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INFLUENCE OF THE MOLECULAR CHARACTER AND DEGREE OF CROSSLINKING ON THE INTERACTION OF CROSSLINKED POLYACRYLAMIDE-SUPPORTED AMINES WITH Cu(II) IONS

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ABSTRACT

Amino groups were incorporated into polyacrylamides with 2–20 mol% of crosslinking agents by transamidation with ethylenediamine. Divinylbenzene, *N,N'*-methylene-bis-acrylamide, and tetraethyleneglycol diacrylate were used as the crosslinking agents. The complexation of these resins, which contain ligand functions in different macromolecular structural environments, was investigated with Cu(II) ions. The Cu(II) uptake of these different resins was correlated with the molecular character and degree of crosslinking in the polymer matrix. The time course and kinetics of complexation depend on the nature of the crosslinking agent in the polymer matrix. The swelling behavior of the uncomplexed and complexed resins, structural characteristics, and thermal decomposition behavior were followed by IR, EPR, and thermal analysis. The swelling characteristics of the complexed resins are lower than those of the uncomplexed resins. Complexation resulted in shifting of the IR absorptions. The EPR parameters depend on the nature of crosslinking and are in agreement with the distorted tetragonal geometry of the Cu(II) complexes. The thermal decomposition behavior also depends on the nature and the degree of crosslinking in the polymer matrix.

INTRODUCTION

Recent developments in the area of structure-reactivity correlation of polymers permit the design of macromolecular systems with relatively well-defined characteristics [1-3]. The overall three-dimensional macromolecular structure, which is decided by the chemical nature of the monomer, the molecular character and degree of crosslinking, and the separation of the reactive sites from the insoluble macromolecular matrix, are decisive in dictating the nature and reactivity of attached functional groups [4-6]. The dependence of the reactivity of the attached functional groups on polymers has been the subject of contemporary interest in the chemistry of functional and speciality polymers [7-10].

In a polymer-supported ligand, the ligand group is only an infinitesimal part of the solid polymer-support, and hence it is subject to a multitude of structural variations compared to a low molecular weight ligand [11-13]. This indicates a definite dependence of the nature and degree of complexing ability of the polymeric ligand with metal ions. Correlation between the trends of complexation and the structural factors characteristic of the macromolecular matrix is important in the design and development of new and selective complexing agents for metal ions.

This paper attempts to draw a correlation between such variables of a macromolecular matrix as the molecular character and degree of crosslinking on the complexing ability, and the physicochemical characteristics and thermal decomposition behavior of the derived amino ligands. For this, polyacrylamides with 2-20 mol% of divinylbenzene (DVB), *N,N′*-methylene-bis-acrylamide (NNMBA), and tetraethyleneglycol diacrylate (TEDGA) crosslinks were selected. Complexation with Cu(II) ion is taken as the model reaction for these investigations.

EXPERIMENTAL

All the reagents used were of certified ACS reagent grade. IR spectra were recorded on a Shimadzu 470 IR spectrophotometer and EPR spectra on a Varian E-12 spectrometer. TG curves were recorded on a Delta Series TGA 7 Thermal Analyser at a heating rate of 20°C/min under nitrogen atmosphere.

Preparation of Functional Polyacrylamides

The preparation and functionalization of polyacrylamides with 2-20 mol% of DVB, NNMBA, and TEGDA crosslinks are reported [14-17]. Amino functions were introduced into the crosslinked polyacrylamide matrices in different structural environments by transamidation with excess ethylenediamine.

Preparation of Copper(II) Complexes

The complexation of the different resins was carried out by the batch equilibration method at its natural pH. Each resin (200 mg) was stirred with a definite concentration of excess cupric sulfate solution (0.015 meq/L) for 24 hours. The complexed resins were collected by filtration, washed with excess deionized water, and dried. The concentration of copper salt solutions was determined by iodometry [18].

Time Course of Complexation

Each of the 4% crosslinked amino resins (500 mg) was mixed with 100 mL cupric sulfate solution (0.03 N) and stirred at room temperature. Aliquots were withdrawn from the test solution and determined at regular intervals.

Kinetics of Complexation

Different sets of 8% crosslinked amino resins (100 mg) were stirred with cupric sulfate solution (6.5×10^{-3} N, 100 mL) at two different temperatures in a thermostatically controlled system for varying time intervals. The remaining concentration of Cu(II) ions in each case was determined.

Adsorption Studies

Different sets of 100 mg of 8% crosslinked amino resins were equilibrated with Cu(II) salt solution of varying concentrations at two different temperatures. The Langmuir and Frumkin equations are used for adsorption studies.

Swelling Studies

Each of the amino resins (500 mg) was equilibrated with 30 mL distilled water for 48 hours. The swollen resins were collected by filtration (adhering traces of water were removed by pressing with filter paper and weighed), dried in vacuum for 24 hours, and weighed. Another set of resins was equilibrated with 30 mL cupric sulfate solution containing 0.66 meq Cu(II), and the weights of the wet and dried resins were recorded. From the swollen and dried weights of the samples, the equilibrium water content (EWC) was calculated by using the equation

