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High Polymer Chelates—V. Structure and Physico-Chemical Properties of Polymeric Chelates*

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Summary

There are two important classes of polymeric chelates. Those formed by reaction of heavy metals cations with a preformed chelating polymer offer many interesting examples of highly selective ion-exchangers; on the other hand, the chelation may promote important and reversible modifications of the macromolecular shape.

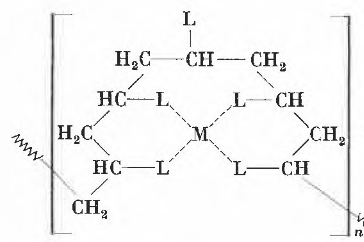
When a polychelate is formed by a reaction between a multivalent heavy metal cation and a bis-bidentate ligand, chains are formed which enjoy new physical properties; the most interesting one is the semiconductivity of the polychelates having a conjugated structure: their amazing electronic properties are discussed.

Introduction

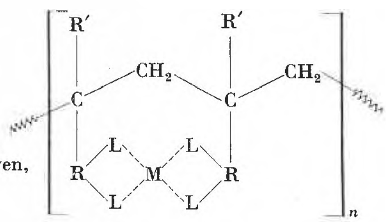
During the past decade, a very abundant although sometimes confusing literature appeared, dealing with the synthesis of polymers containing chelated metal atoms. Excellent reviews[1–3] were devoted to the covering of these investigations, which were mostly exploratory in character, and the present discussion would by no means pretend to be a new additional exhaustive compilation of this type: its aim is to present, on the basis of several recent experimental results, a tentative analysis of the most interesting outcomes and prospects of the chemistry of these polymeric chelates.

Under the name of "polymeric chelates", one could include every type of a polymeric chain containing chemically bonded chelate rings, which are the well-known coordination complexes formed by a metal ion and two (ore more) electron-donor groups of a single "chelating" molecule, or ligand: the resulting ring formation imparts to the chelate a high stability and remarkable properties.

It is possible to conceive, and prepare, two fundamentally different classes of polymeric chelates. The first one is generally obtained by reacting a metal ion with a preformed ligand polymer: the metal atom is not an essential part of the polymer backbone, and as a consequence can be exchanged without modification of the chain's chemical structure; these polymeric chelates may be schematized f.i. by the following formulae, where L denotes an electron-donating group:

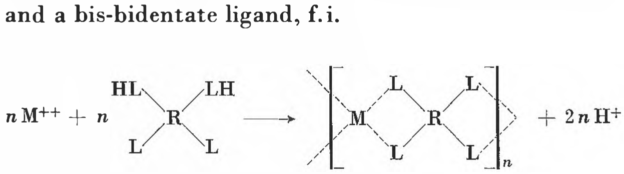


or even,



and wherein the aliphatic backbone could be replaced by any kind of structure, such as aromatic rings, heteroatomic backbone ...

The second class polymers are prepared by a "polychelation" reaction between a multivalent metal atom and a bis-bidentate ligand, f.i.



which is a peculiar type of a polycondensation reaction. In this case however the metal atom is an essential part of the polymeric chain (which is in fact an heteroatomic one) and its exchange or removal brings about the breaking of this chain; these polymers are very often referred to as "polychelates".

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These two types of polymers have very different properties, owing to their different chemical structures. As already indicated, the chelating polymers where the metal ion is bound on the outside of the chain, are able to undergo ion-exchange, in a selective manner depending on the relative stabilities of the formed complexes: this behaviour gives rise to interesting analytical applications; on the other hand, the chelation process induces very important modifications of the chain's shape, and we could presume interesting applications of this chemical-to-mechanical energy conversion; f. i. under the form of a "chelating muscle".

The "polychelates", where the metal is a vital part of the polymeric chain, have a structure which prevents their use as ion-exchangers; but insofar as they have a conjugated structure (this point will be discussed later in detail) they exhibit a bulk of very interesting properties that could be referred to under the name of "quantum properties": many of these products are resistent to high temperatures (200 to 300 °C), have a catalytic effect on several chemical reactions, and enjoy some electric and electronic properties which were gathered under the rather misleading appellation of "semiconducting properties".

