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Macromolecular Complexes as Chemical Reaction Catalysts

S.L.Davydova, N.A.Plate, and V.A.Kargin

The wide potential applications of catalysis by macromolecular compounds have aroused universal interest in this relatively new branch of chemical science: the number of publications devoted to this problem has been growing continuously since the 1950's. Thus, many papers have dealt with the use of sulphonic acid resins as catalysts for hydrolysis and esterification, hydration and dehydration, alkylation, and also various condensations (see review by Polyanskii[1], recent Japanese work[2], etc.). A substantial fund of knowledge has accumulated also on the use of macromolecular catalysts and initiators in polymerisation reactions. For example, the above sulphonic acid resins have been used as polymerisation catalysts for isopentene, butene, dienes[1] and vinyl alkyl esters[3]. Macromolecular radicals obtained by chain transfer reactions[4], illumination, mechanical methods[5], or by chemical changes of reactive groups[6] are already used extensively in the synthesis of graft or block copolymers. These and other polymer systems can be synthesised also on macromolecular anions obtained as macromolecular Ziegler-Natta catalysts[7], macromolecular anion-radicals, or dianions[8], on macromolecular organometallic compounds of the polylithiumpolystyrene[9] or polylithiumpolyethylene[10] type, etc.
Papers on the catalysis of reactions by macromolecular complexes relate to the same field of research. The present review, without attempting to be fully comprehensive, deals with the most important papers (published up to 1968) on the catalysis of organic and of inorganic reactions by macromolecular complexes. For comparison, low-molecular-weight complexes are considered in a number of instances. 84 references.

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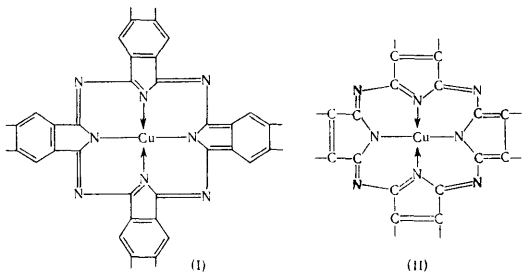
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1. REDOX REACTIONS AND DECOMPOSITIONS

Since the earliest days of the study of catalysis by macromolecular complexes, the catalytic action of these materials towards various oxidation–reduction reactions has attracted most attention†. Among the first papers to be published in this field were those of Roginskii and coworkers[11,12], who studied the catalytic properties of macromolecular chelates with a system of conjugated bonds.

Thus, Roginskii and coworkers[11] investigated the activity of a series of poly(copper phthalocyanines) having different electrophysical properties towards the decomposition of H_2O_2. The greatest catalytic activity was found in the polyphthalocyanine which had the highest electrical conductivity at room temperature and the lowest activation energy for electrical conduction. The lowest activity was observed with the polymers of lowest electrical conductivity and highest E_{act}. The authors attempted to correlate the electrophysical properties and the catalytic activity of these polyphthalocyanines. They also attempted a correlation in their study of the oxidation of alkylaromatic and cyclic hydrocarbons on macromolecular phthalocyanines[12].

These workers compared the rates of oxidation of various hydrocarbons on copper phthalocyanines of type (I), and also the catalytic activity of polymeric and monomeric copper phthalocyanines towards the oxidation of cumene to the hydroperoxide, with the activity of polymeric complexes of tetracyanoethylene and copper, which are presumably macrocyclic azoporphyrin structures of type (II):



(I) (II)

It was found that the polyphthalocyanines are more active than their monomeric analogues and that the tetracyanoethylene polymers are more active than the polyphthalocyanines: the underlying reasons were not discussed. Manecke and coworkers[13] also examined polychelates of this type, prepared from metal acetylacetonates and tetracyanothiophen (or tetracyanofuran), *p*-phenylenedimalononitrile, or *o*-phthalodinitrile.

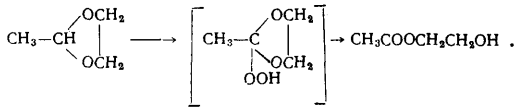
To explain the mechanism of the catalytic action of macromolecular complexes with conjugated bonds, Berlin and coworkers[14] suggest that the presence of acetylacetonate residues in the azoporphyrin structures (II) causes initiation of a chain decomposition of the polymer with formation of peroxide radicals. These workers conclude that in the oxidation of, for example, cumene, in the presence of poly(copper phthalocyanine), oxygen must be present as

† Data on the catalytic properties of low-molecular-weight complexes have long been available: for convenience in presentation we shall discuss them and compare them with the catalytic properties of macromolecular complexes of similar structure;

undissociated molecules or as radical-ions on the catalyst surface.

The catalytic activity of mixed Cu, Fe polyphthalocyanines in the heterogeneous oxidation of aldehyde acetals by oxygen was recently discussed in some interesting papers by Inoue and coworkers[15,16].

Assuming that the main product of the oxidation of acetaldehyde ethylene acetal [2-methyl-1,3-dioxolane (Ed. of Translation)] is 2-hydroxyethyl acetate (as well as acetic acid, acetaldehyde, ethylene glycol, and water), the authors propose the following reaction scheme:



The catalytic activity of this polymeric complex towards the oxidation of other acetals or of cumene is considerably lower (see Fig. 1).

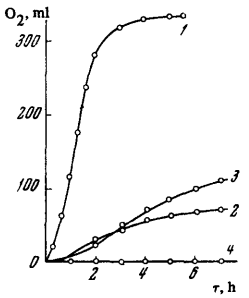


Figure 1. Rate of absorption of O_2 in the presence of Cu, Fe-polyphthalocyanine in the following oxidation reactions:
1) acetaldehyde ethylene acetal [2-methyl-1,3-dioxolane (Ed. of Translation)]; *2*) benzaldehyde ethylene acetal [2-phenyl-1,3-dioxolane (Ed. of Translation)]; *3*) cumene; *4*) acetaldehyde dimethyl and diethyl acetals.

The catalytic activity is strongly dependent on the ratio of the metals (Cu–Fe or Mo–Fe), and on the activation energy for electrical conduction of the polyphthalocyanine. It has been pointed out that these polymers are highly selective and show a synergic effect due to the interaction of two redox metal atoms through a system of conjugated bonds, since the reaction is catalysed neither by Cu-, Fe-, or Mo-polyphthalocyanines, nor by their mixtures[16].

The oxidation of hydrocarbons in the presence of low-molecular-weight chelates was known in the 1950's, and acetylacetonates as well as other chelate compounds are now used industrially for this purpose.

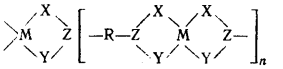
The acetylacetonates of Cu and Co are used, for example, in the liquid-phase oxidation of toluene and ethylbenzene by oxygen or air to the corresponding aldehydes and acids; the rate of the reaction is periodically increased by adding inorganic adsorbents of the Al_2O_3 or kieselguhr type[17].

Cobalt isovalerylacetonate is used industrially as a catalyst for the oxidation of primary and secondary (but not tertiary) alkylbenzenes to the corresponding acids[18]. Salcamine (bis-salicylaldiminatocobalt) is widely used in industry to deodorise petroleum (by oxidising mercaptans to disulphides with atmospheric oxygen[19]) or to remove oxygen-containing impurities dissolved in hydrocarbons[20].

Turning now to oxidation–reduction reactions on macromolecular complexes, we note that the Du Pont company[21] reported in 1962 an investigation of the catalysis of a large number of reactions in the presence of polychelates. These included the oxidation of isovaleraldehyde, metacrolein‡, furfural, and cinnamaldehyde to the corresponding acids, and the oxidation of ascorbic acid to dehydroascorbic acid; the reduction of nitrobenzene to aniline and of nitrocyclohexane to nitrosocyclohexane (cyclohexanone oxime); the reduction of metal ions (Ag, Hg, Fe) to a lower valency, etc. The structure and properties of the polychelates are not quoted: it is stated only that the macromolecular ligands used include salicyl- or resorcinol–formaldehyde resins, polythiosemicarbazides, polyoximes, polyaminostyrene-*NN*-diacetic acids, and other polyfunctional polymers.