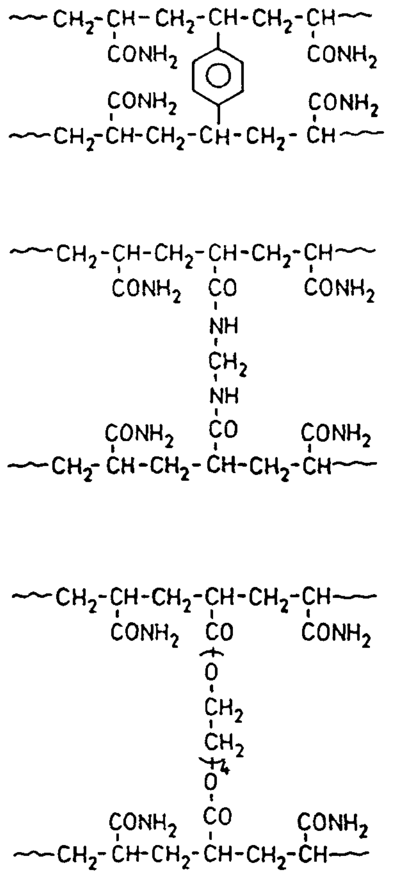
$$\text{EWC}(\%) = \frac{(\text{weight of wet resin}) - (\text{weight of dry resin})}{(\text{weight of wet resin})} \times 100$$

RESULTS AND DISCUSSION

Preparation of Amino Resins

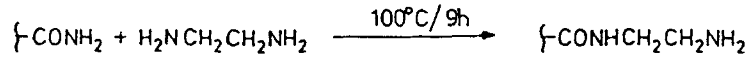
Acrylamide was copolymerized with DVB, NNMBA, and TEGDA (2–20 mol%) by free radical solution polymerization. These crosslinking agents vary widely in their polarity and flexibility. DVB is rigid and hydrophobic while TEGDA is flexible and hydrophilic. A hydrophilic–hydrophobic balance exists in TEGDA because of the presence of the hydrogen bonding ether oxygens and lipophilic dimethylene groups in the crosslinking agent. NNMBA has a rigidity and flexibility intermediate between DVB and TEGDA. The three crosslinked polymeric systems are represented in Scheme 1. An increasing amount of crosslinking agent in the polymer matrix led to increased rigidity because of the increasing number of consecutive crosslinking points.

These resins were converted to the corresponding poly(*N*-2-aminoethylacrylamide)s by transamidation with excess ethylenediamine at 100°C for 10 hours as represented in Scheme 2.



SCHEME 1. From top to bottom, DVB, NNMBA, and TEGDA crosslinked polyacrylamides.

In the DVB-crosslinked system, the amino capacity decreases with increasing rigid and hydrophobic crosslinking. This observation is similar to the decrease in reactivity with the amount of crosslinking agent [19]. For the NNMBA-crosslinked system, the capacity increases with increasing crosslinking, reaches a maximum at 8%, and decreases thereafter. But in the TEGDA-crosslinked system, the amino capacity decreases up to 4% and increases thereafter. These trends in the variation of the extent of functionalization and hence the amino capacity on the nature and degree of crosslinking are depicted in Fig. 1. The high amino capacity of the TEGDA-crosslinked system is expected because of the increased availability of amide groups for transamidation at low crosslinking. The flexible and polar nature of



SCHEME 2. Preparation of polyacrylamide-supported amines.

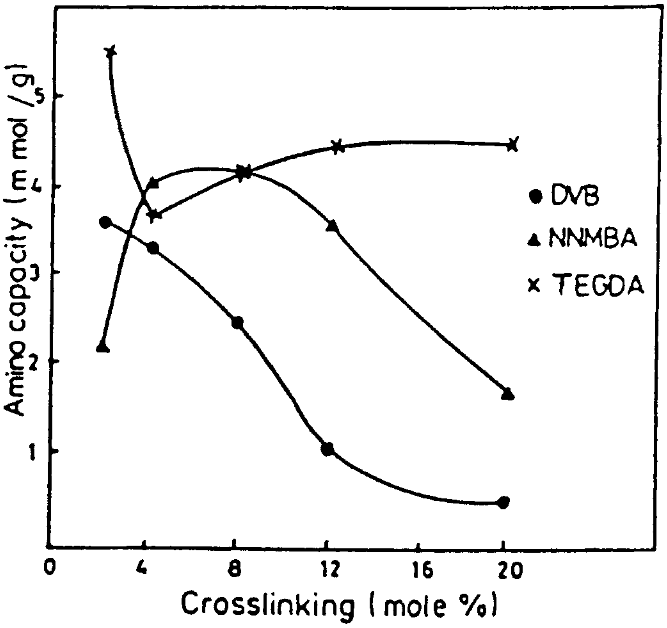


FIG. 1. Dependence of transamidation on the extent of DVB, NNMBA, and TEGDA crosslinking.

the crosslinking agent favors transamidation in the polar surroundings, while the semirigid NNMBA-crosslinked system has intermediate values. The higher capacities of the lightly crosslinked DVB and TEGDA systems can be explained as due to the increased accessibility of the reactive sites for transamidation. The anomalous observation of the low amino capacity of the 2% NNMBA-crosslinked system could be due to the heterogeneity developed in the polymer matrix during polymerization which leads to the formation of microdomains [20]. In this case the capacity increases up to 8% crosslinking and decreases thereafter. Similar observations of increased reactivities of NNMBA-crosslinked polyacrylamides with moderate (8–10 mol%) crosslinks are reported [8, 10], but in the TEGDA system the capacity increases after 8% crosslinking. This appears to be due to the additional contribution of amino groups formed by the cleavage of the ester groups under the basic transamidation conditions. This contribution increases with increasing TEGDA crosslinking. The cleavage of the ester groups of the oligoethyleneglycol diacrylate crosslinks with four or more ethyleneglycol units are reported [21].

