

Thermogravimetric studies of the metal complexes of polyacrylamide-supported amines: effect of the variables of macromolecular structure on thermal stability

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Abstract

The thermal decomposition behaviour of metal complexes of amino functions supported on crosslinked polyacrylamides in different structural environments is followed. The phenomenological and kinetic aspects of the TG curves are investigated. The integral and approximation methods are used for the evaluation of the kinetic parameters. The thermal stabilities of the Cu(II) complexes of aminopolyacrylamides with 2–20 mol.% of DVB crosslinks and 4–20 mol.% of NNMBA crosslinks varied with the extent of crosslinking. The activation energy of decomposition decreases with crosslinking, reaches a minimum, and then increases. The relation between the activation energy and the extent of crosslinking fits into the general equation for a cubic polynomial. The thermal stabilities of the Cu(II) complexes of aminopolyacrylamides with DVB crosslinks are lower than the NNMBA-crosslinked system. This is due to the increased strain energy in the DVB crosslinking points. The thermal stabilities of the amino resins with 4% DVB crosslinks and 2% TTEGDA crosslinks varied with the extent of incorporation of the different metal ions, as well as the unsaturated coordination in the complex.

INTRODUCTION

The complexation of metal ions with polymeric ligands produces metal complexes which possess enhanced thermal stability [1–3]. Elucidation of the structure and thermal stabilities of polymer–metal complexes is of practical importance [4,5]. Thermogravimetry of polymer–metal complexes can reveal the variation of thermal stability by complexation with metal ions [6,7]. The formation of stable ring structures by complexation enhances the thermal stability of the polymeric ligands [8–10]. The characteristics of the polymer matrix, such as the nature of the polymer backbone, and the chemical nature and extent of the crosslinking agent can influence the thermal stability of the polymer–metal complexes. In addition, the

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change in the metal ion content which is dependent on the macromolecular structure is also an important factor affecting the thermal stability.

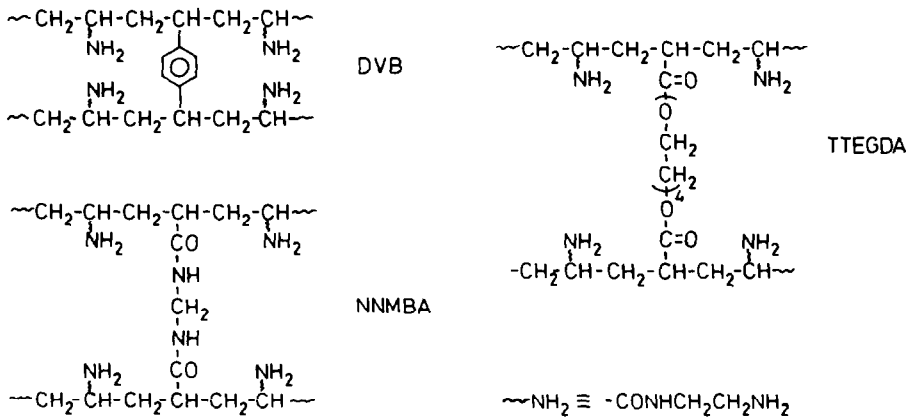
The present investigation is concerned with the thermal decomposition behaviour of the metal complexes of amino functions supported on polyacrylamides in different structural environments. Polyacrylamides with divinylbenzene (DVB), *N,N'*-methylene-bis-acrylamide (NNMBA) and tetraethyleneglycol diacrylate (TTEGDA) crosslinks were selected for the study. These crosslinking agents differ in their relative rigidity and polarity. Cu(II) complexes of aminopolyacrylamides with 2–20 mol.% of DVB crosslinks, various metal complexes of 4% DVB-crosslinked amino resin, amino resins with 4–20 mol.% of NNMBA crosslinks and their Cu(II) complexes, amino resin with 2% TTEGDA crosslinking and its metal complexes were selected for the present study. The present investigation involves the study of the change in the thermal stabilities of the aminopolyacrylamides brought about by the introduction of these crosslinking agents, the variation of the thermal stability on incorporation of a crosslinking agent in different proportions, and the variation of the thermal stability on complexation with different metal ions. The polymeric ligands and the derived complexes were characterised by their IR and ESR spectra. The decomposition of polymeric ligands and the derived complexes fall under the category of solid state reactions that are heterogeneous in nature. The analysis of the TG curves in the present study is limited to non-overlapping and well-defined stages of decomposition. Attempts have been made here to analyse the phenomenological and kinetic aspects revealed by the non-isothermal TG curves. The phenomenological aspects give the thermal stabilities and the regions of thermal decomposition.