The choice of a polymeric ligand to prepare macromolecular chelates for the catalysis of the stated oxidation–reduction reactions is mainly dictated, according to the authors, by the stability of the resulting chelate (though stability or formation constants are not quoted), whereas the metal suitable for complex formation is chosen on the grounds of its redox potential. Both these factors are known to affect the rates of reactions catalysed by low-molecular-weight complexes. Thus, Sn^{II}-polyformaldehyde salicylate reduces silver ions to metallic silver almost instantaneously, whilst Sn^{II}-polyaminostyrene-*NN*-diacetate reduces them in 10–15 min. Nitrocyclohexane is reduced quantitatively to cyclohexanone oxime in the presence of the above polychelates of Fe^{II}, Cu^{I}, and Sn^{II} in times of 24–36, 4, and 1 h respectively[21].

The reactivity of polymeric chelates of transition metals with linear or cross-linked structures (III)



(III)

and of their monomeric analogues was investigated by Boreskov and coworkers[22–25] for a number of reactions; the rates of decomposition were found to be strongly influenced both by the nature of the metal and by the structure of the organic ligand.

No correlation was found when the electrical conductivities of the polychelates were compared with their catalytic activities[22]. Thus, the Zn- and Cu-polychelates of the type 2(S, N)§ thiocarbamate have an electrical conductivity of $10^{-9}\ \Omega^{-1}\ cm^{-1}$, and the corresponding Ni-polychelates have a conductivity of the order of $10^{-13}\ \Omega^{-1}\ cm^{-1}$, and yet the catalytic activity of the Cu and Ni polychelates is high, whereas the Zn polychelates are catalytically inactive. This is probably due to the fact that chemisorption and catalysis are determined not so much by the semiconducting properties of the polymer as a whole as by the electronic state of the metal in the chelate group: the latter criterion is responsible for the strong influence of the environment of the metal in the coordination centre on the catalytic properties of the polymer.

Keier and coworkers[27–30] have shown that studies of X-ray absorption spectra are valuable in establishing the state of the metal in the coordination centres of chelate compounds. In this way, they were able to evaluate and compare the effective charges concentrated on the copper

‡ It is uncertain whether metacrolein $(C_3H_4O)_3$, or methacrolein (methacrylaldehyde, 2-methylprop-2-enal) $CH_2{=}C(CH_3)CHO$, is intended (Ed. of Translation).

§ Complexes can have a variety of coordination centres. According to Calvin and Martell's classification[26], adopted here, these can be designated 2(O,O), 2(O,N), 2(N,N), 2(S,N), 2(O,S), etc. (for bidentate ligands).

atom in the molecules of various chelate compounds, and to establish a correlation between these values and the reactivity of the polymeric chelates. They were also able to identify the direction of changes in the charge on the metal atom accompanying changes in the structure of the ligand. Thus, a direct experimental study of the interaction of polychelates of the Cu–2(S, N) type with the reactants was possible.

For example, in the decomposition of N_2H_4 the effective charge η_π^{eff} remains practically constant during the first hour, and changes by approximately $0.15e$ during the following 15 h. In the oxidation of isopropylbenzene, a change of approximately $0.2e$ (and of the opposite sign) was noted in the charge on the copper atom. Thus, the change in the charge on the central atom of the polychelate is evidence for direct interaction between the reactants and the polymer. In particular, in the decomposition of N_2H_4 partial reduction of the copper during the course of the reaction is indicated by the direction of the shift of the K absorption edge of the copper in the polychelate and by the sign of the change in the charge on the copper atom[27–30]. The X-ray K absorption spectra of copper in polychelates of the type 2(S, N) were used to evaluate η_π^{eff} as a function of molecular weight (between 600 and 3100). On increasing the degree of polymerisation, η_π^{eff} decreases non-uniformly, and on changing from the monomer to a polymer with $M = 1790$ this quantity is hardly affected (but the reactivity of the polychelate is approximately 5–6 times higher than that of the monomer). With further increase in molecular weight η_π^{eff} begins to increase, reaching $0.2e$ for a polychelate with $M = 2560$ (whose reactivity is higher than that of the monomer by a factor of 35).[29]

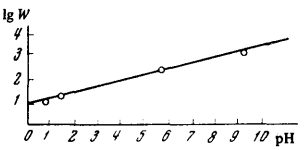


Figure 2. Variation of the rate of decomposition of H_2O_2 on the Cu polychelate of dinitrosoresorcinol with pH at 60°C (W in $cm^3 m^{-2} min^{-1}$).

Because of the lack of solubility, polychelates are difficult to study by physical methods, and the authors were compelled to use much less active monomeric analogues (for example, those prepared from thiopicolineanilides).

Anufrienko and coworkers[31] showed by the ESR method that the M–X,Y bonds in compound (III) have a mainly covalent character, and Zeif and coworkers[32] determined the structure of the complexes as a whole by ultraviolet and infrared spectroscopic studies. Using an approximate quantum-mechanical method of calculation, the nature of the change in effective charge (η_π^{eff}) of the metal ions in the chelate group on varying the structure of the organic ligand was characterised from experimental ultraviolet spectra; in this way, the relationship between the rate of decomposition of hydrazine and the change in effective charge was investigated for a series of chelate complexes. We should note that the application of all these methods has revealed a substantial change in the copper chelate during the decomposition of N_2H_4, which obviously points to chemical (as distinct from catalytic) decomposition of hydrazine under the conditions used in this work[25,33].

According to the same authors[34], the catalytic activity of the polychelates is higher than that of their low-molecular-weight analogues by at least an order of magnitude. They conclude that the higher activity of the polychelates is associated with disorder and distortion in the structure of their chelate groups. Furthermore, the catalytic activity can be influenced by the presence of uncomplexed metal ions at chain ends, which is itself very sensitive to the conditions of preparation of the polymers.

Boreskov and coworkers consider[34] that their observations on the reactions catalysed by macromolecular chelates show a similarity to the characteristic features of the catalytic properties of enzymes, and that chelate polymers are a type of heterogeneous catalyst occupying an intermediate position between inorganic catalysts and enzymes. In this connection, they examined the catalytic activity of synthetic polymeric chelates towards the liquid-phase decomposition of hydrogen peroxide, one of the simplest organometallic enzyme reactions[35]. Kinetic isotherms for this reaction on polychelates of the 2(o, o) type with different metal atoms were obtained; on raising the pH the rate of the reaction increased by almost two orders, evidently as a result of the greater degree of dissociation of the hydrogen peroxide. The reaction rate varies linearly with pH over a wide range of pH values (Fig. 2). The authors believe that the rate of the heterogeneous decomposition of H_2O_2 on each surface centre of the copper polychelate is close to the value found for the enzyme catalase[35].

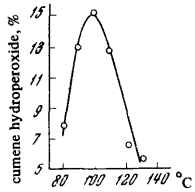


Figure 3. Concentration of cumene hydroperoxide in the oxidised material as a function of temperature of the oxidation in the presence of a 2(S,N) Cu polychelate.

Keier and coworkers[36] studied the catalytic properties of Cu- and Ni-polychelates of the 2(S, N) type based on the bis-thioamides of quinaldine towards various reactions, including the oxidation of isopropylbenzene (cumene) to the hydroperoxide by atmospheric oxygen (Fig. 3). Although in this instance the catalytic activity (which is greatest for the Cu polychelates) and selectivity are determined by the metal ion, the structure of the ligand also plays a role. By introducing electron-donor groups (CH_3, OCH_3) into the biphenyl unit of the polymer chain, and thus raising the electron density on the central metal atom, the rate of the secondary reaction of cumene hydroperoxide is increased, leading to a faster rate of formation of 2-phenylpropan-2-ol:

$$ROOH \rightarrow RO^{\cdot} + OH^{\cdot};\ RO^{\cdot} + RH \rightarrow ROH + R^{\cdot}.$$

A multi-step mechanism has been reported also for the liquid-phase oxidation of isopropylbenzene and ethylbenzene in the presence of heterogeneous catalysts prepared by

depositing 8 wt. % of a Cu polychelate based on 4,4′-bis-(α-thiopicolinamido)biphenyl upon Al_2O_3.[37,38] The catalytic decomposition of the primary oxidation products (the hydroperoxides of ethylbenzene and isopropylbenzene) on the same polychelates is of zero order with respect to hydroperoxide and of first order with respect to the heterogeneous catalyst. E_{act} for the decomposition into radicals is 10.7 kcal mole^{-1} for ethylbenzene and 10.0 kcal mole^{-1} for isopropylbenzene[37].