Examples of these different properties are presented below in more detail, so as a discussion of the structural requirements needed to obtain interesting comparative and useful results.

I. Chelating Polymers, Containing Metal Atoms on the Outside of the Polymeric Backbone

A. Selective Ion-exchange

This was for a long time the most studied application of the chelating polymers, and we will discuss these phenomena in the light of the results obtained in the investigations carried out on two different ligand polymers, namely polymethacroylacetone and polyvinylamine: however the reasons of this choice are worth to be explained previously in some detail. It is true that since the original work of Skogseid, many publications appeared describing the synthesis and the properties of polymers able to form chelate complexes with metallic ions (see f.i. the literature mentioned in references 13 and 14); many of the earlier studies however failed to give really conclusive results, and there seem to be two main reasons for this situation.

First of all, many workers have investigated polymers whose structure was poorly defined and certainly not homogeneous; f.i. the preparation of these chelating resins was very often carried out by performing a classical organic reaction on a preformed polymeric chain: in fact this is not a safe procedure since Smets and coworkers have shown[4–7] that most of these reactions performed on high polymers give rise to important and often determining secondary processes due to intramolecular cyclization, highly favoured by the short distance between two vicinal reactive units. Such mixed structures are highly unfavourable for chelation studies, and these remarks can be extended to many polycondensation process. Therefore, it seems more advisable to consider the preparation of new monomers carrying a well known chelating group, monomer which is subsequently polymerized under mild enough conditions to yield a pure polymer, whose chelating properties can be studied by classical physico-chemical methods.

A second reason for many disappointing results is that the study of these chelating resins was often carried out in a medium with which they are not well compatible; many chelating ligands are very weak acids or bases, showing an hydrophobic character which decreases very much the absorption rate in aqueous medium; therefore it is important either to device hydrophilic polymers to get water compatible chelates to be studied in aqueous medium, or to test the hydrophobic products in such mixed media as water-alcohol, -dioxane, or -dimethyl formamide, where they have a satisfactory solubility; it is worthwhile to mention at this point that the lypophilic character of an ion-exchange polymer can be controlled by insertion of long aliphatic side chains into the resin[8]. It must be admitted that these difficulties have too often prevented a study of a really selective separation, such as that of vicinal transition metal cations like cobalt, nickel, copper and zinc in aqueous solution; it will be shown below that the two polymers selected, which correspond to the criteria discussed above, allow such studies to be made, so as an accurate comparison of the physico-chemical properties of these chelates to those of their low molecular weight analogues.

1° Polymethacroylacetone

Methacroylacetone was synthesized from acetone and methyl methacrylate[9, 10]: this monomeric β-diketone can be easily homopolymerized, or copolymerized with hydrophilic comonomers, and the obtained polymers give the usual neutral chelates with divalent metal ions; it must be pointed out however, that a small fraction of the metal ion is presumably bound by intermolecular chelation, since the polymer obtained is often insoluble: this phenomenon, which is reversible, has to be expected for steric and statistical reasons.

Both the polyligand and its chelate were of high purity (more than 99% for the free ligand, and about 98% for the copper chelate, calculated as a 2 to 1 chelate), as checked by elementary and functional group analysis. A more detailed study of the polymer structure was performed[11] by comparing the infrared spectra of the polymeric ligand and chelates, and those of low molecular weight models having a similar structure, namely pivaloylacetone and its chelates; the spectra are very similar when comparing the ligands or the chelates of the same metal, but moreover one finds the same shift of the carbonyl absorption frequency (1605 cm^{-1}) upon chelation, both for the polymers and their model compounds: this shift should be expected from the nature of the dative bond between the oxygen and the metal atoms[12], and it is rewarding to verify experimentally that it is indeed a function of the metal electro-negativity and the stability of the chelate.

The fact that such chelated polymers had exactly the same structure as their low molecular weight models, promoted a more detailed study of their physico-chemical properties, and more precisely of their formation (or stability) constants. As a matter of fact, many data are now available about the stability of low molecular weight chelates since the publication of tables of formation constants by BJERRUM and SCHWARZENBACH; if an accurate parallelism is found between the thermodynamic properties of these chelates and those of the corresponding polymers, one would dispose there of a very convenient and useful method to design tailored-made resins for specific separation problems, since it is obvious that the metal yielding the most stable chelate would also be the one preferentially adsorbed.