EXPERIMENTAL

The preparation of DVB-, NNMBA- and TTEGDA-crosslinked polyacrylamides with varying extents of crosslinking, its functionalisation to prepare aminopolyacrylamides and complexation with different metal ions were carried out following the procedures reported by the present authors [11,12]. TG curves were recorded on a Delta Series TGA-7 thermal analyser in a nitrogen atmosphere at a heating rate of 20°C min⁻¹.

RESULTS AND DISCUSSION

The preparation of crosslinked polyacrylamides with varying amounts of DVB, NNMBA and TTEGDA crosslinks, the functionalisation with ethylenediamine to yield the poly(*N*-2-aminoethylacrylamide)s, and complexation and characterisation studies are reported [11,12]. The various crosslinked aminopolyacrylamides are given in Scheme 1.

Scheme 1. Poly(*N*-2-aminoethylacrylamide)s with DVB, NNMBA and TTEGDA crosslinks.

Evaluation of the kinetic parameters

The kinetic parameters are calculated using the reported integral (eqn. (1)) [13] and approximation (eqn. (2)) [14] methods using the least-squares technique. The integral equation is used in the form

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

and the approximation equation in the form

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

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 from $\log AR/\phi E$. The left-hand side of eqn. (2) is also plotted against $1/T$. The slope obtained is $0.120394E$. The intercept is $\log AE/\phi R + 8.68703 - 1.921503 \log E$. From this, ΔS is calculated using the equation

$$A = kT_s/h e^{\Delta S/R} \quad (3)$$

where A is the pre-exponential factor, k the Boltzmann constant, ΔS the entropy of activation, R the universal gas constant, h Planck's constant, T the temperature (K) and T_s the peak temperature in the DTG curve.

Metal complexes of DVB-crosslinked polyacrylamide-supported amines

The thermogravimetric studies of the 4% DVB-crosslinked amino resin, its complexes with Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) ions and the Cu(II) complexes of the amino resins with varying extents of DVB crosslinks (2–20 mol.%) are described here.

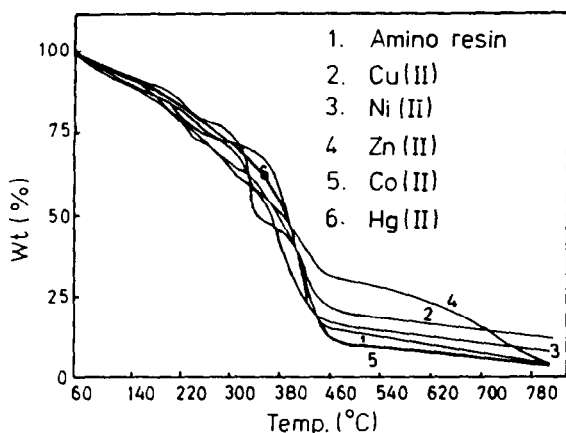


Fig. 1. TG curves of 4% DVB-crosslinked aminopolyacrylamide and metal complexes.