Time-changes in the activity of the polychelate catalyst towards the formation of radicals from the hydroperoxide were examined by measuring initial rates (W_0) of consumption of 1-naphthol (an inhibitor for the resulting radicals) as a function of the time of operation of the catalyst. The rate of formation of radicals is high on a fresh catalyst, but falls off sharply after 20 min, and after 30 min it levels off at 25% of its initial value (Fig. 4). A comparison of the rates of formation of free radicals by thermal and by catalytic decomposition has shown that at 110°C the former (10^{-6} mole min^{-1}) is lower than the latter by a factor of $\sim 10^4$.[37]

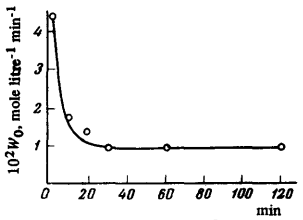
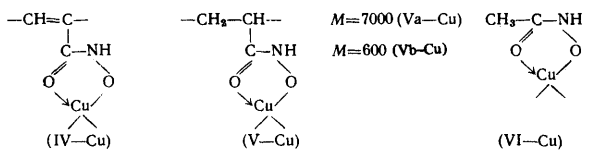


Figure 4. Change of W_0 with time at 90°C; [ROOH] = 3.26 wt. %, c_{cat} = 2.66 mg ml^{-1}.

From their study of the catalytic action of polychelates towards the liquid-phase oxidation of hydrocarbons the authors conclude that free radicals are formed mainly by the catalytic decomposition of the hydroperoxide, and the overall oxidation process is a classical non-branching chain reaction[39].

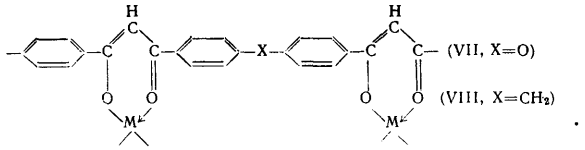
In 1966 a group of Japanese workers[40] prepared some new polychelates (hydroxamic acid derivatives) and studied their catalytic activity towards the decomposition of H_2O_2 in aqueous solutions. Thus, the following copper chelates of polyhydroxamic acid, with (IV) or without (V) a system of conjugated bonds (and Cl residues) in the main chain:



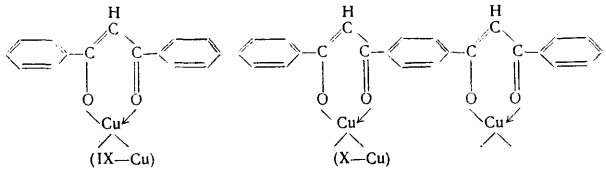
were compared for catalytic activity with the low-molecular-weight Cu chelate of methylhydroxamic acid (VI).

The catalytic activity of these chelates was found to increase in the sequence VI-Cu < Vb-Cu < Va-Cu < IV-Cu, in other words, it was found to be higher in the macromolecular chelates than in their low-molecular-weight analogue. The authors ascribe this behaviour to differences in the polarity of the copper–ligand bond[41].

The same workers[42] studied the catalytic activity of chelates of the poly-(β-diketone) type, which were prepared independently also by Soviet workers[43]:

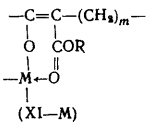


The catalytic activity of the polychelates VII-Cu and VIII-Cu for the decomposition of H_2O_2 is higher than that of their low-molecular-weight analogues IX-Cu and X-Cu



The rate of the decomposition reaction follows a first-order equation with respect to peroxide concentration; the catalytic activity of the chelates is fully reproducible on adding fresh portions of hydrogen peroxide. However, in respect of the catalytic activity of copper chelates of the β-diketone type towards the oxidation of L-ascorbic acid, the activity of the macromolecular chelates is higher than that of their low-molecular-weight analogues but the rate of oxidation shows a zero-order dependence on the concentration of ascorbic acid[42].

The present writers and coworkers[44] have examined the oxidase and catalase activity of a large number of transition metal complexes with macromolecular ligands of the poly-(β-ketoester) type first prepared by the ester polycondensation of dicarboxylic acid diesters[43,45]:



where m = 6, 7, 9; R = C_2H_5; M = Cu, Ni, Fe, Co, Mn.

The catalytic activity of these macromolecular chelates of poly-(β-ketoesters) towards the oxidation of ascorbic acid decreases in the order Cu > Ni ≫ Fe, Mn, Co (Fig. 5), whereas the opposite sequence of catalytic activity is observed in the decomposition of hydrogen peroxide by these complexes: Co > Mn > Fe ≫ Ni, Cu (Fig. 6). This inversion is ascribed to the mechanism of the interaction of the complexes with the substrates. Since the rate-limiting step in the decomposition of H_2O_2 under the influence of complexes is known[46] to be the addition of atomic oxygen, it is to be expected that complexes which are active in this step (and shift the equilibrium to the right) will have low activity in the O_2 absorption reaction which proceeds from right to left, as in the oxidation of ascorbic acid. We note that the catalytic activity of the complex XI-Co (m = 6) is increased very significantly by raising the pH to 10 (Fig. 6, curve *6*), as in the case of the decomposition of H_2O_2 in the presence of polycoordination complexes of type (III) (p.). The catalytic activity of macromolecular chelates of the poly-(β-ketoester) type (XI-M) is strongly dependent on the metal content, for example, copper (in the oxidation of ascorbic acid) or cobalt (in the decomposition of hydrogen peroxide), that is, on the degree of complex formation by the coordination centres (in both instances). As for the polycoordination compounds of

type (III) (p. 985), the catalytic activity of complexes with macromolecular ligands is very sensitive not only to the nature of the metal but also to the nature of the macromolecular ligand, for example, on the length of the polymethylene chain [m in the compound (XI-M)].[44]

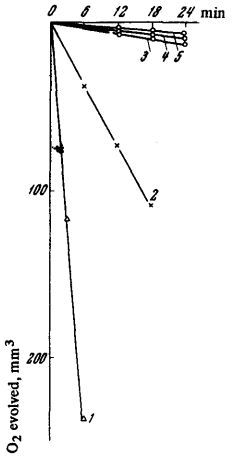


Figure 5. Kinetics of the oxidation of ascorbic acid in the presence of poly-(β-ketoester) complexes (XI)-M, m = 6: *1*) Cu, *2*) Ni, *3*) Mn, *4*) Co, *5*) Fe.

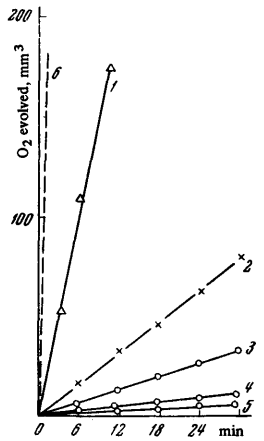
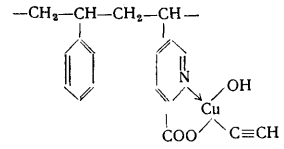


Figure 6. Kinetics of the decomposition of H_2O_2 in the presence of poly-(β-ketoester) complexes (XI)-M, m = 6: *1*) Co, *2*) Mn, *3*) Fe, *4*) Ni, *5*) Cu, *6*) decomposition in the presence of (XI)-Co at pH 10.

