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The spatial organisation of macromolecular metal chelates

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Abstract. **The spatial organisation of metallopolymers (macromolecular metal chelates) is analysed on three levels; local, molecular, and supermolecular. The thermodynamic features of the formation of chelates with polymeric ligands are examined and data are presented concerning the dependence of the structure of the chelate units on various factors. The principal changes which the macrochain may undergo on formation of metal chelate centres are considered. The behaviour of the macromolecular ligands and their low-molecular-mass analogues is compared on the molecular level. The principal characteristics of the formation of intramolecular and intermolecular complexes are listed and the causes of their stability are examined. The bibliography includes 125 references.**

I. Introduction

The problems of the chemistry of macromolecular metal chelates (MMC)† have attracted increased attention by investigators during recent years.[1–9] As a result of the efforts of specialists in various fields (polymer, coordination, bioinorganic, and analytical chemistry, catalysis, etc.), considerable advances have now been achieved in the MMC chemistry. Thus numerous MMC containing virtually any metals in the Periodic System have been obtained, their physicochemical properties have been investigated, and their principal structural characteristics have been elucidated. However, the quantitative parameters of the chelate formation process involving macromolecular ligands have so far been studied inadequately,[11] in contrast to the low-molecular-mass metal chelates‡ (LMC). This has been explained by the need to take into account a whole series of additional factors, in the first place those arising from the chain nature of the ligand. It is useful to examine three levels of the spatial organisation of the MMC:

1. the local level, which reflects the chemical structure of a single chelate unit in the chain molecule (the nature of the complex forming metal and of the electron-donating atoms, the ring size, the steric structure of the ring, etc.);
2. the molecular level, which is determined by the chemical structure of the polymer chain (the chain length, the elemental composition of the repeat units, the shape and conformation of the chain, etc.);
3. the supermolecular level, which reflects the nature of the intermolecular interaction of the macromolecules and the degree of their mutual order.

Taking these three levels of the spatial organisation of the MMC into account, the free energy of formation of the chelates involving macroligands can be represented (on the assumption that its components are additive) by the equation[12]

$$\Delta G = \Delta G_1 + \Delta G_2 + \Delta G_3 , \quad (1)$$

where ΔG_1, ΔG_2, and ΔG_3 are the free energy changes for the local, molecular, and supermolecular levels respectively. Under certain conditions, the free energy change for a particular level may be neglected, which makes it possible to analyse in detail the enthalpy (ΔH) and entropy ($T\Delta S$) contributions to ΔG for each level.

$$\Delta G = \Delta H - T\Delta S \quad (2)$$

Taking this into account, the characteristics of the steric structure of the MMC on each level are analysed in the present review.

II. The local level of the structural organisation of metallopolymers

Initially we shall consider dilute solutions of polymers, i.e. solutions in which chain association may be neglected. Then $\Delta G_3 \to 0$ and Eqn (1) can therefore be expressed in the form

$$\Delta G = \Delta G_1 + \Delta G_2 . \quad (3)$$

† A characteristic feature which makes it possible to identify fairly reliably chemical compounds of this class in the presence of a polymer chain and of metal chelate rings.

‡ The chelate effect in the LMC is one of the most interesting phenomena in the thermodynamics of intermolecular interactions.[10]

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In the case of infinitely long chains ($l \to \infty$) and low degrees of conversion§ with respect to the chain molecule ($\alpha \to 0$), the chelation process may not exert a significant influence on the form and conformation of the macromolecule, so that $\Delta G_2 \to 0$ and hence

$$\Delta G = \Delta G_1 \ . \qquad (4)$$

Thus, in the case of dilute solutions with $l \to \infty$ and $\alpha \to 0$ the chelating macroligand behaves similarly to its low-molecular-mass analogue and the familiar Flory principle then operates: when the components of the model reaction are chosen correctly, the reactivity of the binding centres is independent of whether they belong to the polymer chain or to the low-molecular-mass analogue. This makes it possible to exclude from consideration the molecular and supermolecular levels and to analyse only the local chelate units. The entropy and enthalpy components of ΔG in the case of MMC are determined mainly by the same contributions as in the case of LMC. Since the nature of the complex-forming metal and the electron-donating groups is the same in both cases, the enthalpy of chelate formation changes little on passing from LMC to MMC. For example, ΔH for the chelation of copper(II) ions by type **1** and **3** poly(amido-amines) and their type **2** and **4** low-level-mass analogues are similar (Table 1),[13] which indicates a similar steric structure of the chelate units in these compounds. Therefore, for both MMC and LMC ΔG is determined by the entropy component. This is indicated by the isotypical nature of the dependences of ΔG and ΔS in chelation processes on the degree of conversion (Fig. 1) and also by the independence of ΔH of α (Table 1).

Table 1. Thermodynamic functions for the formation of copper(II) complexes (in kJ mol^{-1} and J mol^{-1} K^{-1}).

Ligand	ΔG	$-\Delta H$	ΔS
1	51.5–47.3[a]	30	72–58[a]
2	57.0	30	90
3	37.2–33.1[b]	16	71–58[b]
4	34.5	17	58

[a] Degree of conversion $\alpha = 0.45-0.85$.
[b] Degree of conversion $\alpha = 0.18-0.88$.

Formally the chelation reaction can be divided into several hypothetical elementary stages and the entropy of the entire process can be expressed as follows:

$$\Delta S_1^0 = \Delta S_{solv} + \Delta S_4^0 = \Delta S_2^0 + \Delta S_3^0 + \Delta S_5^0 + \Delta S_4^0 \ ,$$

§ The degree of conversion α is defined as the ratio of the actual number of metal ions bound to one chain and the maximum possible number.

where ΔS_1^0 is the experimental entropy of the reaction in solution, ΔS_4^0 is the calculated theoretical entropy of the reaction in the gas phase, ΔS_{solv} is the entropy of solvation of the metal ion (ΔS_2^0), of the ligand (ΔS_3^0), and of the complex formed (ΔS_5^0), which is determined as the difference between the entropies in solution and in the gas phase.

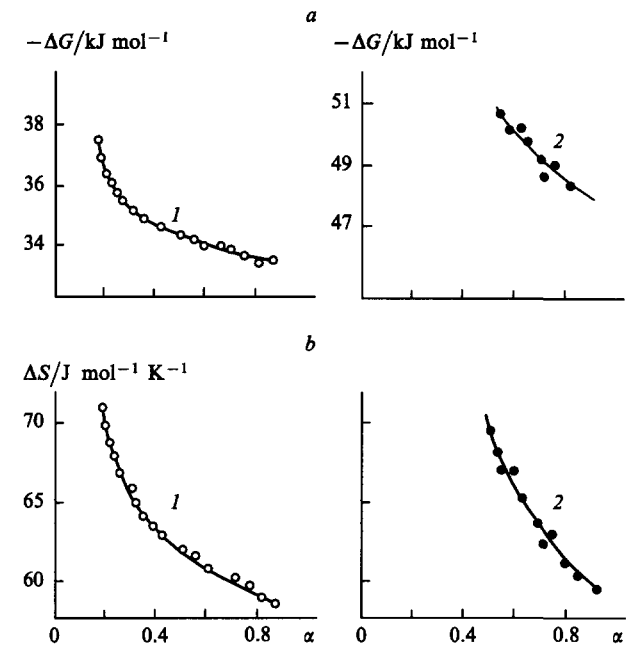


Figure 1. Dependence of ΔG (*a*) and ΔS (*b*) for the formation of copper(II) chelate complexes of poly(amidoamines) of types **1** (curve *1*) and **3** (curve *2*) on the degree of conversion.

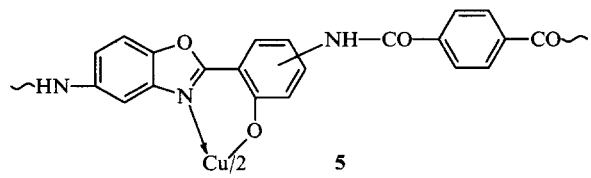
ΔS_4^0 represents in its turn the sum of the entropies of transfer (ΔS_t), internal rotation ($\Delta S_{int.rot}$), symmetry (ΔS_{sym}), isomerisation (ΔS_{isom}), vibration (ΔS_{vib}), and rotation (ΔS_{rot}).[14]

$$\Delta S_1^0 = \Delta S_{solv} + \Delta S_t + \Delta S_{int.rot} + \Delta S_{sym} + \Delta S_{isom} + \Delta S_{vib} + \Delta S_{rot} \ .$$

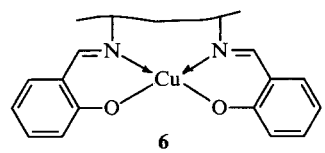
It is assumed[14] that the positive contributions to the entropy component of ΔG come from ΔS_t, ΔS_{rot}, ΔS_{sym}, and ΔS_{isom}. The contribution of ΔS_t, due to the change in the number of species on chelation, apparently changes little on passing from LMC to MMC. Consequently the entropies of chelation are similar in the two cases, since the contribution of the transfer process is the main one. ΔS_{rot} makes a definite contribution to the entropy component. It is smaller in the case of MMC than in the reaction with monodentate ligands because the initial macroligand and the MMC formed are nonrotating species. The symmetry groups for the low- and high-molecular-mass compounds are significantly different and the number of possible isomers of polymeric chelates may be smaller, so that the contribution of isomerisation is in this case reduced. Thus the nickel(II) chelate complexes with salicylaldimine ligands exist in two isomeric forms: planar (green) and tetrahedral (brown). Only a paramagnetic pseudo-tetrahedral form has been obtained on a polymer base[15] even under conditions where the diamagnetic isomer is formed preferentially in the low-molecular-mass system.[16]

ΔS_{vib}, $\Delta S_{int.rot}$, and ΔS_{solv} makes negative contributions to the entropy component.[14] It is postulated that the contributions by the vibration and internal rotation are much lower in the case of the high-molecular-mass system than in the case of the LMC. If the monomeric and polymeric chelating ligands form structurally identical chelate units, then the contribution of solvation is approximately the same in both cases. However, as a rule such cases are rare and the polymer chain exerts a significant influence

on the structure of the local chelate unit with the possibility of the formation of structures which are both less and more distorted than the LMC. As an example, one may quote the copper(II) chelate complex of poly(hydroxyphenylbenzoxazole-terephthalamide) **5**, which has a distorted tetrahedral structure like its low-molecular-mass analogue. However, a somewhat higher value of A and a lower value of g in the EPR spectra compared with the LMC are characteristic of the MMC, which indicates a smaller dihedral angle.[17] On the other hand, in the case of the salicylaldimine ligands the structures of the chelate units are different in the LMC and MMC: planar in the LMC and distorted tetrahedral in the MMC (complex **6**).[15] In conformity with the change in the stereochemistry of the chelate unit, an increase or a decrease in the contribution of solvation is observed.

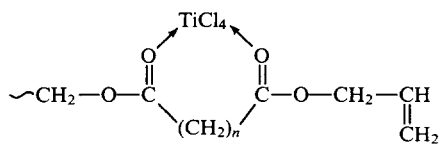


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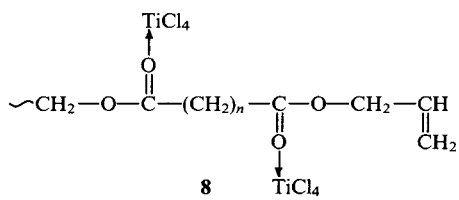


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As for the LMC, the free energy ΔG in the case of polymeric ligands depends to a large extent on the size of the chelate ring. The familiar Chugaev ring rule holds for the MMC: five- and six-membered rings prove to be the most stable. The influence of ring size on the mechanism of the binding of metal ions by polymers can be illustrated in relation to the formation of complexes between $TiCl_4$ and the copolymers of styrene and the diallyl esters of dicarboxylic acids.[18] For n = 1 or 2, a mixture of complexes with the *cis*-disposition (complex **7**) or *trans*-disposition (complex **8**) of the carbonyl groups is formed. Both in the initial ligand and in the MMC, there are two nonequivalent carbonyl groups, but the difference between the vibrational frequencies $\Delta\nu$(C=O) for the *cis*- and *trans*-forms increases from 10–15 to 40–45 cm^{-1}. This indicates a more rigid fixation of the isomers on complex formation. The increase in the size of the separating bridge ($n > 3$) precludes the formation of chelates.



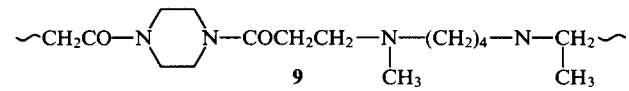
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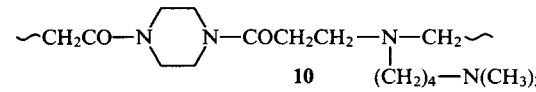
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The study of copper(II) complexes of poly(amidoamines) showed that an increase in the chelate ring size from five-membered to six-membered entails a significant decrease in the stability constants or even precludes the chelation of copper(II) with formation of stable complexes. In this case, the decrease in stability is accounted for mainly by the decrease in enthalpy, since conformational freedom is reduced to a much greater extent in polymers than in low-molecular-mass compounds.[19,20]

The ligands **9** and **10**, which should form seven-membered chelate rings, do not give rise to stable complexes. Thus an increase in the length of the aliphatic chain, linking the nitrogen atoms of the monomer unit, greatly diminishes the complex forming capacity of poly(amidoamines)[19]

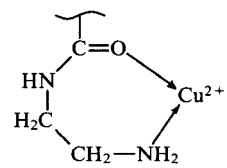


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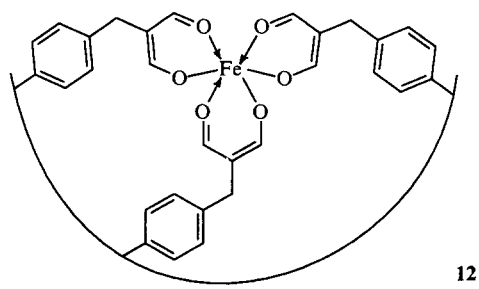
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However, since the polymer chain determines the steric structure of the chelating fragment while the metal ion selects sections of the macromolecular chain with the preferred conformation, there is a possibility of the formation of analogues of metallocycles different from the low-molecular-mass ones. For example, the interaction of copper(II) ions with vinyl polymers containing aminoalkylamide units in the side chain results in the formation of the seven-membered chelate rings **11**, the amine nitrogen atom and the amide C=O groups participating in the coordination to the metal.[21] On the other hand, in the copper(II)–glycylglycine low-molecular-mass system, five-membered rings are formed.[22] Thus, knowing the conformation of the local chelating fragment, it is possible to predict the formation of MMC with metallocycles having a particular size.