Metal complexes of 4% DVB-crosslinked polyacrylamide-supported amine

The TG curves of the 4% DVB-crosslinked polyacrylamide-supported amino resin and its various metal complexes are given in Fig. 1. All the TG curves showed four stages of decomposition. These decompositions varied with the nature of the metal ion. The first-stage decompositions were in the temperature range 304–464 K. The mass loss occurring in this stage was in the range 8–11%. This mass loss is due to the removal of the adsorbed and/or coordinated water molecules present. In general, water of hydration may be considered as either adsorbed within the crystal lattice or coordinated. Water eliminated below 423 K can be considered as lattice water and that eliminated above 423 K may be due to its coordination to the metal ion present in the complex [15]. The mass losses in the case of these complexes can be considered as crystal water.

The second decomposition arises from the decompositions of free amide groups. The mass loss occurred in the temperature range 450–638 K with 4–14% mass loss. The third-stage decomposition is the decomposition of uncoordinated amino groups. The mass losses were in the range 10–21%. The decomposition occurred in the temperature range 461–653 K. The last step is the major decomposition which is used for the kinetic analysis. The temperature of initiation (T_i), temperature of termination (T_f) in TG and the DTG peak temperature (T_g) are given in Table 1.

The kinetic parameters of each system are given in Table 2. The activation energy for the decomposition of the amino resin is higher than that for the complexes. This can arise from the unsaturated coordination structure of the metal complexes. The activation energy decreases in the order amino resin > Zn(II) > Cu(II) > Ni(II) > Hg(II) > Co(II). The lower stabilities of the metal complexes are apparent from the entropies of the complexes. There is no pronounced difference between the entropies of the metal complexes and the uncomplexed resin.

TABLE 1

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

Resin/ complex	Decomposition temp. range in TG (K)		Peak temp. in DTG (K)	Mass loss (%)
	T_i	T_f	T_s	
Amine	575	788	687	52
Co(II)	600	1007	653	51
Ni(II)	603	835	657	42
Cu(II)	561	653	612	21
Zn(II)	550	639	605	21
Hg(II)	593	1073	697	51

Cu(II) complexes of amines with varying extents of DVB crosslinks

The TG curves of the Cu(II) complexes of amino functions supported on polyacrylamides with 2, 4, 8 and 20 mol.% of DVB crosslinks are given in Fig. 2. The TG curves, except that of the 20% crosslinked system, have five stages of decomposition. The 20% crosslinked system has three stages. The first decomposition occurred in the range 307–513 K with mass losses between 7% and 11%. This is the removal of the adsorbed or coordinated water molecules present. The second stage was from 485 to 304 K with mass losses between 8% and 10%. In the 20% crosslinked system, the first-stage decomposition is not very pronounced; it is combined with the second-stage decomposition with 7% mass loss which terminates at 553 K. A slow third stage with mass losses between 8% and 10% is observed in the case of the 2% and 4% crosslinked systems. The third stage of the 8% and 20% crosslinked complexes is used for the kinetic analysis. In the case of the 2% and 4% crosslinked systems the fourth stage is used for the kinetic analysis. The phenomenological data are given in Table 3.

TABLE 2

Kinetic data of the thermal decomposition of 4% DVB-crosslinked polyacrylamide-supported amine and metal complexes

Resin/ complex	Equation (1)				Equation (2)			
	E (kJ mol ⁻¹)	A (s ⁻¹)	ΔS (J)	r	E (kJ mol ⁻¹)	A (s ⁻¹)	ΔS (J)	r
Amine	141.4	8.3×10^5	-138.5	0.9983	142.3	1.5×10^6	-133.6	0.9983
Co(II)	139.1	2.0×10^5	-149.3	0.9968	139.2	3.5×10^5	-144.9	0.9969
Ni(II)	126.3	6.7×10^4	-159.1	0.9891	126.8	1.2×10^5	-154.1	0.9892
Cu(II)	141.1	3.6×10^5	-144.4	0.9928	141.5	6.5×10^5	-139.5	0.9928
Zn(II)	103.5	8.1×10^5	-195.8	0.9999	103.9	4.3×10^2	-201.0	0.9999
Hg(II)	105.0	5.9×10^2	-199.0	0.9995	105.4	1.1×10^3	-194	0.9995