In our view, a quantitative comparison of the catalytic activity of macromolecular complexes with that of their low-molecular-weight analogues (such as the benzoyl- and acetyl-acetonates of the transition metals for VII-M, VIII-M, and IX-M), as Japanese workers[40,42], among others, have attempted, is complicated by the fact that these reactions proceed in a homogeneous medium in the presence of the low-molecular-weight complexes and in a heterogeneous medium in the presence of macromolecular chelates. This difficulty is apparent also with polymeric complexes of a different type—those of polymeric picolinic acid with copper (XII-Cu)—studied by Stepanov and Zosim[47] also in connection with the decomposition of hydrogen peroxide: under conditions of heterogeneous decomposition at room temperature the catalytic activity, expressed in mg-equiv. H_2O_2 per mg-equiv. Cu, is 204, whilst under homogeneous decomposition conditions it is 1540. We note, incidentally, that polymeric complexes of the same type were examined as catalysts for the synthesis of 1,4-butynediol from acetylene and formaldehyde. The copolymer of styrene and vinylpicolinic acid forms polymeric acetylide structures



(XII—Cu)

showing catalytic activity; the Cu complex of polypyridineethanol is practically unreactive towards acetylene under the same conditions. On the other hand the copper complex of the styrene–maleic acid copolymer, in which the copper atom is bound to the macromolecule by ionic forces only, catalyses the formation of butynediol on passing acetylene through a suspension of paraformaldehyde and of the polymeric acetylide[47].

A paper by Gregor and Liu[48] describes a study of catalysis on macromolecular zinc complexes obtained from poly-(*N*-vinylbenzimidazole). These workers investigated the decomposition of carbonic acid, and found that the "coefficient of catalytic activity" for this reaction (λ) is 400 ± 12 for both the Zn^{II} complex of poly-(*N*-vinylimidazole) and for poly-(*N*-vinylimidazole) itself, whereas for the monomeric imidazole λ is 1.5. Thus, the catalytic activity of the polymeric catalysts is significantly higher even for reactions of this type.

2. POLYMERISATION AND COPOLYMERISATION

Before beginning our discussion of the catalytic activity of the macromolecular chelates of transition metals towards the polymerisation of vinyl monomers, we shall dwell on a few examples of the use of low-molecular-weight chelates for the same purpose.

The earliest reports of the use of Co, Ni, and Fe acetylacetonates for the polymerisation and copolymerisation of unsaturated compounds appear in British patents of 1946;[49] subsequently, the use of ethylenediaminetetra-acetic acid complexes in emulsion polymerisation processes was also patented[50]. Later, Strubell[51] used a metal-containing oxidation–reduction system based on the propionylacetonate, benzoin, and benzoyl peroxide to initiate the polymerisation of methyl methacrylate. Fig. 7 shows curves for the increase of viscosity with time of the reaction mixture as a function of the metal in the propionylacetonate. The rate of polymerisation is directly proportional to the amount of added propionylacetonate with the exception of copper propionylacetonate, which activates the reaction strongly whatever amount is added, and of the nickel complex, which has no effect on the rate of polymerisation[51]. Indictor and Linder[52] have recently used a similar system (t-butyl hydroperoxide–acetylacetonate) to study the polymerisation of styrene at 50°C. They found that the initial rate of polymerisation is increased by adding $(1-2) \times 10^{-4}$

mole litre^{-1} of Co^{III}, Cr^{III}, Fe^{III}, or Cu^{II} acetylacetonate to the hydroperoxide, but begins to decrease at higher concentrations of these additives, possibly as a result of the formation of atomic oxygen. According to the authors, the acetylacetonates of other metals are inactive in this particular reaction.

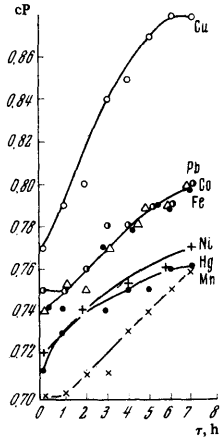


Figure 7. Viscosity of poly(methyl methacrylate) as a function of time of polymerisation in a benzoyl peroxide (1.210 g), benzoin (1.060 g), propionylacetonate (0.60 g) system.

Arnett and Mendelson[53] studied the polymerisation kinetics of styrene in the presence of a large number of acetylacetonates with and without benzoyl peroxide at 110°C, and obtained the following activity series for the metal acetylacetonates:

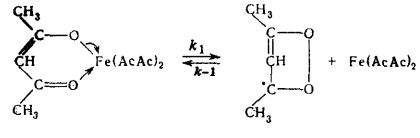
With peroxide: $Co^{III} \simeq Ce^{IV} > Mn^{III} > Fe^{III} > Al^{III} \simeq Cr^{III} \simeq$ without initiator $> V^{III}$.

Without peroxide: $Mn^{III} > Ce^{III} > Co^{III} > Fe^{III} > Al^{III} \simeq Cr^{III} \simeq$ without initiator $> V^{III}$.

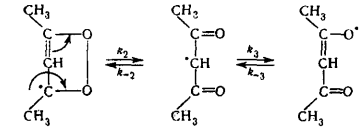
It is interesting to note that these catalytic activity sequences of the acetylacetonates for polymerisation are opposite to the thermal stability sequence obtained by Von Hoene and coworkers[54]:

$$Na^{I} > Cr^{III} > Al^{III} > Ni^{II} > Cu^{II} > Fe^{III} > Co^{II} > Co^{III} > Mn^{III}.$$

The last members of this series begin to decompose in an inert atmosphere at temperatures as low as 150°C, giving acetylacetone as the main decomposition product. Arnett and Mendelson were the first to try to explain the mechanism of formation of radicals on heating the acetylacetonates. Homolytic breaking of the chelate ring (for example, with Fe^{III}) takes place, with formation of Fe^{II} acetylacetonate and a free radical:



which can exist either in the C or in the O form and can initiate the polymerisation of styrene:



Bamford and coworkers[55] also made a study of the initiation of the polymerisation of vinyl monomers by low-molecular-weight metal chelates; they examined, in particular, systems containing the acetylacetonates of Cu^{II} and Co^{II}, and they pointed out that without suitable additives these systems are ineffective for the polymerisation of methyl methacrylate. In conjunction with halogenated compounds of the type CCl_4, CBr_4, CCl_3Br, CCl_3CN, $CCl_3.COONH_4$, and in particular with the last of these the copper chelate is fairly active at a concentration of 1.9×10^{-3} M at 80°C. The authors believe that at low concentrations of CCl_3COONH_4 ($< 6 \times 10^{-4}$ M) the initiating radical is formed by the decomposition of a 1:1 chelate–salt complex, whereas at high concentrations of CCl_3COONH_4 (2.5×10^{-2} M) the initiating radical is formed simply by the interaction of the chelate with the primary decomposition products of the salt[56].

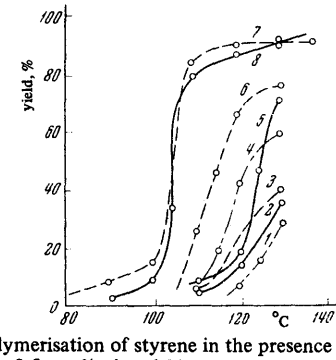


Figure 8. Polymerisation of styrene in the presence of acetylacetonates (concentration 0.5 wt. %, time 1 h):
1) Pd^{II}, *2*) Mn^{II}, *3*) Pt^{IV}, *4*) Ni^{II}, *5*) Rh^{IV}, *6*) Co^{III}, *7*) R_2O_2, *8*) Mn^{III}.

Kastning and coworkers[57] (see also the patents[58,59]) made a detailed study of the efficiency of initiation of the polymerisation of styrene by chelate complexes as a function of the nature of the central metal atom and of the structure of the ligand. It is evident from Fig. 8 that the highest yields of polystyrene are obtained by using the acetylacetonates of metals from Groups VII and VIII of the Periodic Table, and that the rates of polymerisation in the presence of the Mn^{III} chelate or of the peroxide are approximately equal. When the metal can exist in several valency states, the most effective initiators are those in which the metal exhibits the highest valency. The activity of chelates of 1,3-dicarbonyl compounds increases in the order dibenzoylmethane < benzoylacetone < acetylacetone < ethyl acetoacetate (Fig. 9).