11

As well as the contributions from the entropy and enthalpy of chelating common to low- and high-molecular-mass metal chelates, a series of specific contributions are characteristic of the MMC. They include a contribution reflecting the 'adjustment' of the local chelating fragment because the interaction of metal ions with the chelating macroligand is accompanied not only by direct chemical steps (the formation of the metallocycle) but also by a change in the 'local rigidity' ¶ at the reaction site, which is determined by the change in the interaction of the valence-nonbonded chain atoms. The energy of this 'adjustment' is much smaller for soluble macroligands than the energy of chelation, so that the structure of the coordination centres is usually determined by the nature of the complex-forming metal. For example, in the interaction of an iron(III) salt with polystyrene, containing acetylacetone (acac) groups, the 'adjustment' of the polymer chain takes place in such a way that the octahedral structures **12** are formed without appreciable strain.[24]



12

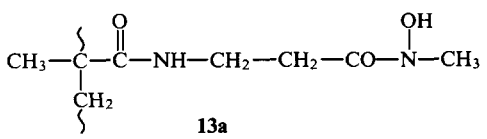
¶ In conformity with the definition given by Landau and Lifshitz,[23] the 'local rigidity' is understood as the resistance to bending of a uniform straight linear filament.

Table 2. Spectroscopic and magnetic characteristics of the monomeric and polymeric nickel and cobalt chelates with ligands of the Bipy and Phen types.

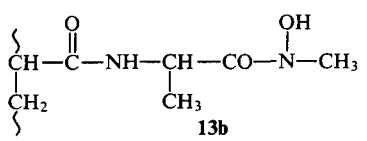
Complex	M	L	IR spectrum (principal frequencies)/cm^{-1}			Dq/cm^{-1}	B'/cm^{-1}	β	μ_{ef}/B.M.
			ν(C=C)	ν(hetero-cycle)	ν(COO$^-$)				
Monomer	Ni	Bipy	1635	1605	1565	1134	773	0.743	3.16
Polymer	Ni	Bipy	1639	1606	1560	1028	837	0.804	2.96
Monomer	Co	Bipy	1637	1610	1560	1152	834	0.859	4.53
Polymer	Co	Bipy	1638	1608	1560	1018	883	0.909	4.75
Monomer	Ni	Phen	1637	1600	1565	1166	830	0.797	3.17
Polymer	Ni	Phen	1640	1600	1560	990	857	0.823	2.95
Monomer	Co	Phen	1635	1605	1565	1163	849	0.874	4.75
Polymer	Co	Phen	1639	1608	1565	1016	884	0.911	4.87

The change in the 'local rigidity' can influence significantly the stereochemistry of the chelate unit formed. Thus the monomeric and polymeric nickel(II) and cobalt(II) chelates with ligands (L) of the type of 2,2'-bipyridyl (Bipy) and 1,10-phenanthroline (Phen) have similar spectroscopic and magnetic characteristics (Table 2), indicating the same steric structure of the chelate units.[25] On the other hand, a decrease in the splitting parameter Dq and an increase in the Racah interelectron repulsion parameter B' have been observed on passing from LMC to MMC. Bearing in mind[26] that $Dq \sim 1/a$,[6] one can assume that the decrease in the splitting parameter indicates an increase in the metal–ligand distance a in the given series. Furthermore, the nephelauxetic parameter β increases in the same series, which indicates a decrease in the degree of covalence in the metal–ligand bond. A consequence of this is, for example, a weakening of the exchange interactions on passing from low-molecular-mass dinuclear nickel(II) chelate complexes of *N*-acylsalicylamides[27] to their polymeric analogues.[28,29] It is known[30] that the bond lengths are altered less than the bond angles, so that a more pronounced distortion of the bond angles compared with the bond lengths can be expected in the MMC.

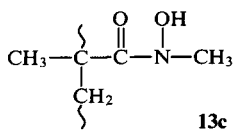
A contribution arising from the 'neighbouring groups' effect also appears in the case of the MMC. This contribution is associated with the influence of both reacted and unreacted units on the free energy of formation of the chelating fragment and hence on the structure of the chelate unit. This effect, which is explained mainly by steric factors, leads to the repulsion of the chelate units and their deformation, hindering chelate formation as the degree of conversion increases. For example, the octahedral iron(III) complexes of hydroxamic acid copolymers **13a–c** are formed without appreciable strain only when the chelating fragments are separated by 11 atoms (compounds **13a**).[31] When the number of atoms between the hydroxamic groups is $t = 7$, a slight strain arises, whereas in the case where $t = 1$ (compound **13c**) the complexes are not formed at all (Fig. 2).



13a



13b



13c

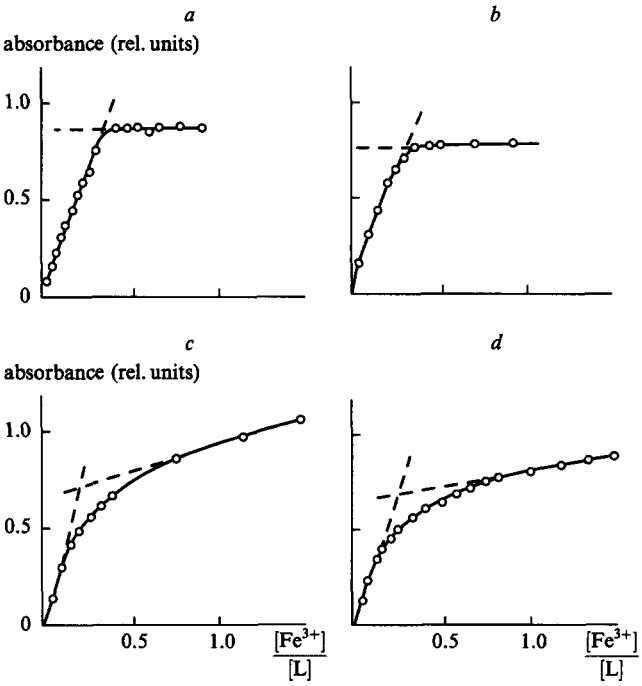
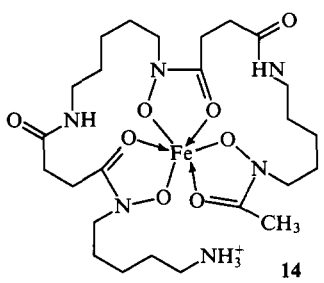


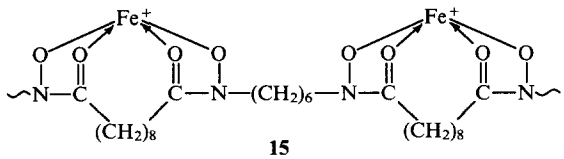
Figure 2. Determination of the composition (inflexion point) of the iron(III) complexes of deferrioxamine (*a*) and poly(hydroxamic acids) **13a** (*b*), **13b** (*c*), and **13c** (*d*).

It is noteworthy that the hydroxamic groups in deferrioxamine **14** [a low-molecular-mass ligand with a high selectivity with respect to iron(III) ions] are separated by nine atoms.



14

In contrast to copolymers containing hydroxamic groups, the formation of complexes with [M]:[L] = 1:3 is not characteristic of the homopolymer — poly(hydroxamic acid).[32] In the presence of the $-(CH_2)_8-$ bridge, the 1:2 complexes **15** are formed preferentially, whereas in the case of the bridge having the composition $-(CH_2)_6-$ a considerable strain arises, as a consequence of which the formation of octahedral complexes becomes impossible.



15

Bulky chelating ligands arranged side by side in the polymer chain preclude exchange interactions between metal ions even at a high concentration of the latter. For example, an increase in the number of copper(II) ions bound to poly(hydroxyphenylbenzoxazole-terephthalamide) (complex **5**) leads to a broadening of the EPR spectral lines as a consequence of magnetic dipole–dipole interaction between the paramagnetic centres (Fig. 3) due to the decrease in the distance between them.[17]

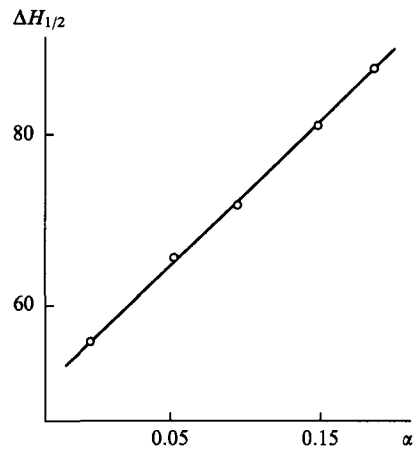


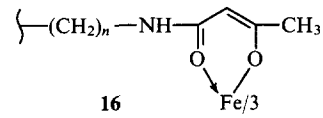
Figure 3. Dependence of the line half-width ($\Delta H_{1/2}$) on the degree of conversion for the copper(II) complex of poly(hydroxyphenylbenzoxazole-terephthalamide) **5**.

However, even for the minimum binding of copper(II) ions to the polymer, the spectrum is not fully converted into a singlet, which indicates the occurrence of exchange interactions between the metal ions. It is known[33] that cooperative effects begin to be manifested over distances of 6–9 Å; consequently the minimum distances between neighbouring copper(II) ions in such MMC exceed this quantity. This distinguishes such complexes from, for example, the copper complexes of linear polyethyleneimine (PEI), in which there is no steric hindrance to exchange interactions between the metal ions.[34] On the other hand, the uncoupling of the chelating fragments leads to the appearance of unfavourable entropy factors. In particular, a decrease in the stability constant ($\lg K$) is observed on passing from the picolinic acid-based LMC to its macromolecular analogue (the copolymer of styrene and vinylpicolinic acid [M = Cu, Ni, Co, Zn, or Mn (Table 3)].[35]

Table 3. The values of $\lg K$ for metal complexes of picolinic acid (A) and its polymeric analogue (B) (dioxane–water).

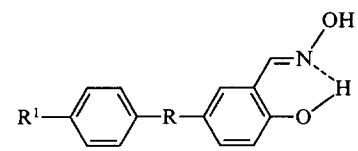
Ligand	Cu^{2+}	Ni^{2+}	Co^{2+}	Zn^{2+}	Mn^{2+}
A	12.80	12.70	12.50	12.72	9.50
B	9.88	9.56	8.28	8.44	8.44

If the chelating fragment is in a side chain, the influence of the main chain depends on the length of the connecting bridge and when the latter increases the difference between the LMC and the MMC vanishes. For example, for type **16** MMC, starting with $n = 2$, the stability of the complexes becomes virtually the same.[36]



16

The chelation process is greatly influenced also by the nature of the connecting bridge between the chelating fragment and the polymer chain. For example, the transfer of copper(II) ions from the aqueous to the organic phase (chloroform, toluene) in the formation of a complex with a hydrophobic low-molecular-mass ligand (compound **17a**) takes place very readily. On the other hand, chelation by its polymeric analogue **17b** takes place ineffectively and only the replacement of the short and hydrophobic methylene bridge in compound **17b** by the long hydrophilic ethylenediamine (compound **17c**) or methylamine (compound **17d**) unit imparts appreciable hydrophilicity and spatial mobility to the chelating fragments, which promotes the diffusion of ions in the polymeric medium and renders the ligands bound to the polymer more mobile.[37]



17a–d

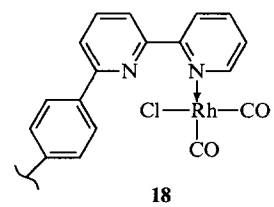
R = CH_2, R^1 = CH_3 (**a**)

R = CH_2, R^1 = polystyrene (**b**)

R = $NHCH_2CH_2NH$, R^1 = polystyrene (**c**)

R = CH_2NH, R^1 = polystyrene (**d**)

On the other hand, if the polymer chain gives rise to hindrance to the formation of chelate complexes, as in the case of polystyrene with bipyridyl groups fixed in the 4-position in the benzene ring,[38] then monodentate binding of the metal with formation of compound **18** is observed.



18

In other words, the selection of the macroligand makes it possible to follow the multistage mechanism of the formation of the MMC, to isolate the intermediates, and to stabilise the unstable (in the case of low-molecular-mass analogues) complexes.

