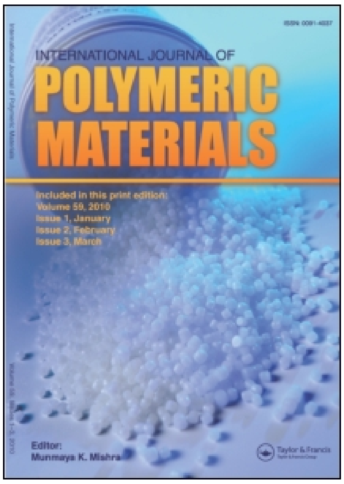

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The Influence of the Polymer Chain on the Catalysis by Variable Valency Metal Complexes*

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The role of the polymeric chain in catalysis has been considered for the case when the chain by itself possesses to catalytic activity. The catalysts studied were the complexes of variable valence metals and polyethyleneglycols of different molecular masses (M). The extreme in dependence of the atomic catalytic activity (ACA) on M (with the amount of the metal in the chain being constant), as well as a drop in ACA with the increase of metal content in the chain (with M being constant), result from irreversible conformations of the intermediates formed on opening of the metal-chain cycle. These dependencies are stipulated by changes in entropy. The activation energy depends solely on the metal nature. The change in the initial reaction rate correlates with the difference of the characteristic viscosities of the starting polymer and its complexes. The use of the "chain" effect in a number of other reactions and catalytic systems is also discussed.

Keywords: Catalysis; variable valence metals; polyethyleneglycols; complexes; atomic catalytic activity; molecular weight dependence

INTRODUCTION

The advances in understanding of transition-metal complexes with polymers are due to their wide applications. Polymer complexes formed as a result of interaction between functional chain groups and molecules or ions of transition metals may be viewed as a new class of

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organoelement compounds having valuable physico-chemical properties. The specific properties of such complexes are the reason for their successful application in diverse chemical processes. A wide variety of polymers are suitable to synthesize catalytic systems with regard to the properties of the reaction medium and the character of active centres. It is now possible to design polyfunctional catalysts for performing various reactions and to studying their mechanism. In particular, in a number of cases the specific properties of enzymatic reactions can be successfully explained.

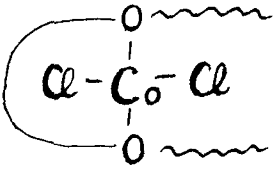
Extensive investigations of catalysis by metal polymer complexes were generalized previously [1, 2].

This paper is devoted to an important aspect of possible participation of the polymer chain in catalysis as a ligand of active centre when the chain itself is catalytically inactive. Catalytic properties of polymer complexes with metals of variable valency soluble in the reaction medium were studied for oxidation reactions of tetralin and cyclohexene (complexes of polyethyleneglycol /PEG/ and polyurethanes with cobalt, manganese, copper, and nickel chlorides), epoxidation of nonene-I (complexes of PEG and crown-esters with acetylacetonate), decomposition of cyclohexenyl hydroperoxide (PEG complexes), synthesis of acetic acid from methanol and CO (PEG complexes with chlorides of noble metals). In all these processes the chain exerts a similar influence on the catalysis. The reaction of tetralin oxidation was studied in greater detail [3, 4], and thus serves as an example.

RESULTS AND DISCUSSION

Metal complexes were prepared by dissolving the calculated amounts of metal salts and polymer in acetone with the subsequent removal of the solvent at 313 K under vacuum. The resultant powders had colours typical of anhydrous chlorides of the corresponding metals. PEG molecular mass (*M*) was widely varied (600 – 100000). The molecular ratio of the metal salt to polymer chain was from 1 to 10. Oxidation was conducted on a gasometric unit in the kinetic region of the reaction. The initial rate of oxygen absorption per metal atom in a weighed catalyst sample was taken as a measure of catalytic activity (atomic catalytic activity – this ACA). At 343–373 K non-catalytic tetralin oxidation can be neglected. Special experiments confirmed the absence of catalytic properties of polymer chains. Salt is not dissolved in the system; therefore, the metal compound is present in the solution only in the form of complexes. Before the reaction the catalyst was dissolved in tetralin in an inert medium at the temperature of the experiment; after that the system was filled with oxygen and oxidation was initiated. The depth of oxidation was 5–10%. ACA was determined for low catalyst concentrations where the growth of the initial oxygen absorption rate depends linearly on complex concentration (within this concentration range the chain association can be disregarded). Consequently, the reactions took place in the region of diluted polymer solutions which is confirmed by the study of the intrinsic viscosity of the systems (Fig. 1).