Calvin and Wilson[60] showed that the stability constants (K_{st}) of Cu^{II} chelates increase in the same order.

One drawback of the acetylacetonates is the need to use relatively high polymerisation temperatures: these initiators were therefore activated by irradiation or by additives. Both in the presence and in the absence of activators the rate of polymerisation was proportional to the square root of the concentration of initiator[57].

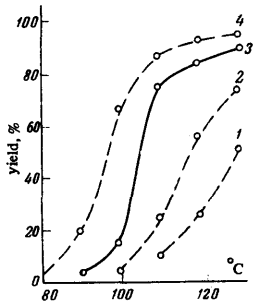


Figure 9. Polymerisation of styrene in the presence of Mn^{II} chelates (concentration 0.5 wt. %, time 1 h): *1*) dibenzoylmethane, *2*) benzoylacetone, *3*) acetylacetone, *4*) ethyl acetoacetate.

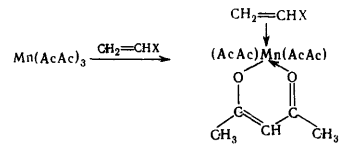
Chelate initiators can be used also for the polymerisation of acrylate and methacrylate esters, ethylene, butadiene, and for the copolymerisation of these monomers. Polymerisation of butadiene and isoprene under the influence of these chelates in solution yields high-molecular-weight polymers containing up to 60% of *cis*-1,4- and up to 10% of 1,2-vinyl units. A recent paper by Riches[61] on the polymerisation kinetics of dienes on Co^{III} acetylacetonate should be mentioned here: the reaction was found to be of one-half order with respect to the initiator and of first order with respect to the monomer (E_{act} = 13 and 20 kcal $mole^{-1}$ for isoprene and butadiene respectively).

The results of Kastning and coworkers[57] on the copolymerisation of vinyl monomers which do not react under the influence of peroxides are particularly interesting. Thus, the polymerisation of a (1 : 1) mixture of styrene and vinyl acetate in the presence of Mn^{III} acetylacetonate at 80°C produces a copolymer containing 28 wt. % of vinyl acetate. (It is well known that for this pair of monomers r_1 = 55 and r_2 = 0.01.) At a higher temperature (100 to 150°C) and 1000–1600 atm pressure styrene and ethylene can be copolymerised with the same initiator. Simple vinyl ethers, which do not polymerise in the presence of chelates, can be made to copolymerise with ethylene to give up to 30% of vinyl ether units in the copolymer.

The authors do not put forward a mechanism for polymerisation in the presence of metal chelate initiators of the type examined, but some of their results are consistent with a free-radical mechanism. They were unable to observe any change in the valency of the central metal atom during polymerisation under the influence of chelates; valency changes took place only for reaction temperatures higher than the decomposition temperature of the chelate[57].

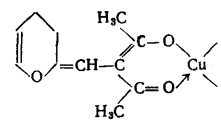
By using tracer atoms and infrared spectroscopy it was shown that the ligand is attached to the growing polymer chain; hence the authors concluded that the polymerisation can be initiated by free radicals formed from the chelate ligands. The microstructure of the resulting polymers does not depend on the nature of the ligand or of the activating additives, which affect only the rate of initiation, and the configuration of the chain is determined only by the nature of the central metal atom.

A group of Japanese workers[62] has measured the copolymerisation constants of vinyl monomers in the presence of metal acetylacetonates (Mn, Co, Fe). Thus, for the styrene–methyl methacrylate system they found r_1 = 0.53 ± 0.08 and r_2 = 0.52 ± 0.05, and for the styrene–methacrylate system r_1 = 0.89 ± 0.02 and r_2 = 0.17 ± 0.02. The authors believe that the first step in the polymerisation is decomposition by monomer attack¶, for example:



Nikolaev and coworkers have shown, in a very recent investigation[63], that their values for the copolymerisation constants of vinyl acetate and styrene (r_1 = 0.01 ± 0.1 and r_2 = 3.9 ± 0.8) suggest a change in the activity of the monomers and the radicals in the presence of $Mn(AcAc)_3$ as compared with copolymerisation in the presence of the usual radical initiators. The valency of manganese changes during the copolymerisation ($Mn^{III} \rightarrow Mn^{II}$), and the rate of the reaction decreases at the same time.

Whereas the above workers found copper acetylacetonate (without appropriate additives) to be inactive towards the polymerisation of vinyl monomers, Uehara and coworkers[64,65] have shown that unsaturated substituents in the pseudo-aromatic ring of Cu^{II} acetylacetonate enable it to initiate the polymerisation of styrene and methyl methacrylate (but not of vinyl acetate) at 0.5% concentration and 70°C. The polymerisation is inhibited by benzoquinone and is accelerated by ammonia and methanol. The reaction order is 0.5 with respect to the initiator and 1.8 with respect to the monomer; the overall activation energy is 20.1 kcal $mole^{-1}$. The infrared spectra suggest that the ligand becomes part of the polymer chain, as in the examples considered above. Initiators of this type (for example, XIII-Cu) have been used also to prepare a styrene–maleic anhydride (1 : 1) copolymer at room temperature:

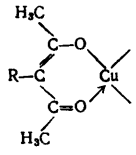


(XIII—Cu) .

We may assume that K_{st} for the (XIII-Cu) chelate, which is not quoted by the authors, is lower than K_{st} for the unsubstituted acetylacetonate, because of conjugation of the chelate ring with the π-system of the dihydropyran ring: we may ascribe the catalytic activity to this effect. The same workers[65,66] have demonstrated the influence of other substituents with double bonds on the activity of substituted copper acetylacetonates in polymerisations. They condensed acetylacetone with propionaldehyde, butyraldehyde,

¶ Subsequently, the reaction proceeds by the schemes shown on p.989.

isobutyraldehyde, and dimethacrolein, and obtained (XIV-Cu)



(XIV—Cu)

where R = CH= (*a*); CH=CH—CH_3 (*b*); CH=CH—CH_2CH_3 (*c*); $CH=C(CH_3)_2$ (*d*); or its hydrogenation products $CH_2CH_2CH_3$ (*e*); $CH_2CH_2CH_2CH_3$ (*f*).

The following activity sequences are given for the XIV-Cu chelates: $a > b > c > f > d > e \simeq 0$ for styrene; $a > c > b > d > e > f \simeq 0$ for methyl methacrylate.

In 1965 Bamford and Lind[67] published the results of a study of the initiation of polymerisation with acetylacetonates without any additives. In contrast to Kastning's results[57], obtained for the polymerisation of styrene at 100°C, these authors (who studied the polymerisation of methyl methacrylate at 80°C) arranged the acetylacetonates examined in their work in the following order: $Mn^{III} > Ni^{II} > V^{III} > Cr^{III} \gg Co^{III} > TiO^{II} > Pb^{II}$. Neither addition of CCl_3COONH_4 (2.77×10^{-4} M) up to a chelate concentration of 2.7×10^{-3} M, nor addition of equimolecular amounts of CCl_4 up to a chelate concentration of 2.8×10^{-2} M, produced any increase in the reaction rate. A more detailed kinetic analysis of a system containing Mn^{III} acetylacetonate (curve *3* of Fig. 10) showed that the rate of polymerisation is proportional to the concentration of chelate raised to the power 1/2:

$$\omega = 1.0 \cdot 10^{-2} [Mn(AcAc)_3]^{1/2} \text{ mole litre}^{-1} \text{ s}^{-1} \text{ (at 80°C)},$$
$$\omega = 0.05 \cdot 10^{-2} [Mn(AcAc)_3]^{1/2} \text{ mole litre}^{-1} \text{ s}^{-1} \text{ (at 70°C)}.$$

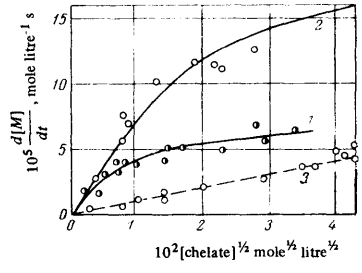


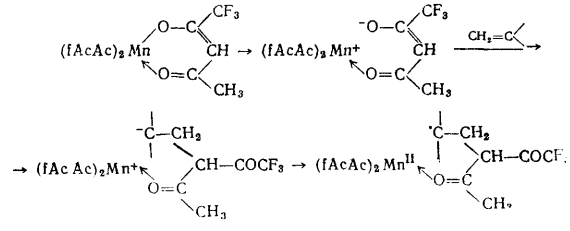
Figure 10. Polymerisation of methyl methacrylate at 80°C on: *1*) Mn^{III}-*p,p'*-dichlorodibenzoylmethane; *2*) Mn^{III} acetylacetonate without additives; *3*) ditto, with CCl_4.