Complexation with Copper(II)

The complexation of amino resins with ligand functions in different structural environments was investigated for Cu(II) ions. The Cu(II) intake by different amino resins is given in Fig. 2. The trend in complexation is similar to the ligand capacities of the resins. For the DVB-crosslinked system, the extent of crosslinking was found to exert a striking influence on the complexing ability in the complexation with copper. The metal ion intake decreases drastically with DVB content. The

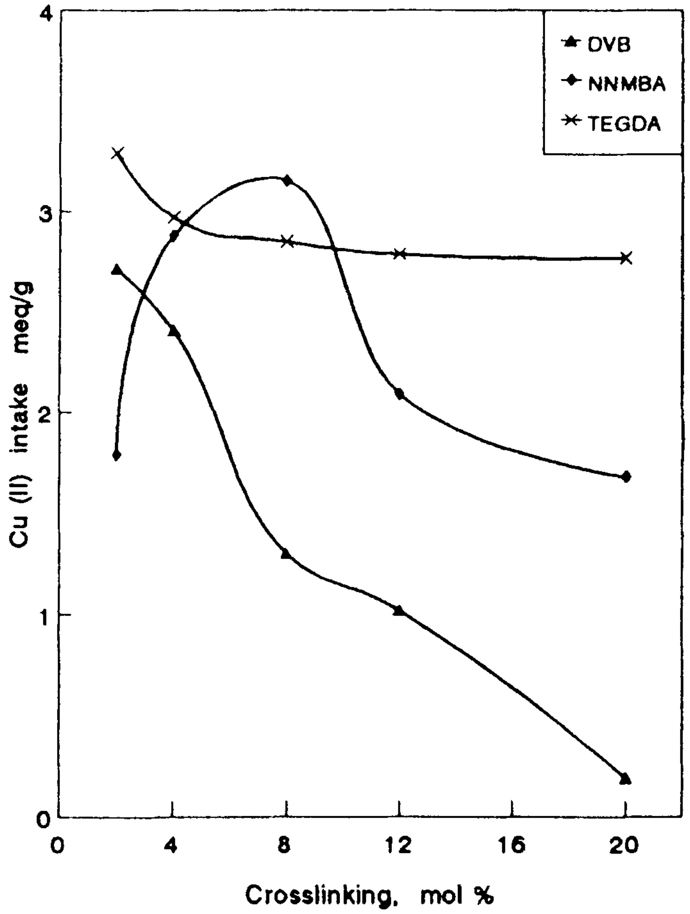


FIG. 2. Comparison of Cu(II) intake by the amino resins.

complexation of NNMBA-crosslinked resins increases with the extent of crosslinking, passes through a maximum at 8%, and then decreases. Generally, a higher metal ion intake would be expected for a low crosslinked system because of the increased availability of ligand functions [22], but the heterogeneity developed in the polymer matrix leads to low metal ion intake for low crosslinked systems. This is also observed in the swelling characteristics of this set of amino resins. The Cu(II) intake by the TEGDA-crosslinked systems decreases gradually with increasing crosslinking and remains almost the same because of the increased concentration of amino functions in the polymer support as well as the increased availability of ligands due to ruptured and random crosslinking.

On comparing these three systems, the influence of the molecular character and degree of crosslinking on complexation is clearly evident. Cu(II) intake by hydrophilic and flexible TEGDA crosslinking is higher while that of the rigid and hydrophobic DVB-crosslinked system is lower. The NNMBA-crosslinked system has values intermediate between these two.

The hydrophilic nature of the polymer matrix is important in the interaction of metal ions in an aqueous medium. The hydrophilic TEGDA crosslinks make for easy interaction of the ligand functions with the metal ions in an aqueous medium. This is exemplified by the very low metal intake of DVB-crosslinked systems. The complexed cupric ions can be eluted using dilute acids. Recyclability of the neutralized amino resins is possible.

Time Course of Complexation

In order to optimize the time required for copper complexation, batch studies were carried out for the 4% crosslinked resins by noting the change in concentrations of the metal salt solutions at regular time intervals. For the DVB-crosslinked system the complexation was completed in 2.5 hours, for the NNMBA-crosslinked system 2 hours, and for the TEGDA-crosslinked system less than 2 hours. The accessibility of reactive sites for metal ions increases with increasing flexibility.

Kinetics of Complexations

In order to evaluate the energy of activation (E) and entropy of activation (S^*) of complexation, parallel studies were carried out at two different temperatures. Aminopolyacrylamides with particles in the 80 to 100 μm range were used for the investigation. The results are in agreement with first-order kinetics. The kinetic parameters were calculated by the Arrhenius equation. In the case of DVB-crosslinked amino resins, the rate constant at higher temperature (318 K) is double that at 306 K. The activation energy for complexation is 82.41 kJ/mol, the Arrhenius parameter is $1.145 \times 10^9 \text{ s}^{-1}$, and the entropy of activation is -71.628 J.

The nature of complexation of NNMBA- and TEGDA-crosslinked amino resins was found to be different from that of the DVB-crosslinked system. This appears to be due to the increased availability of ligands due to diffusion of the solvent molecule with the metal ions into the polymer matrix, and it increases with increasing flexibility/hydrophilicity of the crosslinking agent. Hence, the kinetics of the complexation of TEGDA-crosslinked amino resin could not be followed at higher temperatures. In these two cases, the specific rate constant at higher temperatures was found to be smaller. This arises from the exothermicity of the complexation process and the dissociation of the complex, leading to an overall decrease in the rate.