Thus on the local level the free energy changes are similar when the components of the model reaction involving the LMC and the MMC are chosen correctly. However, it is then necessary to take into account the polymeric nature of the chelating ligand and the contributions arising from this factor to the entropy of chelation. If one considers the reaction

$$[CuX]^+ + Y^- \rightleftharpoons [CuY]^+ + X^-, \quad (5)$$

where Y = poly(amidoamine) and X = its low-molecular-mass analogues, the contribution of the transfer process is zero (the number of species remains unchanged). The free energy change can then be found from the equation

$$\Delta G = -2.303\,RT \lg K = -A_{es} - TS_{st}\,, \quad (6)$$

where A_{es} is the loss of electrostatic energy when the positively charged cation moves away from the negatively charged heteroatom on the polymer to infinity, S_{st} is a statistical factor, and $\lg K$ is defined by the expression

$$\lg K = \lg K_{[CuY]^+} - \lg K_{[CuX]^+} \quad . \tag{7}$$

The enthalpy and entropy of the ligand exchange process (5) are estimated by means of the equations

$$\Delta H = -A_{es}\left[1 + \frac{T}{\varepsilon}\frac{\delta\varepsilon}{\delta T}\right] , \tag{8}$$

$$\Delta S = -A_{es}\left[\frac{1}{\varepsilon}\frac{\delta\varepsilon}{\delta T}\right] + S_{st} , \tag{9}$$

where ε is the effective relative permittivity. As was in fact to be expected, ΔH for this process is zero,[39,40] which indicates an isotypical ligand environment of the copper(II) ions in the LMC and the MMC. On the other hand, the entropy component varies with increasing degree of conversion from positive to negative values (Table 4). It attains zero (i.e. the ΔG for the LMC and the MMC are equal) when half of the negative charges on the polymer are bound to the copper(II) ions or, in other words, when the numbers of the positive and negative charges on the polymer are found to be equal. On the other hand, further addition of copper ions results in the preferential concentration of positive charges on the polymer.

Table 4. Thermodynamic functions of the ligand exchange reaction (5).

$\Delta(\lg K)$	$-\Delta G$/kJ mol^{-1}	TS_{st}/kJ mol^{-1}	S_{st}/J mol^{-1} K^{-1}
0.65	3.72	3.72	12.5
0.45	2.55	2.55	8.6
0.31	1.76	1.76	5.9
0.22	1.26	1.26	4.2
0.06	0.33	0.33	1.1
0.01	0.74	0.04	0.1
−0.02	−0.13	−0.13	−0.4
−0.10	−0.59	−0.59	−2.0
−0.13	−0.75	−0.75	−2.5
−0.20	−1.13	−1.13	−3.8
−0.40	−2.30	−2.30	−7.7
−0.49	−2.80	−2.80	−9.4
−0.73	−4.18	−4.18	−14.0

III. The molecular level of the structural organisation of metallopolymers

With increase in the degree of conversion and/or decrease in the length of the polymer chains, it is necessary to take into account the molecular level of the spatial organisation of the MMC. We shall analyse initially the influence of the degree of conversion on the chelation process for a fixed length of the polymer chains.

The effect consisting in the change of the chain conformation, which is observed after the attainment of a certain degree of conversion and involves different numbers of monomer units, is most frequently manifested. There is then a possibility of both a helix–coil transition, characteristic of charged chains, and of a change in the preferential conformation of the statistical coil.[41] Conformational transitions have been detected in linear poly(amidoamines) on protonation and complex formation.[19] Thus viscometric titration showed that the viscosity of the linear polymer **19** decreases monotonically with increase in the pH (Fig. 4). Analysis of the superposition of the distribution curve on the pH dependence of the viscosity shows that the ratio of the specific viscosity and the concentration (η_{sp}/c) decreases on completion of the formation of the complex CuL and then remains virtually constant until the deprotonation of the ligand is completed. The second small jump corresponds to the formation of HL_2^+ and can be explained by a conformational transition.[39]

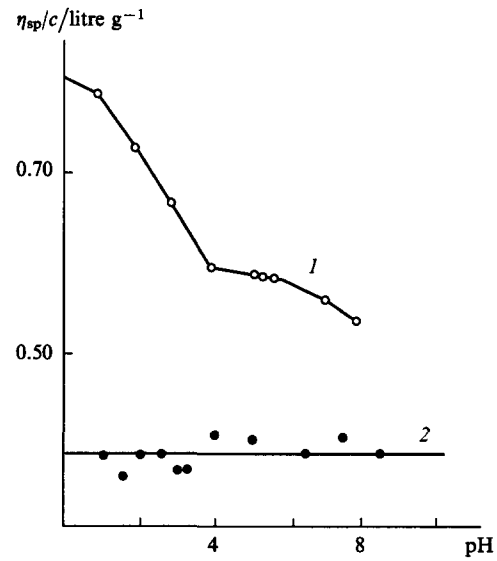
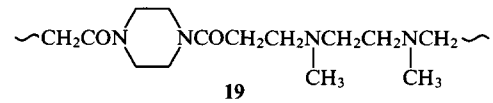
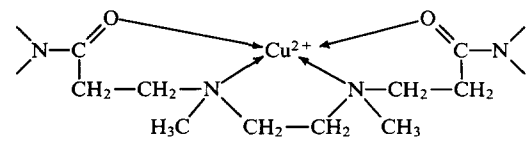


Figure 4. The viscosity and the distribution curves as a function of pH for the copper (II) complexes of linear (compound **19**, curve *1*) and branched (compound **21**, line *2*) poly(amidoamines).

In other words, the involvement in the reactions of the nitrogen atoms of the main chain is accompanied by conformational transitions which influence the properties of the entire macromolecule, since the junctions between different monomer units (six-membered diacylpiperazine chelate rings in complex **20**) are very rigid.

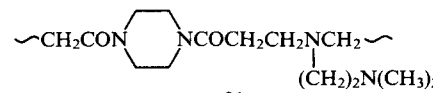


19



20

In the case of the branched polymer **21**, appreciable deviations of η_{sp}/c from a constant value are not observed over the entire pH range (Fig. 4).[40] The weak dependence of the viscosity on the pH and on the degree of conversion for this polymer is unusual and is probably due to the fact that the conformational transition associated with complex formation involves only the side substituents and does not affect significantly the characteristics of the main chain.



21

It has been established[42] that, for the poly-L-lysine.heme and poly-L-lysine.hemin complexes at low degrees of conversion, the fraction of the α-helical structure and the viscosity of the solution do not change. This result shows that the MMC obtained is intramolecular and that the helical structure can be represented schematically in the form of complex **22**. If the degree of conversion exceeds 0.1, then the fraction of the helical structure diminishes, which indicates the existence of steric hindrance to its establishment owing to the coordination of the bulky complexes **23**.

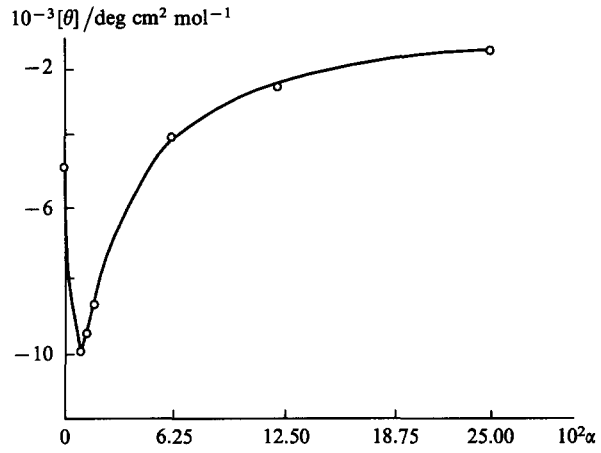
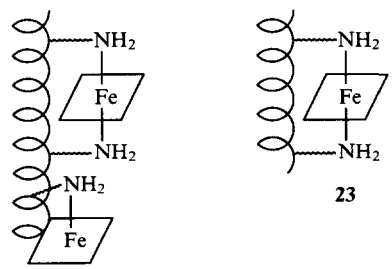


Figure 5. Dependence of the ellipticity θ of poly-*N*(5)-(3-hydroxypropyl)-L-glutamine on the degree of conversion of the Cu^{2+} ions.



In the interaction of copper(II) ions with poly-*N*(5)-(3-hydroxypropyl)-L-glutamine up to a degree of conversion of 6.25×10^{-2}, the α-helical conformation predominates, whilst above this conversion the chain conformation changes (Fig. 5).[43]

The helix–coil transition may be observed in the copper(II)–poly-L-glutamic acid system when a change takes place both in the ratio $[M^{2+}]/[L]$ (Fig.6) and in the pH of the solution for a fixed $[M^{2+}]/[L]$ ratio (Fig.7).[44] If the degree of neutralisation is

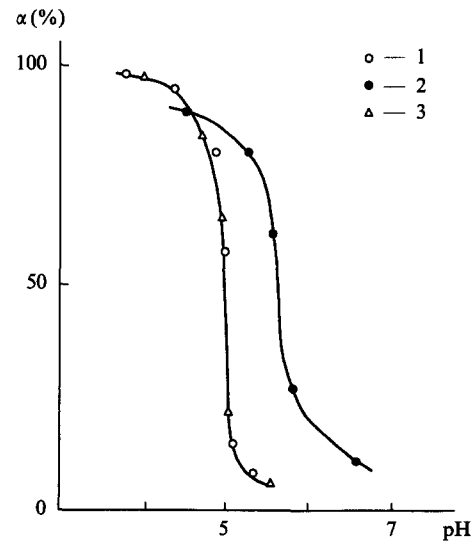


Figure 6. Dependence of the content of the α-helium (α) in poly-L-glutamic acid (*1*) and in its copper complex on pH for $[Cu^{2+}]/[L] = 0.1$ (*2*) and 0.02 (*3*).

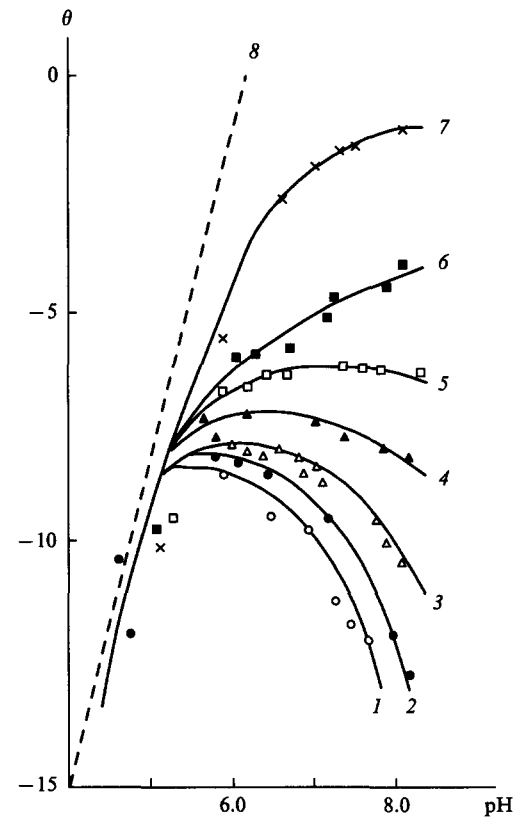


Figure 7. Relation between the molar ellipticity at 222 nm and the pH of Cd^{2+}–polyglutamic acid solutions for different ratios $[Cd^{2+}]/[L]$: (*1*) 1.5; (*2*) 1.0; (*3*) 0.77; (*4*) 0.5; (*5*) 0.4; (*6*) 0.3; (*7*) 0.15; (*8*) 0.0.

less than 0.2, i.e. the polyaminoacid has a helical structure, then the Cu^{2+} ions are hardly bound by the polymer. On the other hand, the interaction of these ions with poly-L-lysine leads to the formation of complexes containing a polymer in the α-helical conformation.[45,46] It is interesting to note that, when Cu^{2+} ions are added, poly-D-lysine undergoes a conformational transition, whereas the addition of other ions, for example, Zn^{2+}, Mg^{2+}, Mn^{2+}, or Ca^{2+}, has no effect whatever on the polymer conformation.[47]

Electrostatic, hydrophobic, or hydrophilic interactions between the components may exert an appreciable influence on the chelation of metal ions. On formation of charged chains, the macromolecules is stretched as a result of the reaction with the metal ion as the degree of conversion increases. Thus the introduction of metal cations into the cavity within the macrocycles of the homopolymers of vinylcrown-ethers may alter significantly the conformation of the polymer chain. In the initial state, such polymers are typical micelles, in which the nonpolar hydrocarbon 'tails' are collected in a coil, whilst the polar 'heads' (crown ethers) emerge into the solution surrounding the micelle. On complex formation, the polymeric crown-ethers are converted into polyelectrolytes, which leads to electrostatic repulsion of the monomer units. This interaction results in the uncoiling of the coil and the assumption by the polymer of the extended chain conformation.[48]

The formation of a complex between uncharged polyvinylpyrrolidinone and copper(II)-chlorophyllin is accompanied by the formation of hydrogen bonds, which leads to a sharp increase in the viscosity of the solution.[49]

The hydrophobic interaction of the LMC with the macroligand is also important. This has been clearly shown in relation to the formation of complexes between heme and water-soluble polmers — poly(ethylene oxide), poly(vinyl alcohol), and polyvinylpyrrolidinone.[50] It was found that the equilibrium between

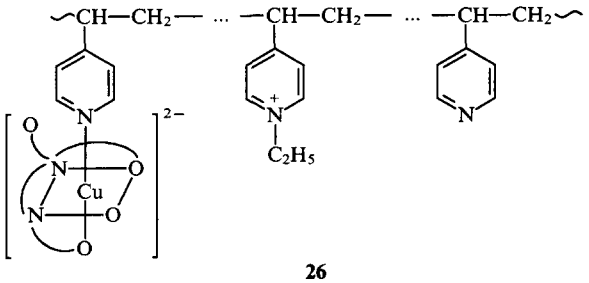
the monomeric and dimeric forms of heme, which obtains in aqueous solution, is fully displaced towards the monomeric form at a high concentration of the polymeric ligand. This effect increases with increasing hydrophobicity of the polymer in the series polyvinylpyrrolidinone > poly(ethylene oxide) > poly-(vinyl alcohol), which led to the conclusion that there is a hydrophobic interaction between heme and the polymer.

Table 5. Stability constants of complexes **26**.