The product $k_p k_t^{-1/2}$ (rate constants for chain propagation and chain termination respectively) is close to the known value for the free-radical polymerisation of methyl methacrylate (0.17 $\text{mole}^{-1/2}$ $\text{litre}^{-1/2}$ $\text{s}^{1/2}$). Hence the authors conclude that polymerisation occurs by a free-radical mechanism in the present system under the influence of radicals formed by the decomposition of the chelate. A similar hypothesis had been put forward by Arnett and Mendelson[53] (see p. 989).

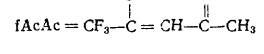
The rates of polymerisation on Mn^{III}-dibenzoylmethane and its *p,p'*-dichloro-derivative (Fig. 10) are proportional to the concentration of the chelate to the power 1/2 for low chelate concentrations ($< 10^{-4}$ M for curve *1* and $< 0.4 \times 10^{-4}$ M for curve *2*). At higher chelate concentrations ($> 10^{-3}$ M) this relationship no longer applies and the product $k_p k_t^{-1/2}$ takes abnormally low values (0.14 and 0.13 $\text{mole}^{-1/2}$ $\text{litre}^{-1/2}$ $\text{s}^{1/2}$ respectively), pointing to some unexplained type of inhibition. Another paper by Bamford and Lind[68], devoted to the selective initiation of free-radical polymerisation in fluorinated derivatives of acetylacetonates, is particularly interesting. In the case of the fluorinated derivative of Mn^{III} acetylacetonate the rate of polymerisation of methyl methacrylate at 80°C is higher by a factor of 7 than the rate corresponding to the non-fluorinated analogue. On the other hand, the polymerisation of styrene is substantially inhibited in the presence of this system: for a given concentration of the fluorinated and the non-fluorinated acetylacetonate (2.5×10^{-4} M), the rates of formation of the polymer are 1.6 and 34 mole litre^{-1} s^{-1} respectively. This inhibition is explained by the fast interaction of the styrene radicals with Mn ions (positively charged) induced by the CF_3 group. The ratio of the rates of polymerisation initiated by benzoyl peroxide in the presence (W) and in the absence (W_0) of the chelate is given by the equation

$$W/W_0 = (Ik_t)^{1/2}/b[C] + a/b \quad (k'/I)^{1/2},$$

where C is the chelate concentration, I is the rate of polymerisation initiated by benzoyl peroxide, a and b are constants which characterise the rates of initiation and of inhibition of the reaction by the chelate. Comparison of the data on the polymerisation of methyl methacrylate and of styrene shows that the action of the fluorinated acetylacetonate of Mn^{III} is highly selective: it induces most effectively the polymerisation of monomers having a strongly polarised double bond. In particular, the rate of polymerisation of acrylonitrile is 70 times higher in the presence of this compound than in the presence of the corresponding acetylacetonate. This is ascribed to the ready attachment of a monomer with relatively high electron-accepting properties to the anion formed by the cleavage of the Mn—O bond. This anion subsequently decomposes with formation of a radical and of the Mn^{II} chelate. The proposed initiation mechanism is consistent with the extremely low (2×10^6 litre mole^{-1} s^{-1}) frequency factor observed in the polymerisation of methyl methacrylate in the presence of the fluorinated chelate:



where

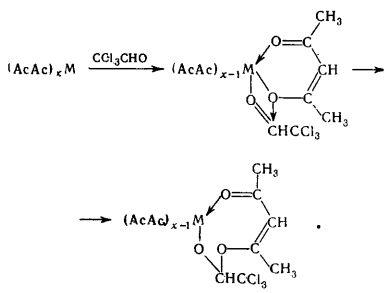


We note that the strong inductive effect of the CF_3 group in $CF_3COCH_2COCH_3$ is responsible for the much lower value of K_{st} of its chelate as compared with the acetylacetonates[26] (see p. 990).

The work of Bamford and Lind[68] provides one of the few examples of selective radical (or, more strictly, radical-ionic) polymerisation processes. We may conclude from this work that a correct choice of the structure of the low-molecular-weight or macromolecular ligand allows the free-radical nature of the process to be retained whilst

adopting some features of the ionic mechanism, thus giving rise to a polymerisation which is intermediate between radical and ionic polymerisation. Thus, under conditions of radical polymerisation it becomes possible to vary the reactivity both of the monomer and of the resulting radical. It may be suggested that the use of chelate complexes is the most efficient way of influencing the reactivity of the radical both in the initiation and in the chain propagation step. In this sense, both the low-molecular-weight and the macromolecular chelates offer interesting possibilities because of the ease of electron transfer in the ligand and of the change in electron density on the metal in the coordination centre.

An interesting example of selective initiation of polymerisation by acetylacetonates of the transition metals Mn^{II} and Mn^{III}, Co^{II} and Co^{III}, was reported by Otsu and coworkers[69]. The polymerisation of chloral, according to these authors, follows a coordination-anionic mechanism according to the scheme



The authors have shown that acetylacetonates of this type can initiate the polymerisation not only of chloral but also of acetaldehyde and of styrene oxide. (The polymerisation of formaldehyde by acetylacetonates had already been disclosed in the patent literature[70].)

In contrast to the views of Kastning[57] and of Bamford[67] (see p. 991), Otsu and coworkers[69] believe that acetylacetonates of metals in both the upper and the lower valency state of the metal can initiate the polymerisation of methyl methacrylate as well as of chloral.

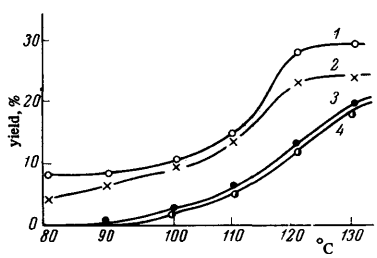
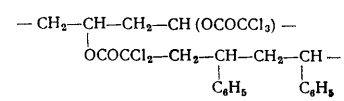


Figure 11. Temperature dependence of the yield of polymerisation products of styrene on poly-(β-ketoester) complexes, (XI)-M, $m = 6$. Time 1 h, concentration of complex 1 wt.%:
1) Co, *2*) Mn, *3*) Ni, *4*) no complex.