Adsorption Approach to Complexation

The complexation of a metal ion by a polymer-supported ligand is a heterogeneous reaction and involves 1) diffusion of metal ions into the polymer matrix, 2) adsorption on the surface, and 3) a reaction which may or may not be followed by desorption. In the case of adsorption, there are two possible approaches: 1) adsorption without any interaction with neighbors—Langmuir Type, and 2) adsorption invoking interaction between the neighbors—Frumkin Type [23, 24]. The two possibilities are considered in the present investigation.

Langmuir Type. The adsorption/complexation of 8% DVB-, NNMBA-, and TEGDA-crosslinked aminopolyacrylamides with Cu(II) ions was carried out at two different temperatures with varying concentrations of metal salt solution until equilibrium was reached. The Langmuir equation was taken in the form

$$\frac{C_f}{C_m} = \frac{1}{KA_s} + \frac{C_f}{C_m}$$

where C_f and C_m are the concentrations of the free and complexed copper ions in meq/L or meq/g, K is the stability constant, and A_s is the surface area covered by the metal ions. Plots of C_f/C_m against C_f are given in Fig. 3. The kinetic parameters were calculated using the Arrhenius equation. The adsorption and kinetic parameters are given in Table 1. The specific rate contant decreased with an increase in temperature, but the free energy of activation becomes more positive with increasing flexibility of the crosslinking agent. The larger the surface area covered, the higher will be the repulsive force. This leads to an increase in the number of collisions for complexation to occur. A more positive value for the free energy of activation suggests a decrease in the spontaneity of the complexation.

The high energy of activation, specific rate constant, and the more negative value of free energy of activation support the view that increased complexation can occur at higher temperatures. With an increase in temperature, the latent reactive sites in the possibly coiled crosslinks become more exposed, thereby enhancing complexation. The entropy of activation shows the disordering of the ordered structure of the polymer matrix by the increased diffusion of the solvents into the crosslinks, making them uncoiled, resulting in increased complexation.

Frumkin Type. In order to investigate the interaction effect in complexation, the Frumkin equation was chosen. The equation is given

$$C_f = \frac{C_m}{(C_f - C_m)K_1} e^{-K_2C_m/C_f}$$

where K_1 is the adsorption constant and K_2 is the interaction constant. The experimental data obtained for the Langmuir Type was used. Plots of $\ln[C_m/C_f(C_f - C_m)]$ vs C_m/C_f are given in Fig. 4. The adsorption and kinetic parameters are given in Table 2. The free energy of activation for interaction is of the same order of magnitude for all systems, but the free energy of interaction is higher than the free energy of adsorption and depends on the nature of the polymer support. In the DVB-crosslinked system, the free energy of interaction is higher than the free energy of adsorption whereas in matrices with flexible crosslinks the free energy of interaction is lower because of the swollen polymer matrix. In the case of the DVB-crosslinked system, the semirigidity of the polymer matrix needs a higher activation energy for complexation.

Swelling Studies

The complexation of a metal ion with a polymer-supported ligand in an aqueous environment is governed by the extent of swelling of the crosslinked polymer in water [25]. The polymer cannot dissolve due to its three-dimensional network structure, but the chains do expand. In this case the transport of metal ions into the polymer network is diffusion-controlled. The extent of swelling depends on the nature and degree of the crosslinking agent. In the complexation of polymeric

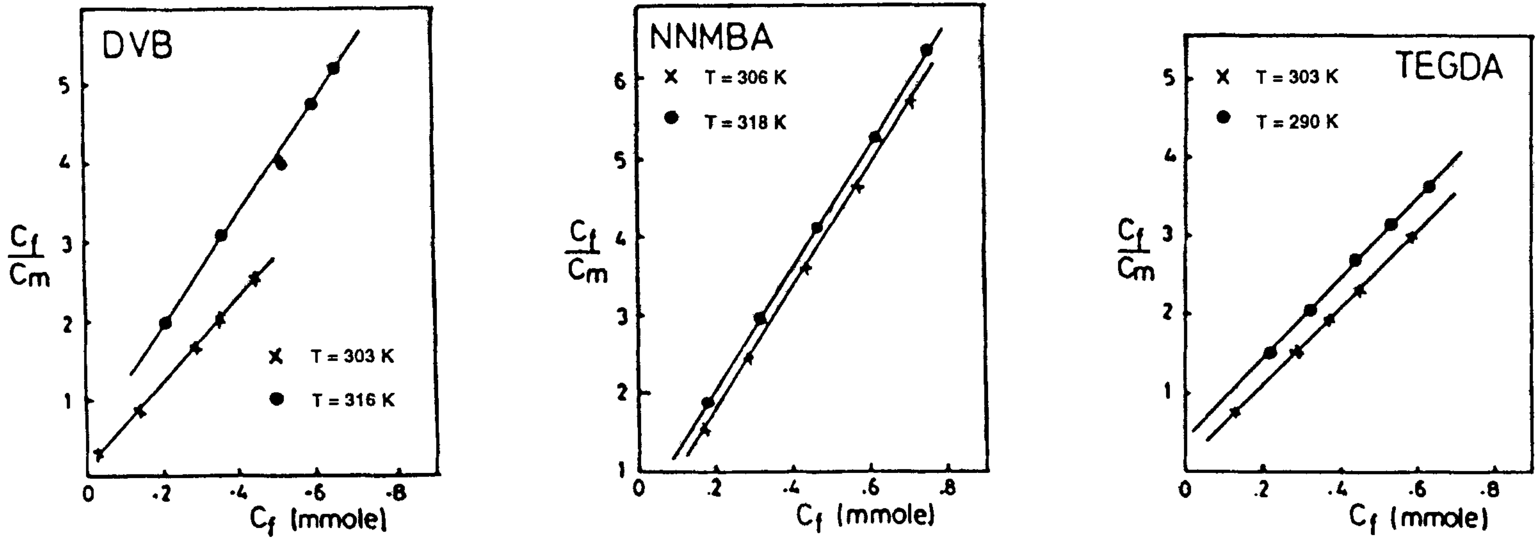


FIG. 3. Langmuir plots for copper intake by 8% DVB, NNMBA, and TEGDA crosslinking.