These ideas were checked first on the polymeric diketone described in this section; to do that, potentiometric titration curves were measured in a mixed medium (dioxane-water) following a method described by FERNELIUS, and the corresponding BJERRUM plots calculated as previously reported[13]; from these data, the relative stability of the different chelates were estimated, and the results are gathered in Table 1, which however deserves a special comment:

Table 1. Formation Constants of the Polymethacroylacetone chelates

M^{++}	Polymethacroylacetone log B_P	log K_f	Pivaloylacetone log B_M	log K_f
UO_2	— 5,7	23,1	— 4,8	22,2
Cu	— 6,0	22,8	— 5,0	22,0
Ni	—11,4	17,4	—10,8	16,2
Zn	—11,3	17,5	—11,2	15,8
Co	—11,7	17,1	—11,2	15,8
Mn	—13,7	15,1	—13,6	13,4
Mg	—15,6	13,2	—15,3	11,7
Ba	—20,0	8,8	–	–

For each compound, a formation constant $K_f = \frac{[ML_2]}{[M]\,[L]^2}$ can be calculated, corresponding to a two steps formation of a chelate containing two diketones for each metal; however, when the ligand is a polymer, the reaction may proceed in one step since there is most of the time a free ligand group in the vicinity of the first chelated species formed, if these equilibria are studied in the presence of an excess ligand; practically, it seems more advisable to compare displacement constants, corresponding to a reaction: $2\,LH + M^{++} \leftrightarrows [ML_2] + 2\,H^+$, and for the polymeric ligands, its best expression corresponds probably to $B_P = \frac{[ML_2]\,[H^+]^2}{[LH]\,[M^{++}]}$.

It may be seen in the table that there is not only a very good parallelism between the polymer and the low molecular weight model, but that even the absolute values of the constants are in a very close agreement if one takes in account the polymeric nature of the ligand as discussed above, by comparing the log B_P for polymethacroylacetone and the log B_M for pivaloylacetone.

This comparison may be drawn still further by plotting the logarithm of the different chelates formation constants versus a function of the electronegativity of the involved metal ion: a direct correlation is obtained (except for the uranyl ion, known to have a collinear polymeric structure), which is completely similar to that obtained with other low molecular weight diketone chelates.

These ideas could be checked for application purposes, assuming that a difference of two units in the logarithms of the formation constants insures a good separation of the corresponding cations when this polymer is used as a selective ion exchanger: table 1 shows the possibility of performing many interesting separations on these bases, and this was proved to be the case with a mixture of copper and nickel ions in aqueous solution; therefore it was necessary to prepare a sample of finely divided polymer (to insure a satisfactory rate of adsorption, despite the rather hydrophobic character of this polymer), and this sample was shaken with a buffered solution of the two ions; it was found that the selectivity is indeed very high: an important fraction of the copper is retained on the polymer but no nickel; the recovery (by a dilute acid solution) is quantitative and the resin may be reused for many cycles. The theoretical capacity of the resin is not fully used, due probably to steric or uncompatibility factors, but it is worthwhile to remind that this capacity is rather high: around 8 meq. per gram of dry resin[14].

Similar results were obtained[15] with polymers of trifluoroacroylacetone, and they could probably be extended to liquid-liquid systems, the polymer being dissolved in the water unmiscible organic phase. At the present time, it seems probable that the most interesting application of this type of polymer would be the recovery of expensive metals dissolved in a mixture of other salts in aqueous solution.

2° Polyvinylamine

A further extension of these ideas and results was sought in the study of a polymer able to perform a selective separation of a complex mixture like that of copper, nickel, cobalt and zinc ions in aqueous solution, which is a problem arising in some hydrometallurgical treatments. From data published for low molecular weight substances[16,17] it appears that such a separation could be achieved with a polyamine resin: therefore it seemed interesting to study the chelation behaviour of pure polyvinylamine, whose synthesis was described by HART[18], since this polymer was water soluble and should allow a rapid metal binding in aqueous solution; moreover the corresponding chelates, which have a highly favourable steric configuration, are water soluble over a wide range of *p*H and ionic strenghts values.