The macromolecular chelates of the poly-(β-keto-ester) type XI-M described by the present writers[43-45,71] were found to initiate the polymerisation of vinyl monomers, such as styrene, methyl methacrylate, etc. Fig. 11 shows the temperature dependence of the degree of conversion of styrene in the presence of various macromolecular chelates of this type. Only the Co and Mn macromolecular chelates are catalytically active under the stated conditions; the degree of conversion in the presence of the Ni chelate is practically the same as in the absence of the chelate. We note that according to Kastning and coworkers[57] the low-molecular-weight chelates of Co and Mn are also the most active in the initiation of the polymerisation of styrene. The rate of block polymerisation of styrene at 80°C in the presence of the manganese chelate (XI-Mn) depends linearly on the concentration of the chelate; addition of benzoquinone (0.2 g litre^{-1}) destroys the polymerisation effect. It was shown that as well as initiation of the reaction, grafting of polystyrene units to the macromolecular initiator (XI-Mn) takes place. The resulting graft copolymers lose their metal atoms as a result of treatment with dilute mineral acids, and become soluble in organic solvents (possibly through the collapse of the three-dimensional network of the initiator macromolecule), whilst retaining the chemical bond between the grafted chain and the macromolecular ligand. When the polymerisation of butadiene was initiated by the poly-(β-diketone) chelates (XI-Mn) and (XI-Co), a significant increase in the yield of polymers can be demonstrated (as compared with initiation by the appropriate acetylacetonates); the product consists of a graft copolymer of butadiene and the poly-(β-ketoester). The degree of grafting of polybutadiene to the macromolecular chelate is 0.80–0.93; the structure of the polybutadiene chains, which contain 20, 34, and 46% of 1,2-, 1,4-*cis*-, and 1,4-*trans*- respectively, is characteristic of polybutadiene prepared by radical initiation.

It is interesting to note that graft (or block) copolymers were obtained by Bamford and coworkers[72] by a different method, namely, by the polymerisation of styrene under the influence of metal carbonyls or acetylacetonates in the presence (as activating additives, see p. 989) of high-molecular-weight halogen compounds, such as poly(vinyl trichloroacetate):



To conclude this Section we note that the catalytic properties of polycoordination polymers (of the quinizarine type) towards the polymerisation of styrene were reported as early as in 1963,[73] but neither the reaction nor the polymerisation products were investigated.

3. CATALYTIC ACTIVITY AND STRUCTURE OF MACROMOLECULAR CHELATES

Whereas the relationship between catalytic activity and structure of low-molecular-weight chelates has been adequately discussed in the literature (see review by Schrauzer et al.[74]), relatively little has been published on this problem regarding macromolecular chelate compounds. Roginskii and his coworkers studied the catalytic activity of semiconductors (for example, polyphthalocyanines) in decompositions and oxidations, and they concluded that the catalytic activity of semiconductors is determined by collective electrical properties[75]. The importance of the collective electrical properties of the system was stressed also by Inoue and coworkers[15,16], who studied the catalysis of the oxidation of the ethyleneacetal of acetaldehyde on mixed polyphthalocyanine semiconductors.

Min'kov and Keier[76] specially pointed out the change in the activity of the catalyst during the reaction in their study of the mechanism of the liquid-phase oxidation of isopropylbenzene on low-molecular-weight copper phthalocyanine chelates. They concluded that initiation in the case of copper phthalocyanine does not involve the activation of oxygen but rather the catalytic decomposition of the reaction products of α-cumyl hydroperoxide into free radicals, which proceeds unimolecularly with specific rate constant $k_{sp} = 1.5 \times 10^3 \exp(-13\,200/RT)$ s^{-1} at 40–70°C and bimolecularly with $k_{sp} = 3.6 \times 10^{10} \exp(-24\,600/RT)$ litre $mole^{-1}$ s^{-1} at 90–100°C. Thus, the decomposition of the hydroperoxide occurs by different mechanisms, depending on the temperature. The activity of the catalyst in this reaction varies with time: at 101°C the rate of decomposition of the hydroperoxide decreases by a factor of 2.5 during the first two hours, and then remains constant, but at 60°C the rate of decomposition of the hydroperoxide has not reached a steady value even after 8.5 h (see Fig. 12).

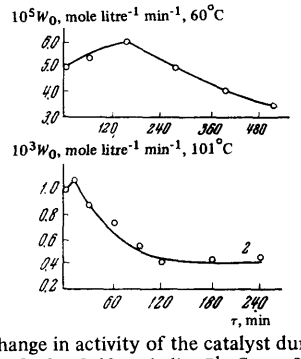


Figure 12. Change in activity of the catalyst during the reaction: *1*) at 60°C, [ROOH] = 0.40 mole litre^{-1}, C_{cat} = 0.66 mg ml^{-1}; *2*) ditto, at 101°C.

On the basis of X-ray diffraction, ESR spectra, and infrared spectra it has been shown that the change in activity of Cu phthalocyanine is associated with a change in the crystal structure of the material (transformation from the α- to the β-modification). As regards the nature of the interaction between the hydroperoxide and the phthalocyanine, the data show that there is no direct interaction between the hydroperoxide and the copper ion: the interaction is with the whole of the π-electron system of the ligand. However, the phthalocyanine itself (metal-free) is inactive towards this reaction. The copper ion exerts a strong polarising effect on the ligand, increasing the π-electron density on the nearest nitrogen atoms and decreasing it on the nitrogen atoms remote from the metal. It is the lower density of π-electrons on the nitrogen atoms not involved in the chelate ring which favours complex formation with the hydroperoxide and activates it in reactions involving its decomposition into free radicals, which finally bring about the oxidation of cumene[77].

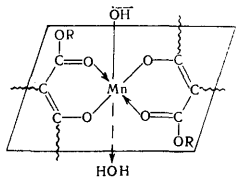
Keier and coworkers[25,35] tried to explain the change in rate of a reaction (for example, the decomposition of hydrazine) on low-molecular-weight complexes of different purity, obtained by recrystallisation. By studying ESR spectra they concluded that crystallisation increases the degree of order of the crystal structure. Polymeric chelates with a more ordered structure also showed a lower reactivity towards the reaction under study. For example, a polychelate with a highly ordered structure which was almost free from defects and planar was similar to its low-molecular analogues in reactivity. This material, prepared in a nitrogen atmosphere, was characterised by a narrow ESR line and by well developed anisotropy[39]. ESR spectral studies before and after vacuum annealing showed that polychelates with a regular structure are not formed under the preparative conditions used. Ordering of the polymer structure takes place during the heat treatment, involving completion of the complex formation and molecular redistribution, and also exchange interaction between the copper ions resulting from the increased conjugation in the polymer. The tetrahedrally distorted structure of the chelate centre becomes planar, and the molecular weight of the polychelate increases. Mutual interconversion of various modifications of the polymer is also possible. All these factors tend to lower the reactivity of the polychelate[39].

The surface of the polychelates plays a well known role in determining their catalytic activity. Thus, the catalytic activity per unit weight of polymer increases by almost two orders of magnitude on increasing the surface area of copper polychelates based on α-thiopicolinamidobiphenyl[34]. In an investigation of the catalytic activity of polychelates towards the decomposition of N_2H_4 it was shown that the chelate suffers fully or partly irreversible changes. Measurements of the decrease in intensity of the ESR signal at the beginning of the reaction give almost quantitative agreement between the number of copper chelate centres which have reacted and the number of decomposed N_2H_4 molecules. The first step of the reaction may consist in the attachment of the reactant to the metal of the chelate centre, accompanied by an electron transfer which alters the charge on the metal and thus weakens the metal–ligand bond[25].

Elimination of the ligand can then take place, with simultaneous attachment of hydrogen atoms at the broken bonds and evolution of NH_3 and H_2 molecules into the gas phase. However, the breakdown of the chelation centre is complete when the copper is reduced to Cu^0, with further increase in the rate of decomposition of the substrate. (The rate of decomposition after 21 h increases to 3 cm^3 h^{-1} as compared with 0.1 cm^3 h^{-1} during the first hour.) In the oxidation of isopropylbenzene (p. 986) the polychelates also react with the substrate and undergo irreversible changes, however (and in contrast to the previous reaction) the deactivation of the catalyst is much slower. Thus, polymeric chelates take part in the formation of free radicals as true heterogeneous catalysts[36].