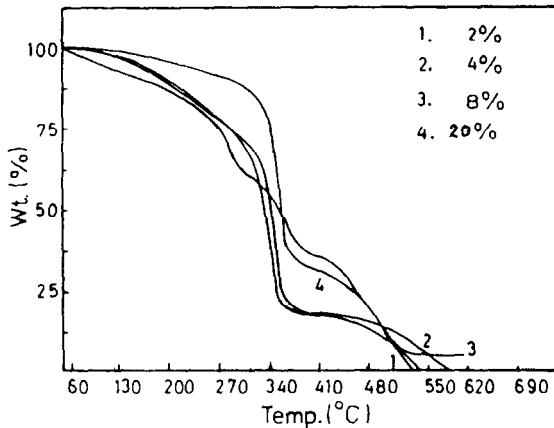


Fig. 2. TG curves of the Cu(II) complexes of aminopolyacrylamides with varying extents of DVB crosslinks.

The activation energy decreases with increasing crosslinking up to 8% crosslinking, and then increases (Table 4). The activation energy (E) and the extent of crosslinking (C) of the Cu(II) complexes fit a cubic poly-

TABLE 3

Phenomenological data of the thermal decomposition of Cu(II) complexes of polyacrylamide-supported amines with varying extent of DVB crosslinks

DVB (mol.%)	Decomposition temp. range in TG (K)		Peak temp. in DTG (K)	Mass loss (%)
	T_i	T_f	T_s	
2	633	795	693	56
4	643	795	709	54
8	577	659	629	19
20	597	783	715	60

TABLE 4

Kinetic parameters of the thermal composition of Cu(II) complexes of polyacrylamide-supported amines with varying extent of DVB crosslinks

DVB (mol.%)	Equation (1)				Equation (2)			
	E (kJ mol ⁻¹)	A (s ⁻¹)	ΔS (J)	r	E (kJ mol ⁻¹)	A (s ⁻¹)	ΔS (J)	r
2	253.0	2.6×10^{14}	+23.9	0.9964	253.5	4.7×10^{14}	+28.9	0.9964
4	250.2	4.2×10^{13}	+08.8	0.9997	250.7	7.7×10^{13}	+13.8	0.9996
8	203.0	2.1×10^{12}	-15.0	0.9957	203.4	3.9×10^{12}	-10.2	0.9957
20	215.1	1.2×10^{11}	-40.1	0.9965	216.5	2.6×10^{11}	-35.7	0.9968

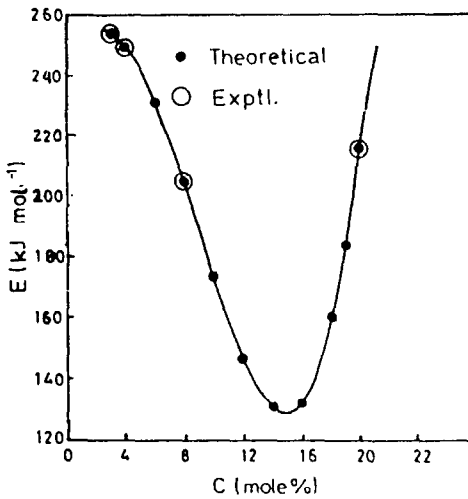


Fig. 3. Activation energy vs. extent of DVB-crosslinking in Cu(II) complexes of aminopolyacrylamides.

mial of the type

$$E = a + bC + cC^2 + dC^3 \quad (4)$$

and the specific equation is

$$E = 233.191 + 16.749C - 3.687C^2 + 0.140C^3$$

The plot of E versus C is given in Fig. 3, with a minimum at 15% crosslinking. A fifth-stage decomposition was observed in 2%, 4% and 8% crosslinked systems from 522 to 780 K with 16–31% mass loss. The decompositions were complete in all cases, leaving the metallic oxide as the residue, resulting from the presence of oxygen in the polyacrylamide support.