The relative stabilities of these chelates were also studied by potentiometric measurements in the presence of the different metal ions; again they follow the same order as that indicated for low molecular weight models, i. e. Cu $\gg$ Ni $>$ Zn $>$ Co, and this situation should allow to perform some separations which are still a challenge in this field, f.i. the removal of zinc traces from cobalt solutions. It was difficult to achieve a calculation of the corresponding formation constants from potentiometric data, since the basicity of the polyamine is a complex function of a strong neighbour-neighbour interaction which does not obey the HENDERSON-HASSELBACH equation, as shown by KATCHALSKY; only a very empirical estimation of these values, was reached by a graphical method[19].

However the selectivities indicated by the potentiometric titrations could be confirmed by dialysis experiments, the polyamine being enclosed in a little cellulose casing bag; the results, as reported earlier[14], show the possibility to catch successively, by a proper adjustment of the *p*H values, the different cations of a mixture of copper, nickel, zinc and cobalt; increasing the *p*H value over 8 led to a decrease of the binding, owing probably to a competitive hydroxide formation. These results confirm the interest of such a chelating polymer, interest which is mostly based on two different properties: the capacity is high, about 80% of the theoretical one (6,3 meq. per gram of dry resin hydrochloride), and the binding is fast in aqueous medium, which is very useful for the applications. Since it is easy to cross-link this polyamine by a reaction with difunctional alkyl halides or isocyanates, the polymer is valuable to be applied to specific separation problems, at least on a laboratory scale.

B. Other physico-chemical properties; polymer shape modifications

The chelates formed by polyvinylamine are water soluble, at least in dilute solutions of low ionic strenght, over a broad range of *p*H values (up to 9–10): this solubility, so as the correlated polyelectrolyte nature of these compounds, induced an investigation[20] of their properties in aqueous solution by classical methods, in order to detect the eventual chelation features corresponding to a specific polymeric behaviour. Copper chelate was choosen as the most stable and simple of these compounds.

A spectrophotometrical study, combined with the results obtained from potentiometric and dialysis experiments, confirmed the preferential formation of a 1-to-4 copper-amine chelate, in which 1 to 2 amine groups over six remain unchelated: this is to be expected, owing to the steric hindrance due to the chelate rings formation and it corresponds to the fact that only 70 to 80% of the complexing groups in the polymer are chelated.

The solubility of this copper chelate corroborates the intramolecular character of the chelation process; however this intramolecular chelation corresponds to the formation of successive tricyclic chelate rings and must be accompanied by a very important contraction of the polymeric chain: therefore, attempts to show this variation of the shape of the macromolecule were carried out by measurements (mostly viscometric) performed on both free and chelated polymers.

To allow a sound interpretation of the data, it is important to exclude any other factor of shape modification, and therefore to perform the experiments under a constant ionic strenght, high enough to ensure an efficient shielding of the intermolecular electrostatic effects; under these conditions, the variation of the chains shape in function of the *p*H or the degree of charge, are due only to intramolecular electrostatic repulsion forces. However, even these variations are negligible, compared to those measured in the presence of transition metal cations: f.i., the dramatic drop in viscosity (more than 10 times) found out upon chelation of the polyvinylamine seems to be effectively due to an important shrinkage of the polymer chain: in this respect, it is interesting to see that for a given metal ion, the *p*H value needed to reduce the initial viscosity of the free ligand polymer by a factor around 10 is exactly the same as the *p*H value corresponding to the half-chelation reaction as determined by potentiometric measurements; this significant parallelism corroborates very well the above conclusions.

This contraction of the polymer chains upon chelation suggests also several applications in the field of the conversion of chemical to mechanical energy, similar to the "synthetic muscles" described by KUHN[21]: one could consider a study of the contraction at constant *p*H, and an evaluation of the energy involved in the chelation process.

These investigations on the polyvinylamine chelate structure were extended by conductometric measurements, which confirmed the formation of a tetracoordinated copper complex, but revealed moreover interesting changes in the macromolecules properties: it was found that the variation of conductance of the free polyamine as well as that of its chelates changed abruptly when the decrease in the degree of charge reached 33%, this change corresponding accurately to a maximum in the viscosity of these products. This unexpected behaviour suggests a still more sensitive structural modification of the chain, and deserves probably a more detailed investigation.