TABLE 1. Adsorption and Kinetic Parameters for the Cu(II) Complexation of 8% DVB-, NNMBA- and TEGDA-Crosslinked Polyacrylamide-Supported Amines

Crosslinking	Kinetic parameters			Temperature,	Adsorption parameters		
(8%)	K, kJ/mol	A_1, S	ΔS, J	K	K, kJ/mol	A_s	A^{ϕ}, kJ/mol
DVB	31.9	8.9×10^9	+8.3	306	32.1	0.1301	−26.4
				318	20.1	0.1286	−26.2
NNMBA	18.6	1.1×10^5	+8.3	303	66.5	0.1871	−92.3
				316	1.6	0.3032	−61.1
TTEGDA	88.8	2.2×10^{20}	−225.5	290	22.5	0.1740	−36.2
				303	109.3	0.1960	−96.5

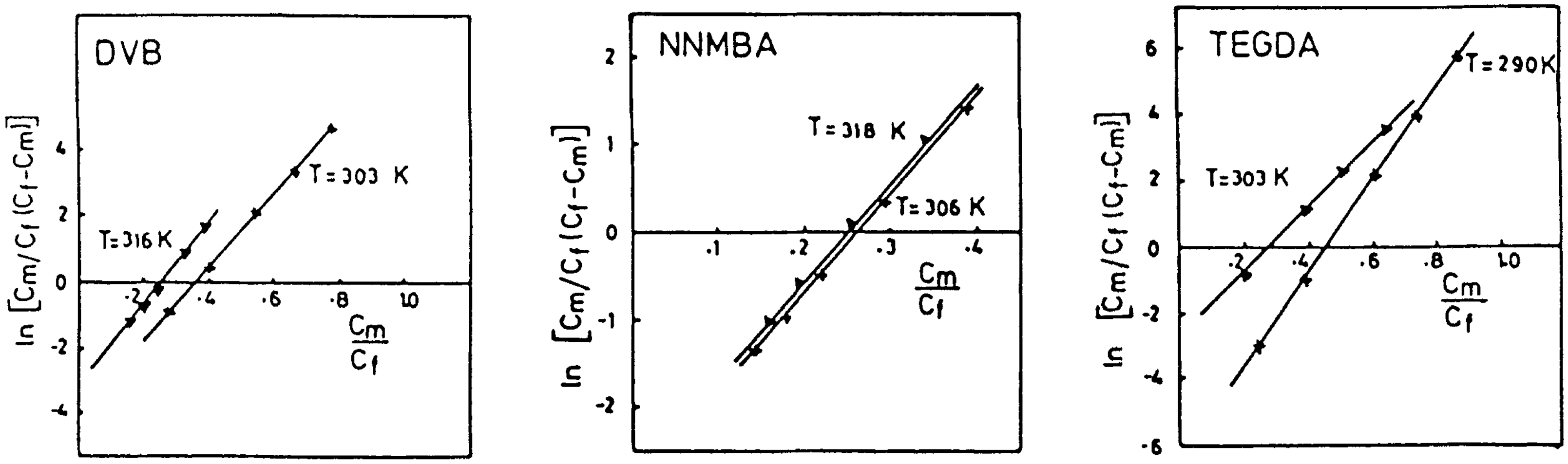


FIG. 4. Frumkin plots for copper intake by 8% DVB, NNMBA, and TEGDA crosslinking.

TABLE 2. Adsorption/Interaction Parameters and Kinetic Parameters of the Cu(II) Complexation of 8% DVB-, NNMBA-, and TEGDA-Crosslinked Polyacrylamide-Supported Amines

Crosslinking	Kinetic parameters			Temperature,	Adsorption/interaction parameters		
(8%)	E, kJ/mol	A_1, S	ΔS, J	K	K, kJ/mol	K_2, kJ/mol	A^{ϕ}, kJ/mol
DVB	6.25	1.3×10^2	−204.7	306	19.05	11.08	−25.07/−23.69
				318	9.00	12.16	−24.90/−24.10
NNMBA	13.1	1.7×10^3	−183.1	303	2.94	9.62	−20.10/−23.10
				316	3.11	11.92	−21.10/−24.70
TTEGDA	2.3	2.4×10^1	−218.63	290	2.30	9.70	−18.60/−22.10
				303	3.20	10.10	−20.30/−23.20

ligands with metal ions, the macromolecular matrix contracts by inter/intrachain complexation with metal ions. For a network structure they are forced to assume a more elongated and less probable configuration as the network expands. Hence high crosslinking lowers the swollen volume whereas in solvents which are compatible with the polymer the swollen volume will increase. A high degree of swelling can minimize possible diffusion problems and make all active sites available for interaction with the metal ion as in a homogeneous reaction.