The entropy decreases with increasing crosslinking in the Cu(II) complexes. In the low crosslinked systems, complexation occurs by the cooperative contribution of the randomly distributed ligands with Cu(II) ions, which causes the polymer chains to distort from their normal positions. This leads to an increase in entropy. As the crosslinking increases, the concentration of the ligand functions on the polymer surface is enhanced. This is due to the reduced availability of the reactive sites, which remain buried within the crosslinks, for transamidation. This is validated in the highly crosslinked systems. The relatively free availability of the ligand functions on the surface of the highly crosslinked systems makes the complexation easier without introducing much strain.

The complexation of metal ions by the amino resins were confirmed by the IR and ESR spectra [12]. The absorptions of the amino groups were

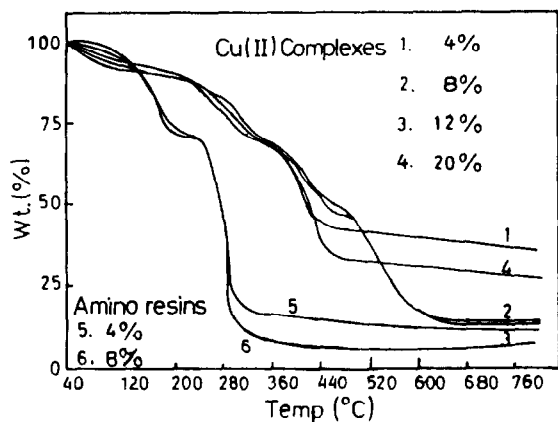


Fig. 4. TG curves of the Cu(II) complexes of aminopolyacrylamides with varying extents of NNMBA crosslinks.

split and shifted to lower frequencies. The ESR parameters suggested that the complex has a distorted tetragonal geometry.

Cu(II) complexes of polyacrylamide-supported amines with varying extents of NNMBA crosslinks

The TG curves of the Cu(II) complexes of amino polyacrylamides with 4, 8, 12 and 20 mol.% of NNMBA crosslinks and of the amino resins with 4% and 8% crosslinks are given in Fig. 4. The thermogravimetric curves of the Cu(II) complexes show four stages of decomposition. The first decompositions were from ambient temperature to 491 K with mass losses between 7% and 14%. This is the removal of the adsorbed or coordinated water molecules present in the complexes. The second stage is the slow decomposition in the temperature range 463–653 K with mass losses in the range 9–13%. This may be the decompositions of unfunctionalised amides and free amino ligands left in the complexes. The third stage was used in all cases for the kinetic analysis, and the phenomenological data of the different systems are given in Table 5.

The kinetic data calculated by the integral and approximation methods are given in Table 6. The activation energy values of the Cu(II) complexes decrease with increasing crosslinking up to 12% crosslinking, and then increase further. The activation energies of the amino resins with 4% and 8% crosslinking are almost the same (Table 6). The activation energy (E) and the extent of crosslinking (C) of the Cu(II) complexes fit a cubic polynomial, the specific equation being

$$E = 378.171 - 21.740C + 0.850C^2 - 0.0024C^3$$

The plot of E versus C for the Cu(II) complexes with varying extents of

TABLE 5

Phenomenological data of the thermal decomposition of polyacrylamide-supported amines and Cu(II) complexes with varying extent of NNMBA crosslinks

NNMBA (mol.%)	Decomposition temp. range in TG (K)		Peak temp. in DTG (K)	Mass loss (%)
	T_i	T_f	T_s	
Cu(II) complexes				
4	572	666	611	23
8	554	646	608	25
12	583	670	618	24
20	594	654	622	16
Amines				
4	583	793	698	64
8	573	823	683	61

NNMBA crosslinking is given in Fig. 5. The activation energy decreases with increasing crosslinking, reaches a minimum at 13% crosslinking, and then increases further. The curve obtained is parabolic in shape within the experimental limits.