C. Prospects of these polymers

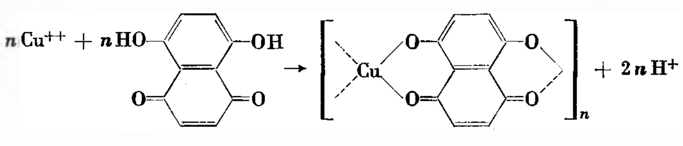
The above discussed examples show that many useful and interesting data can be gained from investigations performed on pure polymers, whose structure is well known and above all homogeneous: these data allow a more precise evaluation of the possibilities of such chelating polymers for different types of applications, even when they are less pure than those used for the basic investigations.

In this respect, a great deal of work remains to be done, which may be rewarding. Even a chemical transformation of a polymer chain may be of interest, if it is performed carefully to completion; an example of this is the synthesis of polysalicylidenevinylamine[22], starting from salicylaldehyde and polyvinylamine itself, first in aqueous medium, and thereafter in a mixed organic medium (dioxane-aldehyde): the reaction yields a very pure and completely soluble SCHIFF's base (99% pure) which is also an interesting polymeric chelating agent: the chelates formed by this ligand have a stability which follows the usual MELLOR's series, as indicated by the shift of the C=N stretching vibration frequency: in the presence of water they undergo an hydrolysis reaction whose rate was found to be inversely proportional to their stability, which corresponds very well to the weakening (by electron donation of the metal) or the basicity of the nitrogen atom which undergoes the protonic attack[23]. It seems also that the cobalt (and eventually iron) chelate could deserve a more careful investigation as a model for some biochemical reactions, f.i. as a polymeric oxygen carrier: this direction is still practically unexplored.

II. Polychelates, Containing Metal Atoms in the Main Polymeric Chains

In this section are discussed the properties of the second family of polymeric chelates, namely those where the metal atom in an essential part of the polymeric backbone.

Although this class of products includes many types of structural arrangements, the most interesting and specific properties appear when a conjugated structure is established throughout the polymeric chain: therefore a bis-bidentate conjugated ligand molecule and a metal atom able to form $d\pi - p\pi$ bonds to both adjacent ligands are required, f.i. copper ion and naphthazarin:



CALVIN already mentioned the possibility of contribution of a conjugated structure involving double-bond character of the metal-to-ligand bond, predicting for the β-diketone chelate rings some aromatic character which is by now chemically confirmed[24]; such effects were also put in evidence by spectrophotometric measurements[25].

In this context, it must be possible to prepare macromolecules in which there is a real conjugation along the chain, through the recurrent metal atoms.

This conjugation gives rise to specific properties, the first one being a stabilization of the macromolecule; that should be reflected by the thermal stability of the products, and it is found in fact that many of these polychelates are resistant to an increase in temperature up to 250, sometimes 350 °C, at least under a non-oxidant atmosphere.

However it must be admitted that their potentialities in the field of thermostable polymers are not very promising, for several reasons: although thermally resistant, they are not very stable against chemicals such as oxidizing, and principally hydrolizing agents promoting a very severe degradation of the main chain; on the other hand their mechanical properties are rather poor and they could not fulfil, in their present state, the strict requirements imposed to the thermostable replacement materials, the more as they face the competition of the extremely satisfactory materials derived from the polyheterocyclic polymers of the general type proposed by MARVEL[26].

A new and interesting set of properties of these polymers was discovered and investigated during the last years, which could be referred to under the name of "quantum properties".

It is generally admitted that conjugation lets promote a good level of conductivity throughout a single macromolecule by its π-electrons: indeed, experiments have shown that many of these polychelates have interesting quantum properties, and among these, conducting properties. The bulk conduction through a conjugated polymer sample requires however an important electronic interaction between the macromolecules: it may be speculated that increasing the degree of conjugation in the chain promotes also an increase of the importance of the π-electrons cloud and consequently a better intermolecular coupling: this should become apparent by a direct correlation between the degree of conjugation in the macromolecule and the bulk conductivity of the polymer sample.