The EWCs (%) of the amino systems and their Cu(II) complexes with a definite Cu(II) content are given in Table 3. The swelling of the TEGDA-crosslinked system is higher than that of NNMBA- and DVB-crosslinked systems. This is due to the hydrophilic nature of the crosslinking agent. In the DVB-crosslinked system, the water intake decreases considerably with crosslinking. This is due to the increasing number of hydrophobic crosslinking points. In the NNMBA-crosslinked system, the swelling in water increases up to 4% crosslinking and the decreases. The 4 and 8% crosslinked systems have almost the same swelling values. The 2% and highly crosslinked systems (12 and 20%) have almost the same water intake because of the possible heterogeneity in this particular polymer support [26]. In the TEGDA-crosslinked system, the decrease in water intake with crosslinking is not very significant because of rupture of crosslinks during transamidation.

The swelling of Cu(II) complexes with 1.73 meq Cu(II)/g of the resins is lower than of uncomplexed resins. This is because of the contraction of the polymer support due to the cooperative contribution of the ligands for complexation [27]. This reduction is much less in the DVB-crosslinked system and decreases with increasingly rigid DVB crosslinks. In highly crosslinked DVB systems the ligand functions are located mainly on the surface and hence are easily available for the metal ions without introducing much distortion of the polymer chains from their normal positions. For the NNMBA-crosslinked system the maximum difference is for 8% crosslinking. In TEGDA-crosslinked systems the difference in swelling by complexation increases with the extent of TEGDA content. The cleavage of a considerable number of the crosslinks during transamidation is the reason for the larger difference in complexation. The complexation of ligands in such a loosely connected network results in a marked decrease in water intake after complexation.

TABLE 3. Swelling Characteristics of DVB-, NNMBA-, and TEGDA-Crosslinked Aminopolyacrylamides and Cu(II) Complexes[a]

	EWC (%), for mol% crosslinking values of				
System	2	4	8	12	20
DVB	78 (72)	68 (61)	56 (53)	40 (37)	34 (32)
NNMBA	63 (60)	80 (78)	78 (59)	63 (55)	57 (53)
TEGDA	84 (74)	82 (72)	80 (70)	76 (68)	74 (55)

[a] Values in parentheses are for complexed resins.

IR Spectra

The IR spectra of the various crosslinked polyacrylamides and amino resins showed characteristic absorptions of the carbonyl, amide, and amine groups in addition to absorptions of the respective crosslinking agents. The carbonyl peak was observed at 1660 cm^{-1}. The peak at 1445 cm^{-1} is the C—N stretch of the amide group. For the DVB-crosslinked polyacrylamide, the peak at 800 cm^{-1} arises from the aromatic ring in the crosslinking agent. For NNMBA, the peak in the 1590-1500 cm^{-1} region is characteristic of the secondary amide group in the crosslinking agent. The absorption at 1100 cm^{-1} corresponds to the ether units in the TEGDA crosslinks.

In the case of the amino resin, the broad N—H peak centered around 3500 cm^{-1} corresponds to a high degree of hydrogen bonding. The N—H stretching frequencies of the Cu(II) complexes are lower than those of the free amines and can be used for the measurement of Cu—N bond strength [28, 29]. Splitting of the broad band at 3500 cm^{-1} into two peaks, one at 3520 cm^{-1} and the other at 3440 cm^{-1}, is a clear indication of the incorporation of the amino groups by coordination with metal ions, preventing hydrogen bonding between the amino groups (Fig. 5). The peaks at 750 and 650 cm^{-1} correspond to the coordinated water molecules. Absorptions in the 400-200 cm^{-1} region are associated with Cu—N translational vibrations.

EPR Spectra

The EPR spectra of the Cu(II) complexes of aminopolyacrylamides with 8% DVB, NNMBA, and TEGDA crosslinks are given in Fig. 6. The EPR parameters are given in Table 4. The values suggest a distorted tetragonal geometry for the Cu(II) complex [29]. The value of $g \leq 2.3$ suggests the covalent nature of the Cu—N bond. The bonding parameter (α^2Cu) of the complex, which is a measure of the in-plane σ-bonding of the Cu—N bond [30], was found to be in the 0.799 to 0.808 range. The covalency of the Cu(II) complex increased with increasing flexibility of the crosslinking agent. The geometry of the complex also became more stable, resulting in decreased strain. A similar variation of the EPR parameters of amine-Cu(II) complexes with the extent of crosslinking and the presence of a spacer between the polymer matrix and the ligand have been reported [31, 32].

Thermogravimetric Studies

In the present investigation the thermal decomposition behavior of the Cu(II) complexes of amino resins for varying numbers of DVB and NNMBA crosslinks were followed in order to trace the dependence of the molecular character and the extent of crosslinking on the thermal decomposition patterns (Fig. 7). The TG curves showed three stages of decomposition. The first decomposition was in the 304 to 513 K temperature range, which corresponds to the removal of adsorbed and coordinated water molecules. The second decomposition occurs by the decomposition of free amide groups. Except in 2 and 4% DVB-crosslinked systems, the third stage is the major decomposition and is used for kinetic analysis. In 2 and 4% DVB-crosslinked systems, the third stage corresponds to the decomposition of un-