CuX^{n-}	Ligand				
	4-ethyl-pyridine	P4VP	QP4VP (20)[a]	QP4VP (25)[a]	QP4VP (61)[a]
24	72	60	123	–	240
25	70	48	–	870	1100

Note. Reaction conditions: aqueous methanol (1:1 by volume), ionic strength of solution 0.1 M, pH 8, T = 298 K.
[a] Here and in Table 6 the numerals in brackets denote the degree of quaternisation.

The macroligand may contain positively or negatively charged atoms, which either promote or interfere with its interaction with metal ions (although they do not in fact influence significantly the formation of a direct chemical bond involving them). This has been noted in a study of the interaction of CuX^{n-}, where X = ethylenediaminetetraacetate (complex **24**) or *N*-(2-hydroxyethyl)ethylenediamine-*N,N',N'*-triacetate (complex **25**), with quaternised poly-4-vinylpyridine (QP4VP) in the formation of type **26** complexes.[51] The stability constants of these complexes (Table 5) increase with increase in the degree of quaternisation despite the fact that steric hindrance should increase in this case. Evidently this is caused by an electrostatic effect; the local concentration of CuX^{n-} should increase with increasing degree of quaternisation by virtue of the Coulombic interaction between the polycation and CuX^{n-}. An increase in the charge on the initial LMC increases its affinity for the polycation and the stability constants also increase in the same sequence.



26

The degree of conversion of metallochlorophyllins (M = Co^{3+}, Fe^{3+}, Ni^{2+}, Cu^{2+}, or Zn^{2+}) in the interaction with QP4VP proved to be unity.[52] The stability constants of these complexes were $\sim 10^3$ litre kg mol^{-1}, i.e. were greater than for the low-molecular-mass analogues. In all probability, the stability of the complexes of the metallochlorophyllins with QP4VP is determined by the electrostatic binding of the carboxylate anion of the LMC to the quaternary pyridinium cation in the polymer chain.

Similar conclusions were reached[51] also in a study of the formation of complexes of methylaquocobaloxime† with pyridine-containing ligands [reaction (10)]. In this case, the stability constants decreases in the sequence 4-ethylpyridine > P4VP > QP4VP(25) > QP4VP(61). The steric hindrance exerted by the polymeric ligand and the positive charge density increase in the same sequence.

† MeCo(dimethylglyoxime monoanion)$_2H_2O$ (Ed. of Translation).

Table 6. The stability constants and rates of formation of complexes by reaction (10).

Constant (method of determination)	Ligand			
	4-ethyl-pyridine	P4VP	QP4VP (25)	QP4VP (61)
K/litre mol^{-1} (a)	3.5×10^3	1.7×10^3	5.3×10^2	95
K/litre mol^{-1} (b)	3.3×10^3	1.8×10^3	4.9×10^2	1.4×10^2
k_1/litre mol^{-1} (a)	20	18	8.4	2.5
k_{-1}/s^{-1} (b)	5.3×10^{-3}	1.0×10^{-2}	1.6×10^{-2}	2.6×10^{-2}
k_{-1}/s^{-1} (a)	6.0×10^{-3}	9.9×10^{-3}	1.7×10^{-2}	1.8×10^{-2}

Note. Method: (*a*) kinetic [aqueous methanol (3:7 by volume), ionic strength of solution 0.05 M, pH 8, T = 298 K]; (*b*) spectrophotometric.

$$CH_3Co(DH)_2H_2O + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3Co(DH)_2L + H_2O \quad (10)$$

(DH = dimethylglyoxime)

Chelation makes it possible comparatively frequently to stabilise conformational and tautomeric forms uncharacteristic of the initial polymer. Thus the addition of the [(2,2',2'',2'''-tetrapyridyl)iron]$^{3+}$ ions to solutions of sodium poly(L-glutamate) increased the content of the α-helical form at pH values where the coil usually predominates.[53] In other words, the metal ion selects the polymer chain conformation which it prefers most.

The chain conformation is determined by many factors (for example, the nature of the solvent) which exerts a significant influence on the entire chelation process. Thus, in the interaction of poly(2-methyl-*N*-vinylimidazole) with the $CoCl_3(en)_2$ system, where en = ethylenediamine, in $H_2O-C_2H_5OH$ mixture, an increase in the ethanol content from 0 mass% to 10 mass% entails a decrease in thermodynamic parameters: from 46.5 to 43.6 kJ mol^{-1} in ΔG, from 97.2 to 41.5 kJ mol^{-1} in ΔH, and from 164.3 to 47.3 J K^{-1} mol^{-1} in ΔS.[50] The solvent also significantly influences the rate constants for forward (k_1) and reverse (k_{-1}) ligand exchange reactions [reactions (11)] (Fig. 8).[54] This can be accounted for by the variation of the conformation of the polymeric ligand as a function of the nature of the solvent; the rate of the ligand exchange reaction of cobaloximes with polymeric ligands, such as the styrene–4-vinylpyridine copolymer, may be controlled by varying the conformation of the macroligand.

$$K = \frac{[ClCo(DH)_2L][DMF]}{[ClCo(DH)_2DMF][L]}$$

$$ClCo(DH)_2DMF + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cl \cdot Co(DH)_2L + DMF \quad (11)$$

The rate constants for the chemical decomposition (k_{decomp}) of the complex between cobaloxime and the styrene–chloromethylstyrene copolymer proved to be smaller by a factor of 4 than the low-molecular-mass benzylcobaloxime (Table 7).[55] This can be explained by the fact that the diffusion of divalent cobalt complexes, formed in the homolytic photochemical decomposition, proceeds less easily as a consequence of steric hindrance by the polymer chain. Furthermore, the alkyl radicals formed are retained by the polymer; the probability of their recombination thus increases compared with the monomeric analogues. However, this type of effect has not been observed in dimethyl sulfoxide (Table 7), because in this solvent cobaloximes are

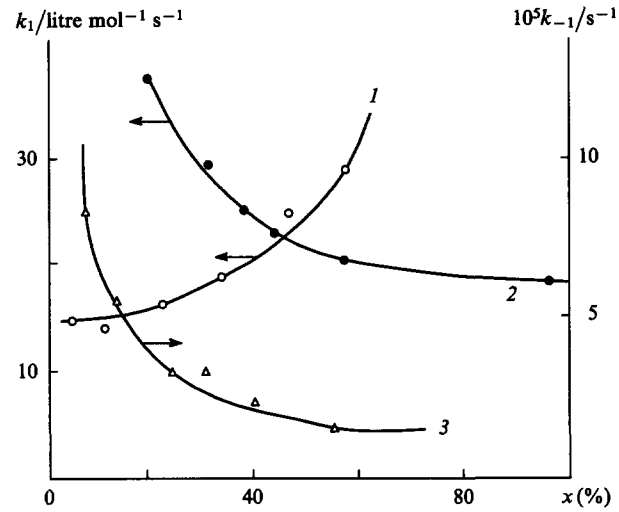


Figure 8. Dependence of the rate constants for the forward (k_1) and reverse (k_{-1}) reactions on the content (x) of 4-vinylpyridine units in the copolymer: (*1*) in benzene; (*2*) and (*3*) in DMF.

localised on the surface of the polymer coil and are not subjected to steric hindrance due to the polymer chain. In mixed solvents (DMSO–benzene), the ratio of the rate constants for the decomposition of the polymer (k^P) and the monomer (k^m) diminishes with increase in the benzene content (Fig. 9). It follows from measurements of the viscosity of the polymer to which cobaloxime is attached that the polymer chain becomes 'extended' with increase in the benzene content in the solvent. Thus the decrease in the rate constant for the photochemical decomposition of the polymer-bound cobaloxime with increase in the benzene content in the solvent is apparently caused by the extension of the polymer chain.

One of the characteristic features of the chelation reaction involving polymeric ligands on the molecular level is the 'neighbouring group' effect caused both by the interaction of the neighbouring chelating fragments and by the statistical nature of the entire chelation process.[56] If blocks containing a smaller number of active centres (functional groups) than required for

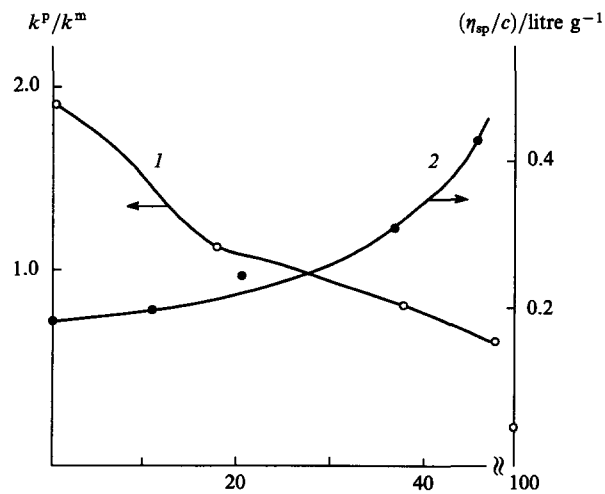


Figure 9. Variation of the relative rate constant (k^P/k^m) for the photochemical decomposition of alkylcobaloximes (curve *1*) and of the ratio η_{sp}/c (curve 2) for MMC as a function of the benzene content in the solvent.

Table 7. Rate constants for the photochemical decomposition of alkylcobaloximes[a]

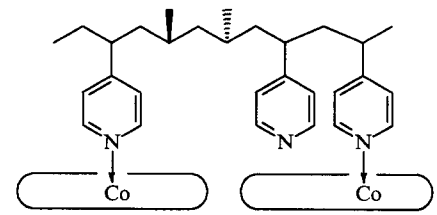
$$RCo(DH)_2L \overset{h\nu}{\rightleftharpoons} R^{\cdot} + Co(DH)_2L$$ [a]

R	Solvent	Irradiation region/nm	$10^2 k_{decomp}$/ s^{-1} [b]
Benzyl	benzene	entire region	4.6
	DMSO	"	1.0
	DMSO	> 350	1.1
	DMSO	> 450	1.1
	DMSO	> 550	< 0.1
Polymer [c]	benzene	entire region	1.1
Polymer [d]	DMSO	entire region	1.4
	DMSO	"	1.4
	DMSO	> 350	1.0
	DMSO	> 450	0.9
	DMSO	> 550	< 0.1

[a] L = Py, C_6H_6, or DMSO.
[b] k_{decomp} was measured on irradiation with light from a tungsten lamp with a constant photointensity.
[c] Contained 8.1 mol% of the cobaloxime.
[d] Contained 2.1 mol% of the cobaloxime.

chelation to the metal ion remain unreacted during the chelation process, then such blocks no longer participate in the coordination, i.e. the concentration of the unreacted centres is not equal to the active concentration of the reacting species. Here it is necessary to take into account the fact that the fraction of the monomer units capable of coordination, among all the unreacted monomer units, depends on the degree of conversion. Various ways of binding the metal to the macroligand are possible.[41] Thus, if there are q metal ions on the chain containing m active centres, then the number of complexes formed, having different structures, is c_m^q (the number of combinations of q molecules with m chain centres).

Low-molecular-mass cobalt(II) chelates, for example of ethylenediamine, have a fairly large volume (diameter about 10 Å), so that during their coordination, even when a close packing is produced, some P4VP units remain uncoordinated for steric reasons (complex **27**).



27

The calculated maximum degree of conversion of P4VP is in this case 0.63, which is close to the experimental values (Fig. 10, see over). A complex of this kind has a rigid rod-shaped structure, in which the mobility of the Co^{2+} chelate is much smaller than that of the monomeric analogues. The decrease in the g-factor in the EPR spectrum of the complex *cis*-$[Cr(en)_2(P4VP)Cl]Cl_2$ with increase in the degree of conversion indicates a decrease in the symmetry of the Cr^{3+} complex (D_{4h}).[8] Such disburbance of the anisotropy is caused by the steric hindrance generated both by the P4VP ligands and the fixed chelates.

For the vinyl imidazole copolymers, the number of ligands axially coordinated to heme is about two, decreasing with decrease in the 1-vinylimidazole content in the copolymer (Table 8, see over). A favourable contribution by the entropy factor, associated according to the authors[57] with the high apparent concentration of the functional groups in the polymer

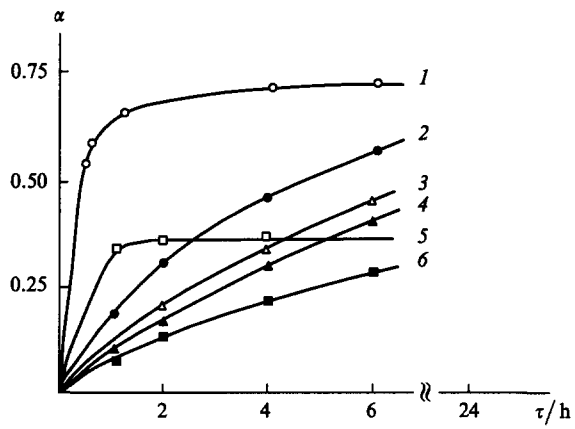


Figure 10. Kinetic curves for the formation of MMC; [chelate] = 0.05 M, [chelate]:[L] = 1, solvent $C_2H_5OH-H_2O$, 353 K: (*1*)Co(acac)$_2$.(P4VP)NO_2; (*2*) $[Co(en)_2(PEI)Cl]Cl_2$; (*3*) $[Co(en)_2(P4VP)Cl]Cl_2$; (*4*) $[Co(en)_2(QP4VP)Cl]Cl_2$ (R = CH_3); (*5*) $[Cr(en)_2(P4VP)Cl]Cl_2$; (*6*) $[Co(en)_2(QP4VP)Cl]Cl_2$ (R = $CH_2C_6H_5$).

Table 8. Parameters of the formation of complexes between heme and the polyvinylimidazole homopolymer and the vinylimidazole–vinylpyrrolidinone copolymer.