The complexes show a fourth stage of decomposition in the temperature range 646–807 K with mass losses between 8% and 19%. The decompositions of the Cu(II) complexes were incomplete even at 1073 K, whereas the decompositions of the Cu(II) uncomplexed resins were complete at the third stage.

The entropies of the Cu(II) complexes are higher than for the uncomplexed amino resin. The negative value of the entropy of the uncomplexed resin suggests a highly ordered structure of the polymer support. Complex-

TABLE 6

Kinetic data of the thermal decomposition of Cu(II) complexes of polyacrylamide-supported amines with varying extent of NNMBA crosslinks

NNMBA (mol.%)	Equation (1)				Equation (2)			
	E (kJ mol ⁻¹)	A (s ⁻¹)	ΔS (J)	r	E (kJ mol ⁻¹)	A (s ⁻¹)	ΔS (J)	r
Cu(II) complexes								
4	304.4	1.9×10^{21}	156.6	0.9953	304.8	3.4×10^{21}	161.5	0.9953
8	257.9	3.3×10^{17}	84.6	0.9999	258.3	5.9×10^{17}	89.4	0.9999
12	235.3	1.6×10^{18}	97.6	0.9952	236.4	3.3×10^{18}	103.6	0.9974
20	264.2	3.6×10^{17}	85.2	0.9990	264.6	6.0×10^{17}	89.3	0.9990
Amines								
4	107.9	1.2×10^3	-193.3	0.9972	108.3	2.1×10^3	-188.3	0.9972
8	107.3	1.2×10^3	-193.0	0.9997	107.7	2.1×10^3	-188.0	0.9997

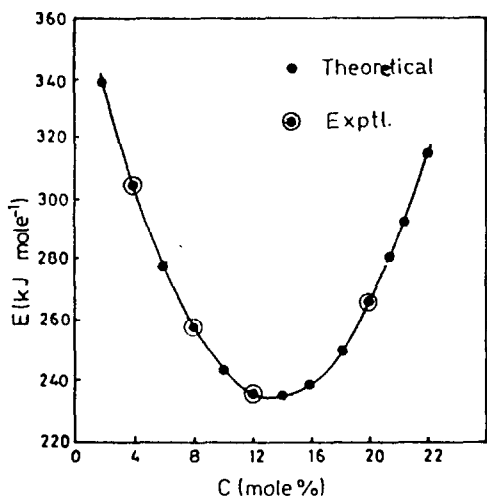


Fig. 5. Activation energy vs. extent of NNMBA crosslinking in Cu(II) complexes of aminopolyacrylamides.

ation with metal ions increases the disorder of the system by the rearrangement of the macromolecular chains for complexation with Cu(II) ions.

Metal complexes of TTEGDA-crosslinked amino resin

The TG curves of the 2% TTEGDA-crosslinked aminopolyacrylamide and its metal complexes are given in Fig. 6. The TG curves of the uncomplexed amino resin and its metal complexes except the Cu(II) complex show three stages of decomposition (Fig. 6). All the TG curves show mass losses in the range 4–14%, up to 482 K. This is attributed to the loss of adsorbed and/or coordinated water molecules present in the

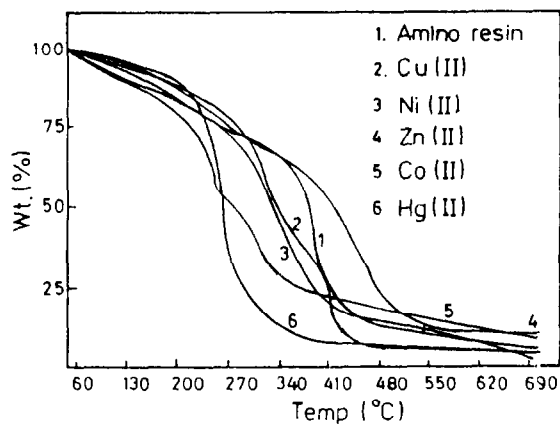


Fig. 6. TG curves of 2% TTEGDA-crosslinked aminopolyacrylamide and metal complexes.