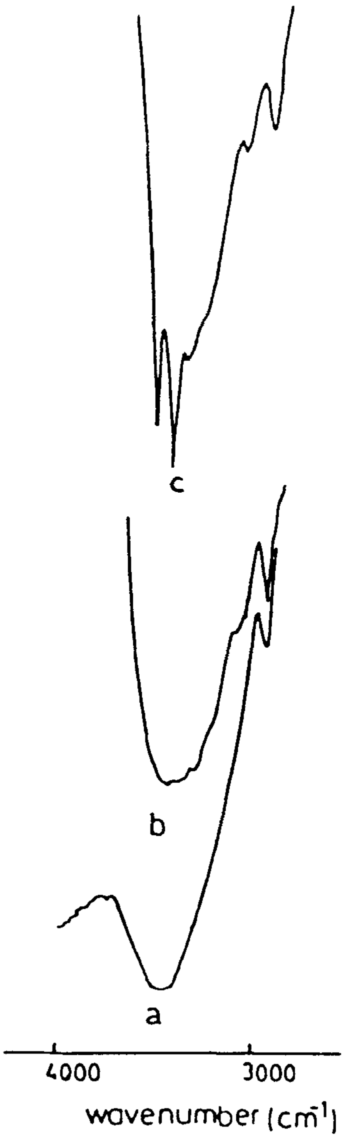


FIG. 5. IR spectra of the NH_2 groups of the (a) amide, (b) amine, and (c) Cu(II) complexed resins.

complexed amino groups. In these two systems, the fourth stage is used for kinetic analysis.

The kinetic parameters were calculated using the approximation equation by the least-squares method [33]. The thermal stabilities of the complexes were found to be higher than those of the uncomplexed resins [34]. The activation energy (*E*) of the DVB-crosslinked aminopolyacrylamides was in the 253.5 to 203.4 kJ/mol range, but in the NNMBA-crosslinked system the *E* values range from 304.4 to

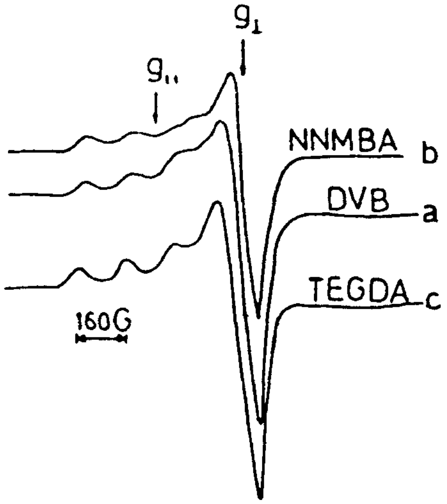


FIG. 6. EPR spectra of the Cu(II) complexes of aminopolyacrylamides with 8% DVB, NNMBA, and TEGDA crosslinking.

235.3 kJ/mol. Thus the thermal stabilities of the rigid DVB-crosslinked system are lower than those of the semirigid NNMBA-crosslinked system. In all these complexes the activation energy (E) and the extent of crosslinking (C) fit into the general equation for a cubic polynomial of the type

$$E = a + bC + cC^2 + dC^3$$

obtained by simplifying a quadratic equation. The specific equation for the DVB-crosslinked system is

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

and for the NNMBA-crosslinked system

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

In the case of amine-copper complexes, the E value decreases with increasing crosslinking, reaches a minimum, and increases thereafter. The curve tends to take the shape of a parabola within experimental limits (Fig. 8). The availability of

TABLE 4. EPR Parameters of the Cu(II) Complexes of Aminopolyacrylamides with 8% Crosslinking

Crosslinking	$g_\parallel$	$g_\perp$	$A_\parallel$	$A_\perp$	α^2Cu
DVB	2.3004	2.0937	155	41.667	0.8083
NNMBA	2.2943	2.0911	155	35.000	0.8010
TEGDA	2.2938	2.0898	160	41.600	0.7999

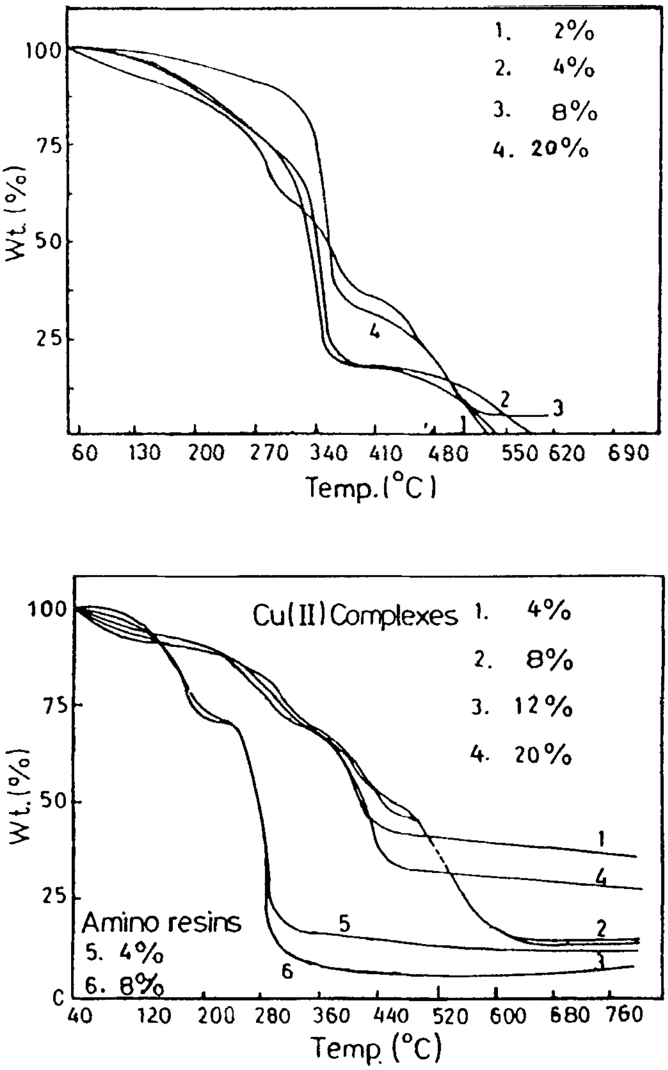


FIG. 7. TGA curves of the Cu(II) complexes of aminopolyacrylamides. Top: DVB crosslinked. Bottom: NNMBA crosslinked.