On these grounds, the properties of three types of diketone polychelates were investigated[27], to elucidate the influence of an increasing degree of conjugation and intermolecular coupling on the electrical properties: these properties are gathered in Table 2.

When the polymer chain is a completely saturated one like in the case of the polymethacroylacetone copper chelate (PMA-Cu), the product behaves like an insulator. In the polytetraacetylethane-copper chelate (PTAE-Cu), the polymer is continuously conjugated and a certain conductivity does appear, characterized by the usual straight-line relationship between the logarithm of the conductivity and the reciprocal of the absolute

Table 2. Electrical properties of bis-diketone polychelates

Chelate		σ348 °K (mho · cm⁻¹)	$E_A^{(a)}$ (eV)	σ_0 (mho · cm⁻¹)
PMA – Cu^{2+}		< 2 · 10^{-17} (b)	–	–
PTAE – Cu^{2+}		4,7 · 10^{-16}	0,83	5 · 10^{-4}
PNTZ – Cu^{2+}	I	3,2 · 10^{-12}	0,95	3 · 10^{2}
	II	2,6 · 10^{-12}	0,84	2,3
PTAE – Fe^{3+}		3,3 · 10^{-11}	0,77	2,3
PNTZ – Fe^{3+}		1,1 · 10^{-7}	0,49	1,4

(a) A plot of log σ in function of the reciprocal of the absolute temperature gives a straight-line relationship between 300 and 400 °K; the measurements were effected under vacuum on carefully purified samples.
(b) Limit of sensitivity of the electrical measurement apparatus.

temperature. In the polynaphthazarine copper chelate (PNTZ-Cu) the same type of conjugation is present, but more effective because the good coplanarity of the ligand-metal system, imposed by the rigidity of the aromatic ligand molecule and the usual square planar structure of the copper chelates: the conductivity increases by four orders of magnitude, the activation energy remaining unchanged; it is worthwhile to point out that these results are reproducible even on samples synthesized independently (I and II).

However the conductivity of these chelates remains relatively low, which indicates a too weak electronic coupling to insure a good probability of intermolecular electron jumping. This difficulty should be overcome by the creation of a conjugated network: therefore polychelates of trivalent metal cations were prepared which would yield (by the binding of three difunctional ligands around each metal atom) the desired cross-linked structure, except that resonance is probably less favoured through an octahedrally coordinated metal site than through a square planar chelate: despite this limitation it is rewarding to verify that for both conjugated ligands, chelation with a trivalent cation enhances the conductibility by five orders of magnitude.

These compounds show also other interesting properties[27]: they have a continuous absorption spectrum extending to the near infrared, they are photoconducting to a variable extent, they exhibit an important SEEBECK effect which gives an indication of the type of the predominating current carriers (*n*-type), and they show also catalytic properties for the decomposition of N_2O and the chain-oxidation of unsaturated hydrocarbons.

But one of the most amazing effects evidenced in this work is the very important influence of an external gas on the bulk conductivity of a polymer sample: a gas like oxygen (or even iodine) decreases this conductivity by three to four orders of magnitude (10.000 times), even when present in such low amounts as about 1% of the total metal content (in moles) of the product under investigation: this result is a good confirmation of the existence of a delocalized electronic structure. On the other hand, electron donating molecules like NH_3, are able to increase the conductivity of the same chelate by a comparable factor of 10^3 to 10^4, yielding for instance ferric chelates having a resistance of 1.000 ohms per centimeter.

Conclusion

Judging from the results published in the last ten years literature, it could be said that after a first wave of exploratory work, there is still much to be done in the field of polymeric chelates.

A little bit paradoxically, it seems that the effort must be focused more on the methods for the preparation of these polymers than on an elaborate study of their properties: there is a great need for products whose structure is homogeneous and exactly known, and also whose molecular weight can be controlled; moreover, for eventual applications, it would be necessary to develop certain specific properties: it would be very interesting to get soluble polymers, whose mechanical properties would be good (i.e. of high molecular weight), and a control of the cristallinity of the samples is also of the utmost importance.

None of these goals has been achieved till now, but they are not beyond the capabilities of interested workers in the field.

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