Ligand	α	K/litre mol^{-1}	ΔH/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}
Homopolymer	1.6	1.6×10^4	–	–
Copolymer (50)[a]	1.3	3.1×10^4	−16.8	30.7
Copolymer (20)[a]	1.2	3.2×10^4	–	–
Copolymer (10)[a]	0.9	4.1×10^4	−22.6	13.0
1-Ethylimidazole	1.3	4.8	−23.0	−42

[a] The numerals in brackets denote the vinylimidazole content in the copolymer.

matrix, is observed. Therefore in most cases the stability constant of the MMC is higher by a factor of 10^2-10^4 than the corresponding constant for the low-molecular-mass analogues.

The pyridine-containing ligands can be arranged in the following sequence in terms of the calculated equilibrium constant (Table 9) of the ligand exchange reaction

Table 9. Equilibrium constants of the ligand exchange reaction (11) as a function of the ligand composition.

Ligand	$10^{-5}K$/litre mol^{-1}
Pyridine	0.68
Styrene–4-vinylpyridine copolymer with different contents of 4-vinylpyridine units (%)	
9.8	0.45
13	1.0
24	1.2
32	1.4
41	1.9
53	1.5
100	0.085

Note. Solvent–DMF (at 20 ± 0.5 °C).

Table 10. Thermodynamic parameters of the ligand exchange reaction (11).

Ligand	ΔG/kJ mol^{-1}	ΔH/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}
Pyridine	−27.2	−14.2	42
P4VP	−22.2	−8.0	50.4
Styrene–4-vinylpyridine copolymer[a]	−29.3	−6.3	79.8

Note. Solvent–DMF (at 20 ± 0.5 °C).
[a] Content of 4-vinylpyridine units 32%.

[Eqn (11)]: styrene–4-vinylpyridine copolymer (13%–53% of 4-vinylpyridine) > Py > styrene–4-vinylpyridine (10% of 4-vinylpyridine) copolymer > poly-4-vinylpyridine.[54] The distance between the pyridine fragments in P4VP is so short that not all the 4-vinylpyridine groups can function as ligands owing to the steric hindrance generated by the coordinated cobaloximes. In the case of the copolymer containing 13%–53% of 4-vinylpyridine fragments, where the steric hindrance between the cobaloxime moieties may be neglected, the equilibrium constant is higher than for the low-molecular-mass analogue (Py). This is also indicated by the calculated thermodynamic parameters of the ligand exchange reaction (Table 10).

The rate of formation of the cobalt chelates with the partly quaternised P4VP diminishes in the following sequence of groups R (the group in the quaternising agent): H > CH_3 > $CH_2C_6H_5$ (Fig. 10), which is due to the steric hindrance arising from the polymeric ligands.[58]

The use of polymeric crown-ethers for the formation of [L]:[M] = 2:1 complexes with a sandwich structure (Fig. 11), i.e. in those cases where the size of the cavity within the macrocycle is too small for the formation of 1:1 complexes, proved to be effective. This is clearly seen in relation to the interaction of the potassium ion with the 15-crown-5-ether (the constant for the extraction of potassium picrate is 0.42×10^3 mol^{-2}) and with its polymeric analogue (extraction constant 2.3×10^3 mol^{-2}). The greater effectiveness of the polymeric crown-ethers in the formation of the 2:1 complexes is caused by the high local concentration of the macrocycles in the polymer chain, which entails the single-stage binding of the metal ion by two neighbouring fragments (Fig. 11). However, one should note that the examination of the macromolecular models of the complexes indicates that the involvement in complex formation of, not neighbouring, but alternate monomer units is preferable.[59]

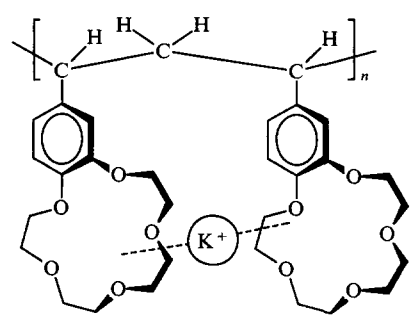


Figure 11. The structure of the sandwich type complex formed by the K^+ ion and the polyvinylbenzo-15-crown-5.

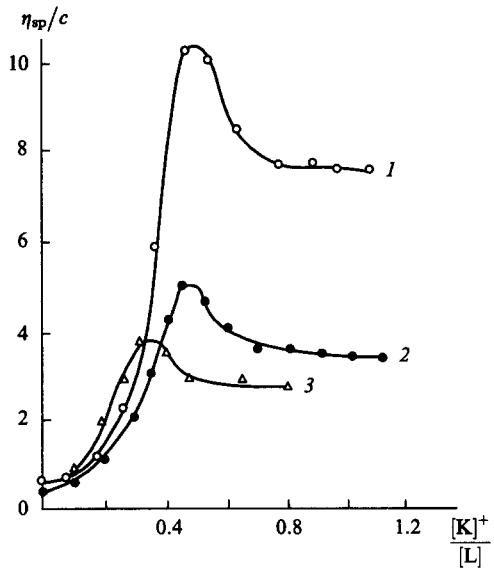
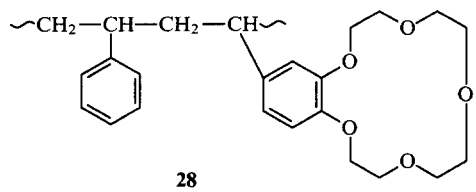


Figure 12. Dependence of the viscosity of the styrene–vinylbenzo-15-crown-5 copolymer on the ratio $[K^+]:[L]$ for different contents of the chelating fragments (%): (*1*) 18; (*2*) 11.8; (*3*) 5.8.

The results of viscometric measurements have shown (Fig. 12) that the maximum values of η_{sp}/c in the potassium ion–copolymers **28** system corresponds to the 2:1 complex and that the content of the crown-ether units does not exceed 20%. In other words, intramolecular metal chelates are formed only when the chelating fragments are separated by less than four (on average) styrene units.[60]



28

In the formation of the MMC, the first step may be regarded as a second-order reaction (first-order with respect to each component), while all the subsequent steps (with formation of the chelate rings) may be regarded as first-order reactions. The overall formation of metal chelates with a single chain is a second-order reaction. Since the rates of complex formation reactions are ususally high, it is difficult to distinguish experimentally the consecutive stages of the process. However, in those comparatively rare cases where this has been achieved the successive stability constants K_i as a rule increase with increase in the degree of conversion. Low-molecular-mass ligands behave differently. Thus, in the case of the low-molecular-mass pivaloylacetone and methacryloylacetone the ratio $K_1/K_2 = 1.08$ and 1.12 respectively (copper complexes are considered). On the other hand, the analogous ratio for polymethacryloylacetone[61] is 0.84, i.e. the stability constants increase with increase in the degree of conversion. This is a consequence of the cooperative 'chain effect', which involves a change in the shape of the macromolecule without change in the contour length on complex formation.[41,59] In particular, the interaction of metal ions with soluble polymers decreases the flexibility of the polymer chains with increase in the degree of conversion. This effect is manifested particularly clearly in the case of polymers containing biypyridyl units in the main chain.[62,63] Appreciable changes in the shape of the macromolecules of poly-2-vinylpyridine have been observed[64] in its interaction with cobalt acetylacetonate. The stability constant of the MMC in the case of polymeric ligands can be expressed in the form

$$K = \prod_{i=1}^{i=N} K_i = \sigma K_j \ ,$$

where $\sigma = K_i/K_{i-1}$ is the parameter of the cooperative effect, showing by what factor the stability constant increases as a result of each successive addition compared with the previous value. It has been postulated that all the consecutive stability constants, other than the first, are the same (since virtually the entire entropy is lost in the first step, the subsequent stages represent intramolecular cyclisation). The 'chain effect' is manifested by the high local concentration of the functional groups, so that the stability constant is not determined by the average concentrations of the components but by their local concentrations in the coils (as in microreactors).[65] After entering a region of a high local concentration of the functional groups, the metal ion immediately forms coordinatively saturated complexes, whilst the groups which remain free participate in the formation of a small number of coordinatively unsaturated structures.

The constancy of the composition of the complexes for different ratios of the reacting components (within wide limits) is a distinctive feature of the reactions of macroligands compared with their low-molecular-mass analogues: it is thermodynamically easier for a macromolecule to form coordinatively saturated complexes (even if their amount is smaller) than the unsaturated complexes. Thus a study of copper(II) complexes of a polymer aminated by ethylenediamine, diethylenetriamine, and trimethylenediamine demonstrated[66] small differences between the values of $A_{||}$ and $g_{||}$ as well as α^2 (the unpaired electron density on the coordination ion) for the LMC and the MMC (Table 11). These differences indicate the existence of some steric hindrance to the formation of the tetracoordinate complex CuN_4 in the case of the polymer. When the content of copper ions in the MMC is <0.05 mmol g^{-1}, the EPR spectrum is satisfactorily resolved and corresponds to isolated mononuclear complex species having the same composition. When the copper concentration increases, the EPR spectrum represents the superposition of an anisotropic multiplet (due to the isolated complexes) and a singlet with a g-factor of about 2.08–2.10. The amplitude of the latter increases with increase in the copper content in the MMC. The singlet is evidently due to the existence of regions with a higher local concentration of copper ions, where the distance between neighbouring ions does not exceed 7–9 Å and where there is a strong spin-exchange interaction between them. The composition of the copper complexes in such regions apparently correspond to the formulae CuN_4, CuN_3, CuN_2, or CuN—i.e. in the course of chelation coordinatively saturated complexes are formed initially as the degree of conversion increases and then coordinatively unsaturated complexes are produced.

In the case of an acrylic acid copolymer containing phenanthroline units, a 1:1 complex (this complex has the highest stability constant) and then a 1:2 complex are formed in succession with increase in the degree of conversion.[67] On passing from the

Table 11. Parameters of the EPR spectra of the copper complexes of a polymer aminated by polymethylene amines and of its low-molecular-mass analogues at 77 K.

Complex	$A_{\|} \pm 3$/G	$g_{\|} \pm 0.005$	$g_{\perp} \pm 0.005$	α^2
MMC	180	2.214	2.050	0.79
MMC[a]	175.5	2.205	2.049	–
Cu(en)	184	2.235	–	0.81
$Cu(en)_2$	190	2.201	2.045	0.80

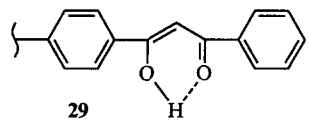
[a] Temperature—298 K.



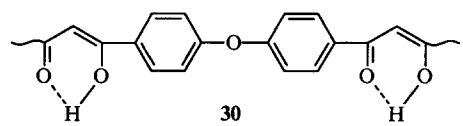
Figure 13. Emission spectra of the europium(III) complexes of poly-*p*-benzoylacetylstyrene (curve *1*) and dibenzoylmethane (curve *2*).

first complex to the second, a slight increase in $A_{||}$ and an appreciable decrease in α^2 (by 0.05) are observed, which indicates slight tetrahedral distortions of the coordination unit. This can be explained by the steric hindrance arising when four coordinated nitrogen atoms are located in a single plane.

Together with the main peak at 613 nm due to the $^5D_0 \rightarrow {}^7F_2$ transition (as in the low-molecular-mass analogue dibenzoylmethane), an additional peak at 580 nm, corresponding to the forbidden $^5D_0 \rightarrow {}^7F_0$ transition,[68] appears in the emission spectrum of the Eu^{3+} complex of poly(*p*-benzoylacetylstyrene) **29** (Fig. 13). The appearance of this peak is associated with the decrease in symmetry around the Eu^{3+} ion (owing to the steric hindrance arising in the formation of the polycyclic complex). An increase in the degree of conversion in this instance leads to the formation of 1:2 and 1:1 complexes with the [M]:[L] = 1:3 complex. The fluorescence intensity remains almost constant until the attainment of the maximum at low Eu^{3+} concentrations (Fig. 14). In other words, the maximum intensity corresponds to the 1:3 complex. When the β-diketone fragment is introduced into the main chain (the ligand **30**), the formation of 1:3 complexes becomes more difficult and the 1:2 complex, characterised by a low fluorescence intensity, becomes the main product.



29



30

The reaction of iron(III) ions with the low-molecular-mass ligand bipyridyl produced an equilibrium mixture of 1:1, 1:2, and 1:3 complexes, whereas the formation of only 1:1 chelate is characteristic of poly(6-vinyl-2,2′-bipyridyl).[69] Thus the polymeric ligand makes it possible to stabilise complexes having a specified composition.

One of the manifestations of the chain effect in metallopolymer systems is also the independence of the thermodynamic parameters of the chelation process of the chain length (molecular mass) of the polymeric ligand.[70] Thus, in the formation of copper(II) complexes of poly(hydroxamic acids), the stability constants of the latter diminish with increase in the molecular mass of the polymer (from 3000 to 15 000).[71] Fig. 15 presents the spectra of the copper complexes of methylhydroxamic acid and its polymeric analogues in the far infrared. In this case, the absorption band at 550 cm^{-1} in the IR spectrum of the LMC refers to the Cu–O and C–N bond vibrations. This band undergoes a bathochromic shift with increase in the molecular mass of the polymer. The band at 516 cm^{-1}, assigned to the deformation vibration of the ring and the O=C–C– group, shifts in the same direction. Bearing in mind that the order in which the frequencies of the stretching vibrations and their force constants vary corresponds to the order of the variation of the stability constants of the complexes of β-diketones, one may postulate that the stability of the copper complexes of poly(hydroxamic acid) diminishes with increase in molecular mass.[72]

The formation of low-molecular-mass chelates involving cobalt(II) and P4VP with a lower degree of polymerisation also proceeds more readily.

