin are due to the formation of stable ring structures of the complexes.

Except in the case of the Zn(II) complex, the entropies of the metal complexes are higher than that of the uncomplexed resin. This is because of the rearrangement of the macromolecular chains for complexation with metal ions. The difference between the activation energies of the Zn(II) complex and the uncomplexed resin is smaller. A similar trend is also observed in the case of entropy values.

TABLE 8

Kinetic data of the thermal decompositions of 2 mol.% TTEGDA-crosslinked polyacrylamide-supported dithiocarbamate and metal complexes

Resin/complex	Eqn. (1)				Eqn. (2)			
	E (kJ mol^{-1})	A (s^{-1})	ΔS (J)	r	E (kJ mol^{-1})	A (s^{-1})	ΔS (J)	r
DTC	110.7	3.6×10^3	−183.6	0.9936	111.1	6.4×10^3	−178.7	0.9937
Co(II)	179.7	2.0×10^7	−73.6	0.0066	180.1	3.6×10^9	−68.7	0.9966
Ni(II)	119.7	1.8×10^4	−170.3	0.9989	120.2	3.2×10^4	−165.4	0.9989
Cu(II)	156.2	1.2×10^7	−116.5	0.9918	156.7	2.1×10^7	−111.6	0.9919
Zn(II)	112.2	2.5×10^3	−186.6	0.9993	112.6	4.5×10^3	−181.7	0.9930
Rg(II)	123.2	8.4×10^4	−157.1	0.9917	123.2	1.5×10^5	−165.5	0.9918

IR spectra

The polymeric dithiocarbamates showed the absorptions of the amides and dithiocarbamates. The absorptions at 1660 and 3400 cm^{-1} are the C=O and N–H absorptions of the amides. The absorption at 1550–1450 cm^{-1} is associated with the thioureide vibration and is the C–N vibration of the CS_2–NR_2 bond [11]. The absorption in the 1050–950 cm^{-1} region is the ν(CSS) vibration. In the metal complexes this peak is broadened and shows a splitting of 20 cm^{-1}, indicating the bidentate coordination of the dithiocarbamates [6]. The IR spectral region between 400 and 200 cm^{-1} is associated with the M–S translational vibrations [12].

CONCLUSION

The foregoing investigations of the phenomenological and kinetic analyses of the thermal decompositions of the differently crosslinked polyacrylamide-supported dithiocarbamates and their metal complexes by the thermogravimetric technique revealed increased stability for the metal complexes compared to that for the uncomplexed resins. In the Cu(II) and Ni(II) complexes of NNMBA-crosslinked polyacrylamide-supported dithiocarbamates, the thermal stability varies with the extent of NNMBA crosslinking. In the Cu(II) complexes, the activation energy decreases with increasing crosslinking up to 11 mol.% and increases thereafter, but in the case of the Ni(II) complexes, the thermal stability is at a minimum at 7 mol.%, increases up to 17 mol.% crosslinking and then decreases with further crosslinking. The entropies of the metal complexes are more positive than those of the uncomplexed resins. This arises from the deformation of the polymer chains for complex formation with the increase in disorder of the polymer support.

REFERENCES

1 A. Warshawsky, Polymeric ligands in hydrometallurgy, in D.C. Sherrington and P. Hodge (Eds.), Syntheses and Separations Using Functional Polymers, Wiley, New York, 1988, p. 325.
2 H. Egawa, T. Nonaka and M. Nakayama, J. Macromol. Sci. Chem., 25 (10/11) (1988) 1407.
3 H. Nishide, N. Shimidzu and E. Tsuchida, J. Appl. Polym. Sci., 27 (1982) 4161.
4 A.Z. El-Sonbati and M.A. Diab, Polym. Deg. Stab., 22 (1988) 295.
5 T. Desai and B. Suthar, Synth. React. Inorg. Met. Org. Chem., 16 (1986) 675.
6 P.C.H. Mitchell and M.G. Taylor, Polyhedron, 1 (1982) 225.
7 B. Mathew and V.N.R. Pillai, in S. Sivaram (Ed.), Polymer Science: Contemporary Themes, Vol. 1, McGraw-Hill, New Delhi, 1991, p. 422.
8 A.W. Coats and J.P. Redfern, Nature, 201 (1964) 68.
9 P.M. Madhusudanan, K. Krishnan and K.N. Ninan, Thermochim. Acta, 97 (1986) 189.

10 A.V. Nikolaev, V.A. Logvinenko and L.I. Myachine, Thermal Analysis, Vol. 2, Academic Press, New York, 1969.
11 D. Coucouvanis, Prog. Inorg. Chem., 11 (1970) 283.
12 I. Ojima, T. Onishi, T. Iwamoto, N. Inamoto and K. Tamaru, Inorg. Nucl. Chem. Lett., 6 (1970) 65.