ligands for the formation of stable ring structures decreases with increasing crosslinking because of the reduced availability of ligands with an increasing number of crosslinks. After 8–15 mol% crosslinks, the functionalization presumably occurs mainly on the surface of the polymer matrix. Thus the availability of ligands for complexation results in stable ring structures after a definite extent of crosslinking. This results in increased thermal stability of the complexes after a particular level of crosslinking.

The entropies of activation for the decomposition of Cu(II) complexes are higher than those of uncomplexed resins. This arises from the distortion of the

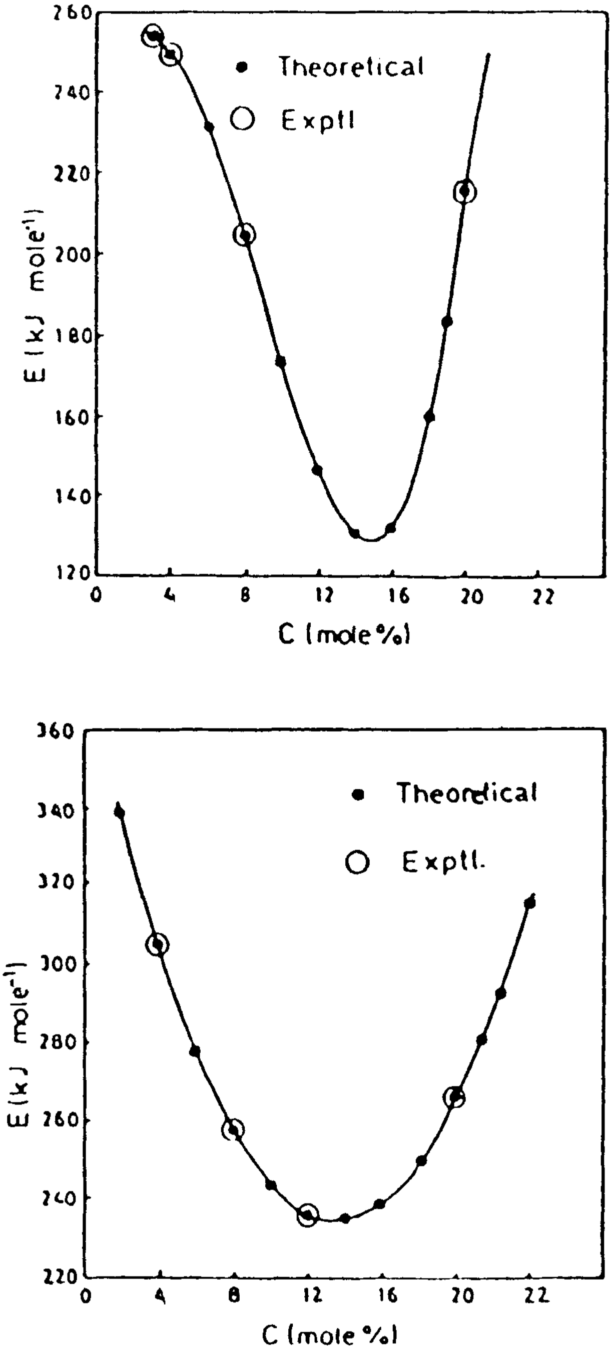


FIG. 8. Activation energy vs extent of DVB (top) and NNMBA (bottom) crosslinking in Cu(II) complexes of polyacrylamides with amino functions.

polymer chains from their normal positions for complexation with metal ions. In the DVB-crosslinked system the entropy of activation decreases with increasing crosslinking (+28.9 → −37.7 J). This arises from the decreased distortion of the polymeric ligand with increasing rigid DVB crosslinking. In the highly crosslinked system the ligands are concentrated mainly on the surface and are easily available for the metal ions. This results in a decreased change in entropy. In the NNMBA-crosslinked system the entropy of decomposition did not show a general trend. The values are 161.5 J (4%), 89.4 J (8%), 103.6 J (12%), and 89.3 J (20%). The entropy of activation for decomposition is more positive in the Cu(II) complexes of the NNMBA-crosslinked system. This is because of the decreased rigidity of the NNMBA crosslinks which cause more distortion of the polymer chains compared to their normal positions on complexation. In Cu(II) complexes with varying extents of NNMBA crosslinking, the entropy variation is similar to the activation energy variation.

CONCLUSION

The extent of functionalization, metal ion intake, kinetics of complexation, interaction between complexed species, and swelling characteristics of the resins are decided by the relative rigidity/flexibility as well as the polarity and extent of crosslinking agents in the insoluble polymer support. Complexation leads to shifting and splitting of the IR absorptions of the ligands. The EPR parameters of the amine–Cu(II) complexes suggest a more stable tetragonal geometry for the flexible TEGDA-crosslinked system. The thermal stabilities of the Cu(II) complexes are higher than those of the uncomplexed resins. This points to the possibility of modification of the physicochemical, thermal, and mechanical properties of the macromolecular metal complexes by adjusting the most important structural parameters, the molecular character, and the extent of crosslinking in the three-dimensional polymer matrix.

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