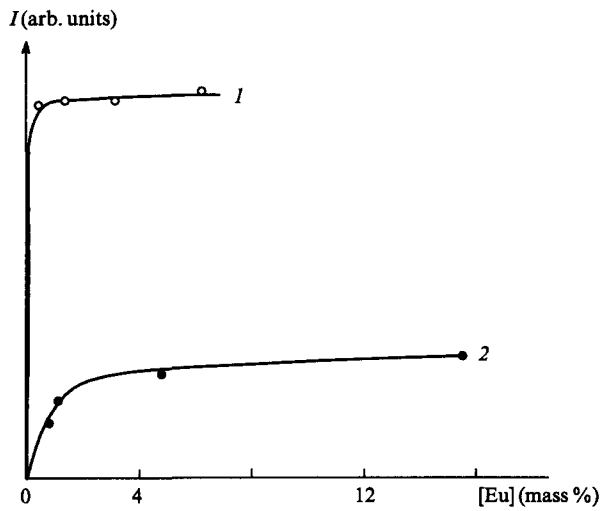


Figure 14. Dependence of fluorescence intensity at λ = 613 nm on the europium content in the macrocomplexes of **29** (curve *1*) and **30** (curve *2*).

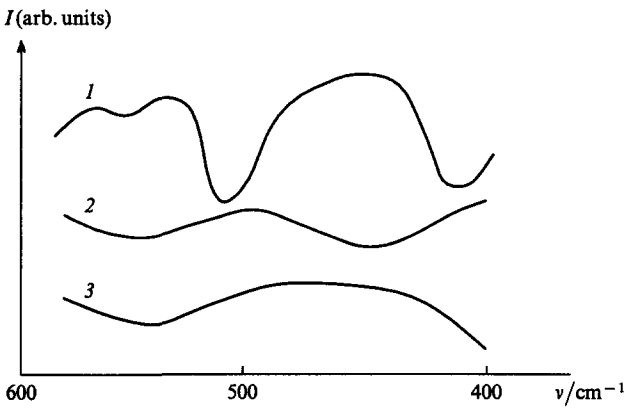


Figure 15. IR spectra of the copper(II) complexes of methylhydroxamic acid (curve *1*) and poly(hydroxamic acids) with M_n = 640 (curve *2*) and 17 000 (curve *3*).

The chelating fragments of one (intramolecular metal chelates) or two polymer chains (intermolecular metal chelates) may participate in the formation of macromolecular metal chelates. A typical manifestation of the chain effect is intramolecular (and not intermolecular) cyclisation in dilute solutions. For example, the interaction of poly(6,6'-dimethyl-5-vinyl-2,2'-bipyridyl) with cobalt(II), copper(II), and zinc(II) chlorides in ethanol at 298 K results in the formation of 1:1 complexes with M←N bonds.[73] The decrease in the viscosity of the solutions of the MMC in dimethylformamide (DMF) on dilution (Fig. 16) indicates their polyelectrolyte nature. The solubility of these compounds indicates the absence of intermolecular cross-linking, i.e. the bipyridyl groups behave like the usual chelating ligands in the side chains of the polymer. Similar results have also been obtained for the VO^{2+} and Co^{2+} complexes of polyureas incorporating the bipyridyl group.[74]

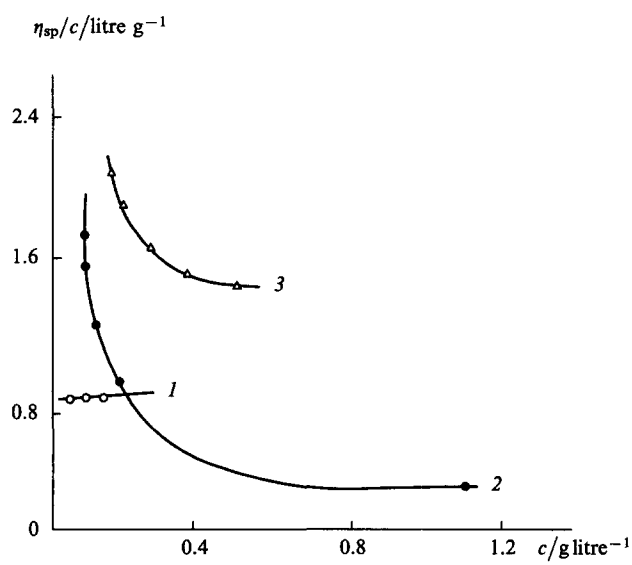
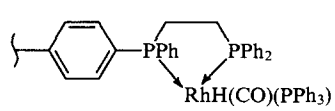


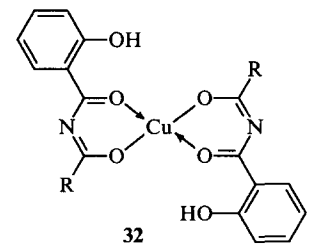
Figure 16. Concentration dependences of the ratio η_{sp}/c for poly-4-methyl-4'-vinyl-2,2'-bipyridyl (curve 1) and its complexes with $ZnCl_2$ for [Zn]:[L] = 0.3 (curve *2*) and 0.6 (curve *3*).

The features of the formation of chelates with participation of polymeric ligands noted above may lead both to the appearance of new reactions, uncharacteristic of the low-molecular-mass compounds,[75] and to a change in the mode of the complex formation reactions known for the LMC.[76] Thus it has been shown that the polymer modified by 1,2-bis(diphenylphosphino)ethane forms the mononuclear complex **31** on interaction with $RhH(CO)(PPh_3)_3$,[77] whereas the low-molecular-mass analogues — 1,3-bis(diphenylphosphino)propane and 1,4-bis(diphenylphosphino)butane — give rise to dimeric rhodium complexes.

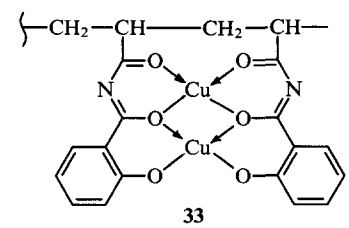


31

The low-molecular-mass chelating ligands *N*-acylsalicylamides afford mononuclear metal chelates on interaction with copper(II) ions and, of the two possible coordination centres, the diacylamine fragment participates in the complex formation reaction (complex **32**).[27] However, the *N*-acylsalicylamide on the polymer base immediately gives rise to the dinuclear copper complexes **33**.[78]



32



33

Another characteristic example is the shift of the monomer ⇄ dimer equilibrium in solution of metallophthalocyanines towards the monomeric form on formation of complexes with polymeric ligands, which is indicated, for example, by the increase in the intensity of the monomer peak with a simultaneous decrease in the intensity of the dimer peak in the UV spectra of the metallophthalocyanines (Fig. 17).[79] This shows that the large size of the polymer chain prevents the aggregation of the metallophthalocyanine units. Evidently the dimer cannot arise if only one metal chelate molecule is present in each polymer coil. The mole fraction X_i of the metal chelate bound to the polymer chains, each of which contains k metal chelate molecules, may be calculated by the equation[79]

$$X_i = \frac{k(1-p^2)(p\alpha)^{k-1}}{(1-p+p\alpha)^{k+1}}, \qquad (12)$$

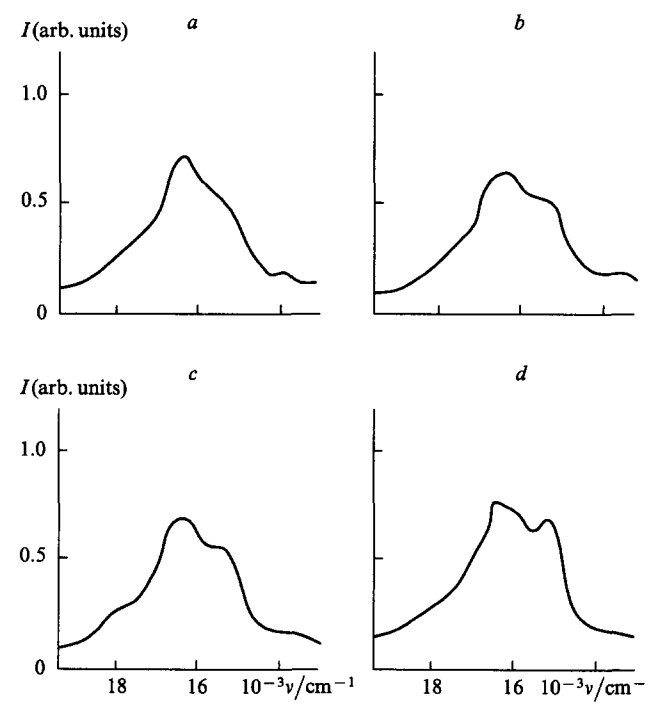


Figure 17. Absorption spectra in the visible region of complexes of cobalt-tetrasulfophthalocyanine (concentration 2.5 μM) with PVA at different concentrations of the latter (mM): (*a*) 2.5; (*b*) 5.9; (*c*) 10.0; (*d*) 25.0.

where $p = 1 - 1/P_n$ (P_n is the number-average degree of polymerisation). Calculations showed (Table 12) that, in the case of a polymer with a relatively low molecular mass (P_n = 50), X_i for isolated (k = 1) metal chelate molecules is extremely large and diminishes slowly with increase in α. On the other hand, in the case of a polymer with a high molecular mass (P_n = 1680), the fraction of polymer chains containing only one metal chelate molecule attains high values at low degrees of conversion.

Table 12. Calculated amounts (in mol%) of isolated molecules of metallophthalocyanines bound to polyvinylamine.

$10^2\alpha$	P_n = 50	P_n = 1680
1	45.04	0.32
0.2	82.95	5.27
0.1	90.88	13.93
0.02	98.07	56.04
0.01	99.03	73.31

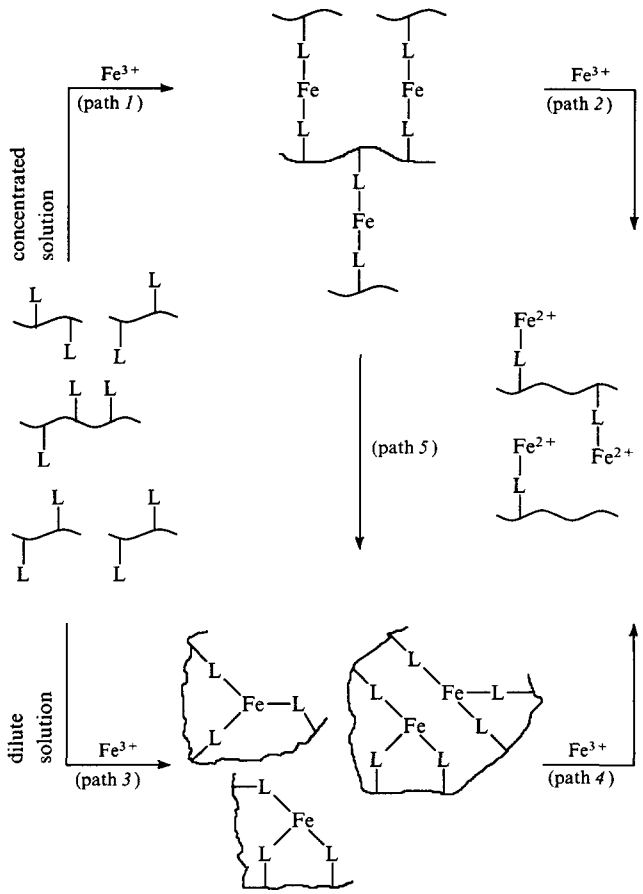
At the molecular level there are spatial organisation requirements which distingish macromolecular metal chelates from their low-molecular-mass analogues. The principal polymer chain effects are fully manifested on this level: the changes in the conformation of the chain, neighbouring groups, etc. In certain cases, these effects can be separated, which makes it possible to discover their characteristic features.

IV. The supermolecular level of the structural organisation of metallopolymers

On passing from a dilute to a concentrated solution and further to a massive specimen, there is a significant increase in the extent of the intermolecular interaction of both the initial polymers and of the metal chelates based on them, which makes it necessary to take into account a third (supermolecular) level of the spatial organisation of the MMC. Studies have shown that the reactions of metal ions with concentrated solutions of macroligands, cross-linked or graft polymers, are distinguished primarily by the greater free energy changes in the process. In concentrated solutions, the polymeric nature of the ligands considered should be manifested more strongly than in dilute solution and the characteristics of the chelation process associated with their polymeric character should be more pronounced. Therefore, in considering the kinetic and thermodynamic features of the chelation process on the supermolecular level, one has to take into account all the principal effects of the polymer chain.

With increase in the macroligand solution concentration, there is an appreciable increase in the probability of the formation of intermolecular (and not intramolecular) metal chelates.[80,81] By varying the degree of conversion, it is possible to observe the reversible transition between the intermolecular and intramolecular metal chelates. We shall demonstrate this with the aid of the scheme, presented below, for the formation of complexes between iron(III) ions and poly(hydroxamic acids) (Scheme 1).[82] At high polymer concentrations, the hydroxamic groups from different polymer chains are disposed closer to one another than the chelating fragments in the same chain. This increases the probability of the formation of intermolecular bonds (path *1* in Scheme 1), whereupon cross-linking becomes a significant feature of the process. The cross-linking of the polymer chain is accompanied by an increase in the viscosity of the solution (Fig. 18). Increase in viscosity by virtue of intermolecular cross-linking via the formation of metal chelates has been observed[60] after the addition of alkali metal salts to styrene–crown-ether copolymers. As a result of further addition of iron(III) ions, the cross-linked complexes with the composition [L]:[M] = 3:1 are converted into 1:1 complexes (path *2*) and, by virtue of the rupture of

Scheme 1



the cross-links, each iron ion is bound to only one hydroxamic group (path *4* also leads to the same products).