TABLE 7

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

Resin/ complex	Decomposition temp. range in TG (K)		Peak temp. in DTG (K)	Mass loss (%)
	T_i	T_f	T_s	
Amine	562	1017	665	67
Co(II)	513	625	520	31
Ni(II)	532	815	599	45
Cu(II)	566	653	596	26
Zn(II)	589	828	668	49
Hg(II)	497	1102	605	85

complexes as mentioned earlier. The second stage is the slow decomposition which is perhaps the decomposition of unfunctionalised amide groups and of the free ligands present in the complexes. This stage occurs in the temperature range 445–624 K with mass losses in the range 3–19%. The third stage is the major decomposition and this is used for the kinetic analysis. The T_i , T_f and T_s value of the different systems are given in Table 7. The kinetic parameters are given in Table 8. The activation energies decrease in the order Cu(II) > amino resin > Ni(II) > Co(II) > Hg(II) > Zn(II). The lower stabilities of the metal complexes other than that of the Cu(II) complex, appear to be due to the unsaturated coordination structures of the complexes.

The entropy of the Cu(II) complex is much higher than those of the uncomplexed resin and the other metal complexes. This also indicates the higher thermal stability of the Cu(II) complex as a result of the complete coordination sphere. For the other metal ions, the entropies are more or less the same as for the uncomplexed resin, suggesting the decreased

TABLE 8

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

Resin/ complex	Equation (1)				Equation (2)			
	E (kJ mol ⁻¹)	A (s ⁻¹)	ΔS (J)	r	E (kJ mol ⁻¹)	A (s ⁻¹)	ΔS (J)	r
Amine	140.3	9.5×10^5	-137.2	0.9938	140.8	2.4×10^6	-132.3	0.9996
Co(II)	120.6	8.0×10^5	-136.5	0.9984	121.0	1.4×10^6	-131.7	0.9984
Ni(II)	139.6	2.6×10^7	-108.6	0.9989	140.0	4.7×10^7	-103.8	0.9989
Cu(II)	252.5	4.9×10^{17}	+88.0	0.9995	252.9	8.7×10^{17}	-103.8	0.9989
Zn(II)	83.3	1.3×10	-230.2	0.9968	85.1	3.2×10	-222.9	0.9969
Hg(II)	104.5	2.0×10^4	-168.5	0.9979	104.9	3.6×10^4	-163.6	0.9979

rearrangement of the polymer chains for complexation with metal ion which leads to the development of an unsaturated coordination structure.

CONCLUSIONS

The above phenomenological and kinetic analyses of the thermal decompositions of the differently crosslinked polyacrylamide-supported amines by the thermogravimetric method revealed that the thermal stabilities of the polymer-supported ligands vary significantly by complexation with metal ions. The thermal stabilities of the Cu(II) complexes of the amino functions supported on DVB- and NNMBA-crosslinked polyacrylamides with different amounts of the crosslinking agent are dependent on the nature and the amount of the crosslinking agent. The Cu(II) complexes of the 8% DVB-crosslinked and 12% NNMBA-crosslinked systems have the minimum thermal stabilities. The thermal stability of the NNMBA-crosslinked system is higher than that of the DVB-crosslinked system because of the increased strain energy at the rigid DVB-crosslinking points. The thermal stabilities of most of the metal complexes of 2% TTEGDA- and 4% DVB-crosslinked systems are lower than the uncomplexed resins. This may arise from the unsaturated coordination structure of the complexes.

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