In order to identify the type of metal–polymer bond and the valency state of the metal in the chelates with macromolecular ligands (XI-M) prepared by the present writers, their magnetic moments μ_{eff} were measured[78]. The μ_{eff} values (in Bohr magnetons) were 3.83 and 4.87 respectively for different samples of XI-Mn, which corresponds to three and four unpaired d-electrons. Thus, the samples were spin-free and contained Mn^{IV} and Mn^{III} ions. It is not easy to envisage a coordination of three (or four) macromolecular ligands around the central manganese atom, as the Stewart–Briglebb molecular model clearly shows. Hence we may imagine that the manganese atom is surrounded by six oxygen atoms, four of which belong to polymeric ligands and the other two to two hydroxyls (for Mn^{IV}) or to one

hydroxyl and one solvent water molecule (for Mn^{III}), which thus complete the coordination octahedron:



Some of the centres may be coordinated to one macromolecular ligand and two solvent water molecules[71].

In this instance, as with the macromolecular chelates of type (III),[34] the high catalytic activity can be ascribed[78,79] to the formation of disordered, incompletely saturated coordination centres in the polymer chain, with a distorted geometrical configuration.

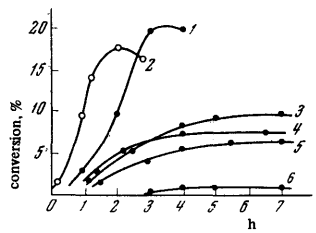


Figure 13. Liquid-phase oxidation of acrolein in the presence of the following acetylacetonates:
1) Mn, *2*) Co, *3*) Fe, *4*) Cu, *5*) Ni, *6*) acetylacetone; concentration 1×10^{-3} mole litre^{-1}.

Japanese workers have put forward[80] some interesting ideas on the changes in the coordination centre of the catalyst in the course of the catalytic reaction. The activity of acetylacetonates decreases in the series Co > Mn ≫ Fe ≃ Cu > Ni (Fig. 13) for the liquid-phase oxidation of acrolein to acrylic and peracrylic acid, and acrylic acid polymers. (The solvent used for the oxidation determines the relative yield of these products.) The authors believe that the reaction occurs by a radical mechanism, and that the initial and the final products (including polymeric products) enter into the coordination centre of the catalyst (for example, Co^{III} acetylacetonate) as they are formed.

The most important thermodynamic characteristic of complexes in general (and macromolecular complexes in particular) is their so-called stability (or instability) constant. Thus, according to Kenney[81], K_{st} of polycoordination polymers (that is, the equilibrium constant of the reaction $M^{m+} + mA^- \rightleftharpoons [MA_m]$) is a measure of the free energy change attending complex formation. The values of this constant for bivalent metals increase in the series Mg < Mn < Fe < Co < Ni < Cu < Zn.[81] Thus, it is particularly relevant to establish the dependence of the activity of macromolecular chelates upon their stability—for example, for the complexes of the 2(O, O) type considered here. The Japanese workers already mentioned[40,42] observed a correlation between the catalytic activity series of the poly-(β-diketone) copper chelates (see p. 987), VII-Cu > VIII-Cu > IX-Cu > X-Cu, and the shifts of the absorption maxima in the visible region of the spectrum towards longer waves (λ_{max} 388, 375, 370, 368 mμm respectively). This is evidence that the energy of the electronic transitions in the macromolecular ligands and their chelates decreases in the stated order, and therefore the strength of the bond between the macromolecular ligand and the metal must also decrease in the same order.

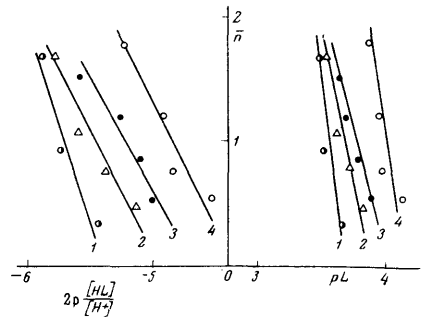


Figure 14. Curves for the formation of poly-(β-ketoester) complexes, (XI)-M, $m = 6$:
1) Mn, *2*) Co, *3*) Ni, *4*) Cu.

The present writers and their coworkers[82] have measured the acid–base dissociation constants of the macromolecular ligands of the poly-(β-ketoester) type XI and the formation (or stability) constants of their complexes with transition metal cations. The acid–base dissociation constant K_a of the macromolecular ligand (XI, $m = 6$) was found to be $10^{-6.4}$ (that is, $pK_a = 6.4$). This value was obtained from the Henderson–Hasselbach equation $pH = pK_a - n\lg[(1 - \alpha)/\alpha]$, where α is the degree of neutralisation, and n is a constant independent of the extent of polymerisation whose value varies between 1 and 2 and increases with dilution of the solution. The formation constants (or stability constants) of the macromolecular chelates XI-M decrease in the series Cu > Ni > Co > Mn (Fig. 14). We note that the same sequence also describes the increase in catalytic activity of the poly-(β-ketoester) complexes XI-M for the decomposition of hydrogen peroxide, and the decrease in the activity of these complexes for the oxidation of ascorbic acid (see Figs. 6 and 5 respectively, and p. 987).

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Published data show that the field of macromolecular complexes is an interesting one from many viewpoints. Leaving aside the problem of preparing thermally stable polychelates[83], it is obvious that macromolecular complexes are vitally important as catalytic systems which are active towards a wide range of reactions including the polymerisation of vinyl monomers.

These systems are interesting also from the standpoint of structural studies, since their structure allows mutual interaction of coordination centres through the polymer chain.

Macromolecular complexes containing metals can be treated as model compounds for the substances which take part in a number of biochemical processes, such as the assimilation of metal ions (Cu, Fe), the blocking of functional groups (Mn), redox reactions of the cell (Cu, Fe, Co), and others[84].

Each of the two main classes of macromolecular complexes, prepared either by polycoordination of multivalent ions with multidentate low-molecular-weight ligands or from previously synthesised macromolecular ligands, has some advantages as a catalytic system: the former because of the presence of a conjugated system and of the concomitant synergic effect (that is, the collective electronic property of the macromolecule), the latter because of the presence of a macromolecule which is not destroyed by the removal or replacement of some metal atoms by others, and also because of the solubility of the initial macromolecular ligand.

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The Inhomogeneity of Copolymers with Respect to Composition

V.A.Myagchenkov and S.Ya.Frenkel'

The inhomogeneity of composition (i.c.) which arises in copolymerisation not only influences the physical and physicochemical properties of the copolymers formed but also, when it is correctly assessed, makes it possible to arrive at certain conclusions concerning the copolymerisation mechanism. The review deals mainly with binary statistical copolymerisation. A critical analysis is given of the "classical" Mayo-Lewis concept, according to which the copolymerisation constants remain unchanged throughout the process. Regarding such systems as "normal" or standard, the authors have derived expressions for their distribution functions with respect to composition. Further it is noted that the case where r_1 and r_2 are constant is more likely to be an exception rather than the rule and possible causes of the departure from such constancy are indicated. The principles of the derivation of the integral and differential distribution functions with respect to composition for copolymerising systems are discussed in detail. Analytical expressions are proposed for numerical estimates of inhomogeneity with respect to composition. In their statistical significance the expressions obtained resemble equations of different degrees governing the molecular weight ratios in homopolymerisation. The deviations from the "norm" in the copolymerisation of ionogenic monomers in aqueous solution are considered as an example of the application of these expressions. In this case the copolymerisation constants depend on the conversion due to the changes in the degree of ionisation of the "bound" monomers compared with the free monomers and due to the overall change in ionic strength. In conclusion a critical analysis is given of the existing experimental methods for the determination of inhomogeneity of composition and the prospects for the further development of the statistical theory of copolymerisation are discussed. The bibliography includes 111 references.

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I. INTRODUCTION

The polydispersity of copolymers is not restricted to differences in chain length. Individual macromolecules can differ also in their chemical composition (inhomogeneity of composition) or in their shape (molecular polymorphism)[1,2]. All three types of polydispersity are a consequence of certain processes occurring in copolymerisation. Their analysis may provide valuable information about the kinetics and mechanism of copolymerisation—by analogy with the detailed information about the homopolymerisation mechanism derived from the analysis of molecular weight distribution (m.w.d.). In addition, inhomogeneity of composition and molecular polymorphism have a