At low concentrations of the chelating macroligand, where the neighbouring hydroxamic acid groups in the same chain are disposed closer to one another than the groups from different polymer chains, the iron complex is formed intramolecularly (path *3*, Fig. 18), which diminishes the limiting size of the disordered polymer coil and hence diminishes the viscosity. With increase in polymer concentration, the change in viscosity becomes more appreciable, since the density of the cross-links

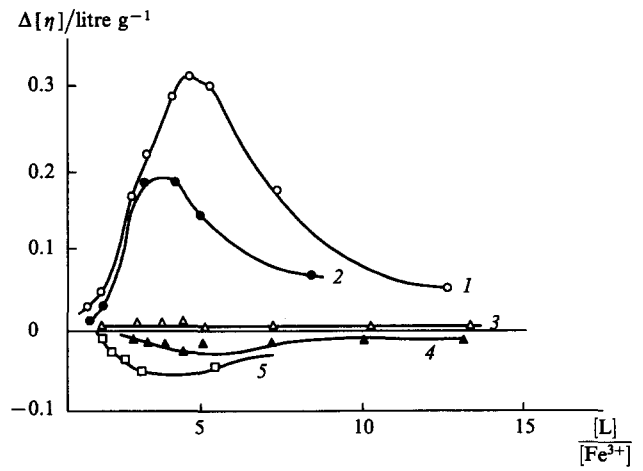


Figure 18. Dependence of the change in the intrinsic viscosity of the polymer containing 0.749 mol% of hydroxamic acid units on the ratio [L]:[Fe] for different concentrations of the polymer (g litre^{-1}): (*1*) 4.90; (*2*) 3.25; (*3*) 1.0; (*4*) 0.75; (*5*) 0.50.

increases. It is noteworthy that the molecular mass of the polymer has a greater influence on the viscosity than the content of the chelating fragments.[82]

The cross-linked polymers formed at high concentrations are 'kinetic' products, which after a time are converted into thermodynamically more stable intramolecular complexes (path *5*). The transition between the intramolecular and intermolecular complexes is reversible

Since the chemical bond is the same in both cases, the enthalpy of the transition ΔH should be zero and hence the transformation is determined by entropy factors. The conversion of intermolecular chelates into intramolecular ones is a first-order reaction, the rate constants for which are 5.21×10^{-6} s^{-1} at 303 K and 49.7×10^{-6} s^{-1} at 333 K. The activation energy and the entropy are 63.3 kJ mol^{-1} and 4.2 J mol^{-1} K^{-1} respectively.

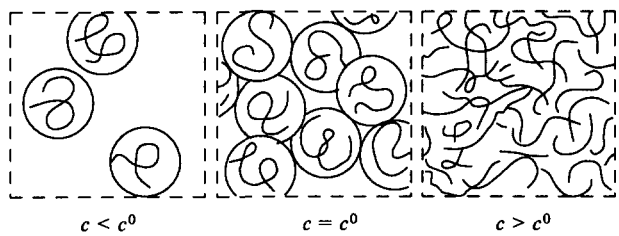


Figure 19. Schematic representation of the polymer at different concentrations of the latter.

The following two parameters are most important for the formation reactions of intermolecular metal chelates: the critical polymer concentration c^0 and the temperature T_t of the liquid ⇄ gel transition.

The quantity c^0 represents the concentration above which the intermolecular interaction becomes significant (Fig. 19).[83] It is noteworthy that the critical concentration of the polymer is inversely proportional to its molecular mass.[84] Above the critical concentration, the transition temperature T_t is almost independent of the concentration and molecular mass of the polymer (Fig. 20). It has been suggested that Eqn (13), obtained from the classical theory of gel formation, be used to calculate T_t.[85] This equation shows that T_t is determined mainly by the thermodynamic characteristics associated with the formation of metal–polymer bonds (i.e. ΔH and ΔS).

$$T_t = \frac{\Delta H}{\Delta S - R \ln[(c - c^0)/c^0]} \tag{13}$$

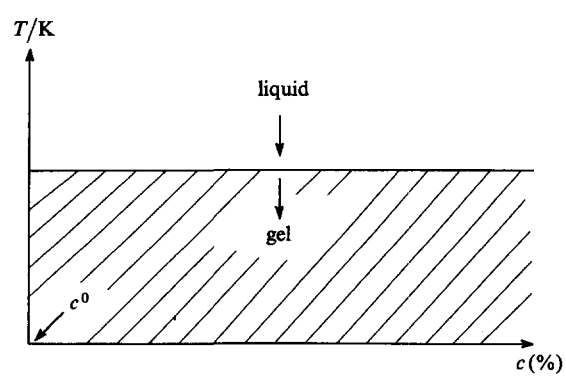


Figure 20. Liquid ⇄ gel phase diagram.

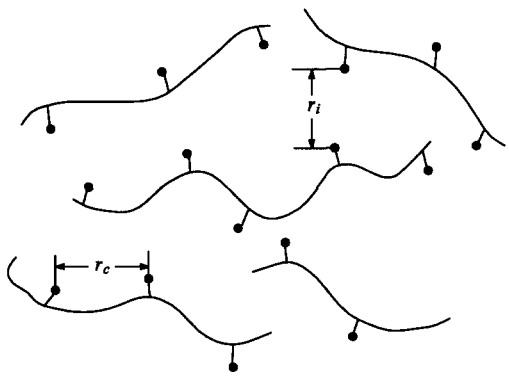


Figure 21. Schematic illustration of the formation of intramolecular (r_c) and intermolecular (r_i) chelates.

The distance between the chelating fragments on formation of the intramolecular (r_c) and intermolecular (r_i) metal chelates (Fig. 21) can be determined by means of statistical analysis, adopting the spheres in contact model. The distance r_i is determined from the equation

$$r_i = \frac{S}{(N_c/2)^{1/3}} , \tag{14}$$

where S is the length of the side of a box made up of close-packed spheres (1 cm) and N_c is the number of chelating fragments in 1 cm^3. The latter quantity is calculated as follows:

$$N_c = \frac{c_p}{100\, M_s} X N_A , \tag{15}$$

where c_p is the polymer concentration at the gel formation point (g litre^{-1}), M_s the average molecular mass of the elementary unit, X the mole fraction of the chelating fragments in the polymer, and N_A the Avogadro number.

The distance between the chelating fragments in one chain (r_c) is a function of the mole fraction of the chelating unit in the polymer and of the size of the polymer, which are determined by the solvent. Assuming that the polymer in solution consists of a disordered coil, r_c can be calculated by the equations

$$r_c = r_0 \beta , \tag{16}$$

$$r_0^2 = c_\infty t l^2 , \tag{17}$$

where r_0^2 is the mean square of the distance between neighbouring chelating fragments; t the average number of chemical bonds separating the chelating fragments, l the bond length (0.154 nm), c_∞ the characteristic ratio taking into account the increase in the size of the polymer as a result of short-range effects in the disordered coil model, and β the expansion factor taking into account the increase in the size of the polymer by virtue of its interaction with the solvent.

As an example, one may quote the results of the calculation of the quantities r_c and r_i for hydroxamic acid copolymers (Table 13).[82] Analysis of these data indicates that the hydroxamic acid groups of the polymer react in a 'disordered' fashion and

Table 13. Comparison of the values of r_c and r_i for hydroxamic acid copolymers.

Content of hydroxamic fragments in the copolymer (mol %)	r_c/nm	r_i/nm	Difference (%)
0.259	12.8	11.2	13
0.749	6.8	6.4	6
1.80	4.2	4.9	15

form infinite networks only when the probability of the intermolecular binding of the metal exceeds 50%.

In the analysis of the kinetics of reactions involving insoluble polymers, one must take into account both diffusional (transfer of the functional groups after the system has passed through the glass point) and topological (virtually complete absence of the translational diffusion of the functional groups grafted to the polymer skeleton) difficulties. In comparatively early studies,[86] it was shown that the rate-limiting stage of chelation by cross-linked macroligands is diffusion. Because of this, the surface chelating groups are the first to react and the access of metal ions to the interior of the block is restricted. In particular, the study of the kinetics of the chelation of metal ions by cross-linked polyamine ligands confirmed the appreciable influence of diffusion on this process: for polymer particles whose size is up to 0.1 mm, external diffusion is rate-limiting, whilst for particles with sizes in excess of 0.1 mm internal diffusion into the deep layers is rate-limiting.[87] In the case of linear polymers, the rate of complex formation is appreciably higher than for cross-linked polymers because it is determined by the rate of diffusion of the metal ions to the functional groups. The formation of chelates is preceded by the formation of outer-sphere complexes and their transformation into inner-sphere complexes with subsequent diffusion of the metal to the second ligand of the polymer, and so on. As a consequence of the lower metal concentrations at the reaction site, the overall composition of the complex may be different from that in the case of linear polymers and low-molecular-mass analogues. The significant difference in the binding of metal ions by the soluble and cross-linked macroligands also consists in the fact that in the latter the overall macroligand concentration is constant and independent of the dilution of the suspension by the solvent.

The small difference between the stability constants of the low-molecular-mass and high-molecular-mass hydroxyquinoline metal chelates indicates isotypical spatial environments of the metal ion in these compounds. Polymers with 8-hydroxyquinoline groups have been obtained by the polymerisation of[88] or polycondensation[89] method. The composition of the complexes corresponds in this case to the ratio [M] : [L] = 1 : (1.5 – 2.0), which is close to the ratio 1 : 2 corresponding to the stoichiometry of divalent metal complexes. On the other hand, the formation of 1 : 1 complexes is characteristic of cross-linked polymers.[90] Furthermore, the stability constants of complexes based on cross-linked polymers are lower than those of the low-molecular-mass analogues (Table 14).[91]

Table 14. *Stability constants of 8-hydroxyquinoline complexes.*

Metal	MMC			LMC		
	$\lg K_1$	$\lg K_2$	$\lg K_3$	$\lg K_1$	$\lg K_2$	$\lg K_3$
Cu	7.45	6.65	14.10	13.49	12.73	26.22
Ni	5.60	5.35	10.96	11.44	9.94	21.38
Mg	3.18	2.82	6.00	6.38	5.43	11.81

In terms of the stability of the complexes with 8-mercaptoquinoline polymer, divalent metals can be arranged in the sequence Hg > Cu > Ni > Co > Zn > Pb, which is the same as the stability series of the 8-mercaptoquinoline chelate complexes of these metals. However, in contrast to low-molecular-mass analogues, the macroligands form 1 : 1 complexes and the selectivity of 8-mercaptoquinoline in relation to certain metal ions is retained when this group is introduced into the polymer.[92]

The composition and stability of the MMC formed are also influenced by the physical state of the macroligand. As a result, their transition from the nonporous (gel) to porous structures is accompanied by a decrease in the overall stability constant of the complexes owing to the closer packing of the chains and the lower mobility of the functional groups, which leads to appreciable free energy losses on complex formation.

It is interesting to note that the time required for the saturation of the macroligand by the metal increases with increase in the size of grains in the latter.[93]

An increase in the degree of cross-linking leads, on the one hand, to a decrease in stability of the macrocomplexes as a consequence of the increase in strain in the twisted chain on formation of the second and subsequent coordination centres and, on the other, to a change in the nature of the intermolecular interaction. In particular, the rate of interaction of vanadyl acetylacetonate with the chloromethylated styrene – divinylbenzene copolymer modified by catechol groups is much lower when the degree of cross-linking of the polymer is 20% than when it is 2%. The rate increases if the polymer with a 20% degree of cross-linking is ground (Fig. 22).[94] The ratio of the initial rates of absorption of vanadyl ions from a solution of the polymers with 2% and 20% degrees of cross-linking is ~3.9.

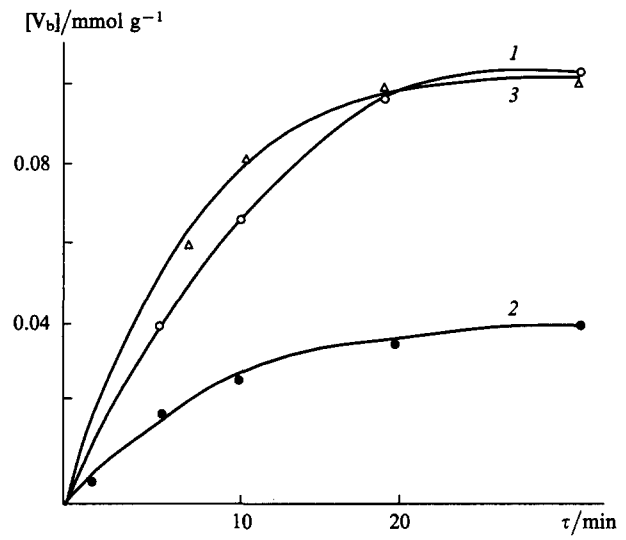


Figure 22. Absorption of vanadyl ions from a solution by a polymer containing catechol groups; (*1*) degree of cross-linking of the polymer 2%; (*2*) degree of cross-linking of the polymer 20%; (*3*) ground polymer with a degree of cross-linking of 20%.

An increase in the degree of cross-linking of the polymeric ligand may alter the steric configuration of the chelate unit: thus it changes from square planar to tetrahedral in the nickel complexes.[15]

The intermolecular interaction in a polymer is known[95] to be much more pronounced than in the analogous low-molecular-mass compounds. Apparently in the MMC it is still stronger than in the initial ligands. This happens both as a consequence of the decrease in chain flexibility on formation of the complex and as a result of the increase in the energy of the local intermolecular interaction. The parameters of the intermolecular interaction in the MMC are influenced by the electron-donating capacity of the functional groups, their distance from the main chain, and also the presence and size of other substituents which do not participate in the complex formation reaction. As a result of these factors, the polymeric complexes frequently give rise to more ideal morphological structures than the original macroligand. Thus the structural changes in the styrene – divinylbenzene copolymer during its alkylation by 5-chloromethyl-8-hydroxyquinoline in nitrobenzene in the presence of $AlCl_3$ have been elucidated in detail.[96] In the stage involving the attachment of the complex to the polymer, the latter undergoes a reorganisation — micronetwork rearrangements and twisting of

the polymer. The structural changes in the polymer obey the steric requirements of the complex-forming metal (minimum free energy loss) and in all cases the capacity of the chain molecules for twisting depends on the rigidity of the chain, the nature of the solvent, etc. By operating with these factors, it is possible to weaken or, conversely, to intensify the twisting or extension of the chain. It is then necessary to take into account the increase in the rigidity of the chain at the binding sites with increase in the degree of conversion.

In particular, the change in the chain rigidity, which depends on the number of bound functional groups, affects the stability of the complexes: the most stable complexes are formed for low degrees of conversion and the least stable are formed for higher conversions. With increase in the degree of conversion, the stability constants of the copper(II) chelate complexes of poly(acrylohydroxamic acid) pass through a maximum (Table 15): they increase with increase in η in the region of low conversions and diminish in the region of high values of η.[97]

Table 15. Stability constants of copper(II) chelate complexes of poly(acrylohydroxamic acid) {293 K, [$NaNO_3$] = 0.2 M}.

α	B_1	B_2	B
0.087	−1.9	−2.9	−4.8
0.26	−0.75	−1.85	−2.6
0.43	−1.1	−2.4	−3.5
0.69	−1.0	−2.8	−3.8

Note. $B_1 = K_1K_a$; $B_2 = K_2K_a$; $B = B_1B_2 = KK_a^2$.

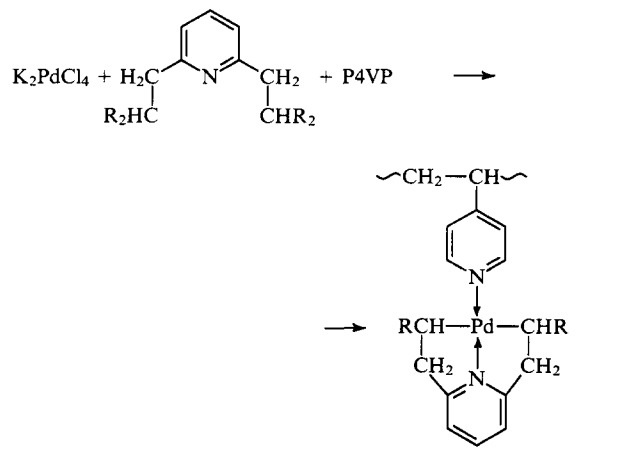
The stability of the MMC is influenced significantly also by the valence of the metal. Thus the stability of poly(enol-ketone) chelates based on oxidised poly(vinyl alcohol) films increases in the following sequence of ions: $M^+ > M^{2+} > M^{3+}$.[98] An important factor is that oxidation of the films promotes the permeation of the metal ions into their deep layers.

The dependence of the properties of the complexes formed and of the degree of conversion on the method of preparation of the complexes is characteristic of the MMC based on cross-linked macroligands.[99-101] As was to be expected, if the polymer does not swell in the given solvent, then the chelation reaction either does not occur or proceeds with a very low percentage binding of the metal.[102] This conclusion has been confirmed yet again by a study of the interaction of transition metal compounds with polymers based on 2,2′-dipyridylmethane.[103] The composition of the complexes formed with participation of this polymer also depends on the nature of the metal and the ligands bound to it.

The influence of temperature on the chelation process may be demonstrated in relation to the interaction of K_2PdCl_4 with 2,6-derivatives of pyridine[104] in the presence of P4VP or the styrene–4-vinylpyridine copolymer. The interaction results in the formation of complex **34** (Scheme 2).

Macromolecular metal chelates have been obtained at 298 and 360 K. It was found that the P4VP-based MMC, obtained at 298 K, are bright yellow in colour and dissolve readily in ethanol, while the polymer obtained at 360 K is dark yellow and is only slightly soluble in ethanol. This can be explained by the different conformations of P4VP in ethanol at different temperatures. On the other hand, the palladium chelate based on the styrene–4-vinylpyridine copolymer, the conformations of which are the same at these temperatures, dissolves readily both in ethanol and chloroform regardless of the temperature at which it is obtained. The degree of conversion, found from elemental analysis and NMR spectra, was 25% in all cases under these conditions. In other words, by varying the temperature, it is possible to obtain complexes having the same composition but with different steric structures.

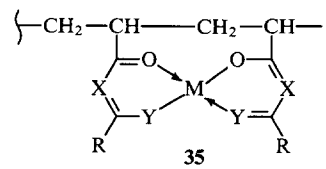
Scheme 2



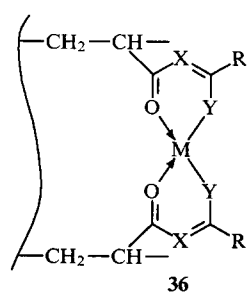
34 (R = COOAlk)

The structure of the complexes is in many respects determined by the conditions of their preparation. It is apparently necessary to take into account the relaxation time of the products formed, which are in a stationary state, and hence the dynamics of the variation of the required properties. The interchain cross-links arising in the rigid chain polymers alter appreciably their supermolecular organisation, which increases the rigidity of the chain. This should be manifested by a change in the relaxation transitions within the chains and the segments. Evidently, the α-relaxation, associated with the micro-Brownian motion of the long sections of the chains near the glass point, is more subject to such influences. For low degrees of saturation of the macroligand, the overall restriction of the chain mobility is slight. With increase in the degree of saturation, an ever increasing number of cross-links are formed between neighbouring chains, which should lead to an increase in the glass point T_g. In the region of β-relaxation, the glass point is almost independent of the metal content and intermolecular cross-linking leads to its increase. On cyclisation, T_g should increase with increasing metal content as a consequence of the increase in the rigidity of the individual sections and the decrease in the mobility of the entire chain.

Macroligands with chelating fragments grafted to the surface (the readily swelling functional group coating on an insoluble substrate) occupy an intermediate position between the soluble and cross-linked polymers.[1,65] The interaction of metal ions with such macroligands simulates to a large extent complex formation in solutions. As a rule, in both cases the free energy changes are similar.[105,106] Intramolecular cyclisation (complex **35**), and not intermolecular cyclisation (complex **36**), is characteristic of grafted macroligands, as for soluble polymers.[28,29,107]



35



36

In order to assess the interactions in transition metal ion–grafted macroligand systems, the modified Langmuir equation is usually employed:

$$\frac{c}{c_b} = \frac{1}{kf_{max}} + \frac{1}{f_{max}}, \quad (18)$$

in which c and c_b are the concentrations of the dissolved and bound metal, k is the stability constant, and f_{max} is a constant characterising the limiting degree of binding (limiting adsorption) of the metal to the functional groups of the polymer. This equation is valid only for low degrees of conversion when the concentration of the unreacted and unreactive centres may be neglected.

In particular, the adsorption of copper(II) ions on polymeric ligands with grafted iminodiacetic acid groups is described by the Langmuir equation (Fig. 23).[108] The parameters of the Langmuir equation, calculated from the relations presented in Fig. 23, are listed in Table 16. The constant f_{max} increases with increase in the degree of grafting to ~0.3. This quantity indicates that the number of centres capable of binding Cu^{2+} ions increases to 30% depending on the number of bis(carboxymethyl)amino-groups.

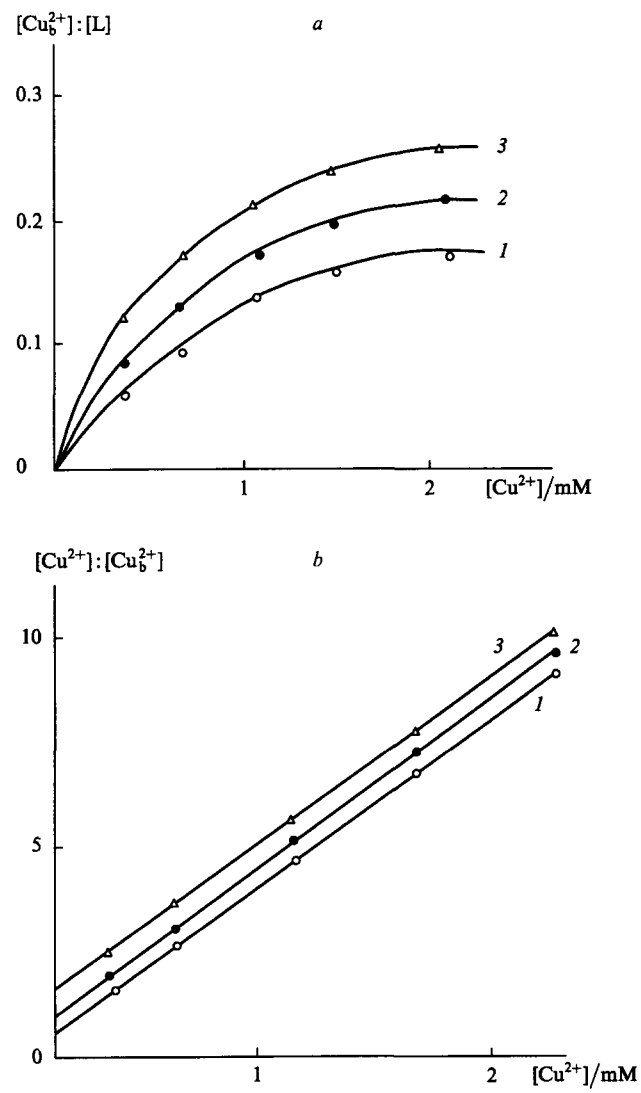


Figure 23. Relation between the amount of Cu^{2+} ions and their concentration in solution (*a*) and the corresponding Langmuir relation (*b*) for different degrees of grafting of the chelating fragments (%): (*1*) 24.4; (*2*) 31.8; (*3*) 40.5.

Table 16. Parameters of Eqn (18) for the chelation of copper(II) ions by polymers with grafted iminodiacetic acid groups.

Degree of grafting	$10^{-4}K$/litre mol^{-1}	f_{max}/mmol g^{-1}
24.0	1.8	0.24
31.8	2.2	0.26
40.5	3.1	0.29

The constant K also increases with increasing degree of grafting. These results show that the ability of the ligand groups of the grafted chains to chelate Cu^{2+} ions increases with increasing degree of grafting. The complexes formed become more stable apparently by virtue of the fact that, as soon as the Cu^{2+} ion has been coordinated to one ligand, other ligand groups coordinate to it more readily. On the other hand, the adsorption of Cu^{2+} by a polymer containing the same number of bis(carboxymethyl)-amino-groups bound directly to the main chain is described by the Langmuir equation with the parameters $K = 3.5 \times 10^3$ litre mol^{-1} and $f_{max} = 0.075$ mmol g^{-1} under the same conditions.[109] Thus the chelating capacity of the polymers improves after the introduction of a grafted chain as a bridge.

V. Conclusion

Analysis of the three levels of the structural organisation of the MMC shows that the characteristics of their formation differ significantly from those of the formation of the LMC. For the latter, the second and third levels are not as a rule considered. Therefore the methods for the estimation of the thermodynamic parameters of the MMC and the LMC should also differ. On the most thoroughly investigated local level, important information about the mechanism of the formation reaction can be obtained precisely by comparing the thermodynamic parameters.

Examination of the second level leads to the conclusion that, in the calculation of the thermodynamic parameters, account must be taken of the principal polymer effects, as for the kinetics of chemical reactions with participation of macromolecular reagents. Only this approach permits the quantitative estimation of the differences between the processes involving the formation of the LMC and of the complexes in the macrochain–MX_n systems. In ideal cases, it is possible to estimate the contribution of each effect (or at least to discover which is the dominant one) to the thermodynamics of the process, which helps in understanding the characteristic features of the formation and structure of the MMC.

The third, supermolecular level has been least investigated. This is associated, on the one hand, with the dependence of its parameters on the degree of conversion in the chelation process and, on the other, with the possibility of the occurrence of the so called 'stationary states' characteristic of long-chain molecules. The properties of the MMC obtained differ appreciably from the equilibrium ones. Unfortunately, not only the properties of the system in a specified 'stationary state' but also the very conditions of the appearance of such a state still remain uninvestigated.

In the general case, the observed equilibrium constant can be represented to a first approximation as the product of the equilibrium constants for different levels. Unfortunately, the number of kinetic studies on MMC is still insufficient for more specific generalisations.

Here we may also note that the importance of the problems under consideration is determined, firstly, by the need for a purposeful approach to the synthesis of MMC with specific homogeneous structures.[110] Secondly, there is a possibility of synthesising deliberately MMC designed for different practical applications (in the first place as metallopolymer composite materials in metal complex immobilised catalysts). Among comparatively new aspects, we may point out the use of

MMC in 'non silver' photographic processes,[111] as sensitisers of photodynamic cancer therapy,[112] and as high-temperature superconducting materials (ceramic material consisting of polymers with YBC-chelates ‡).[113]

The structural organisation considered in the present review mainly in relation to polymerisation MMC is characteristic also of the MMC of the coordination and condensation types,[113-116] liquid-crystal polymeric chelates,[117-121] and also MMC obtained by methods involving the polymerisation and copolymerisation of the corresponding metal-containing monomers.[122] The formation of complexes between a metal-containing monomer of the chelate type and a template during radical copolymerisation and polymerisation makes it possible to regulate the position of the metal ion in the polymer matrix, while the high degree of cross-linking promotes the stabilisation of the functional group environment.[123] Such template polymerisation strategy is promising from the standpoint of the construction of highly specific catalysts, sorbents, and synthetic receptors for the recognition of complex biomolecules. In other words, the MMC, i.e. organised polymolecular *ensembles* (especially in thin Langmuir–Blodgett metallopolymer films),[124] are potential objects for the vigorously developing supramolecular chemistry[125] — the constructional chemistry of intermolecular bonds.

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