The linear dependence of η_{sp}/C on C and intrinsic viscosity indicate that no dissociation of complexes occurs in the solution and that the end-to-end distance in the chain is shorter. These data, together with spectral characteristics and solubility of the compounds, allow us to assign the following structure to the complexes;



Other metal complexes differing only in the number of chain-metal bonds have a similar structure of intramolecular cycles.

The initial and reaction products were analyzed and the inhibitor concentration was determined by gas–liquid chromatography [5]. Tetralin hydroperoxide was analyzed iodometrically.

In all cases a strong dependence of ACA on M was observed. Figure 2 illustrates this dependence for the $CoCl_2$/PEG complex (1:1).

The maximum increase in the rate is observed at $M = 40000$. The greater the difference in the intrinsic viscosities of the initial polymer and the complex, the higher the increase in the reaction rate. The extreme in dependence can not be accounted for by a change in the character of interaction between PEG and tetralin. The experimental values of the intrinsic viscosities of fractions processed by the Mark-

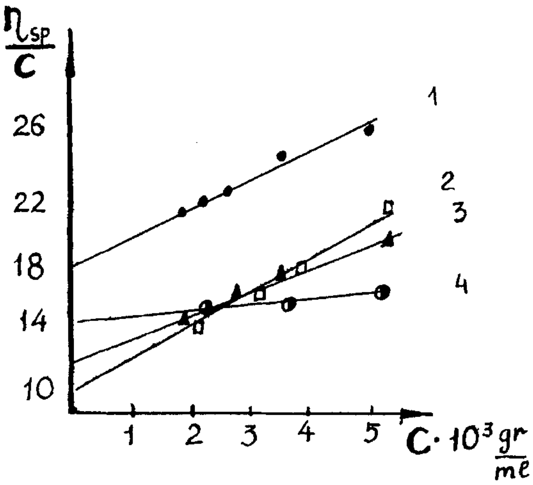


FIGURE 1 The dependence of a reduced viscosity of PEG ($M = 20000$) and its complexes with $MeCl_2$ (1:1) on concentrations in tetralin (353 K); 1-PEG; 2-$CuCl_2$/PEG; 3-$MnCl_2$/PEG; 4-$CoCl_2$/PEG.

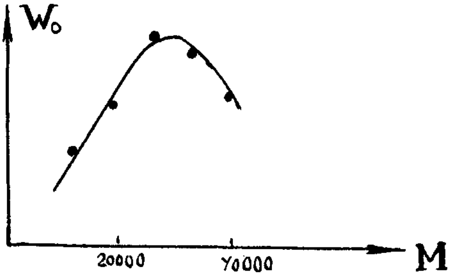


FIGURE 2 The dependence of ACA on M in $CoCl_2$/PEG complex (1:1).

Houvink equation ($\eta_{sp} = KM^{\alpha}$) showed tetralin to be a Θ-solvent ($\alpha = 0.5$). Consequently, the shape of the polymer coil within the investigated range of M and interaction of tetralin with the chain remain unchanged. Similar dependence for the complex with 1:1 ratio in the $CoCl_2$/PEG system showed that α is close to 0.5, and therefore, the observed dependence is related only to specific properties of the chain molecule.

The dependence of the rate constant on chain length was observed earlier, for example in [6, 7]. An apparent constant of the second order reaction rate was slowly increasing during solvolysis of *n*-nitrophenyl acetate catalysed by oligoimidazoles in a propanol-water mixture at 229 K; this growth slowed down with increasing *M*. In the literature the growth of the constant rate is attributed to the fact that the reaction inside the coil occurs in specific microreactors where the most favourable arrangement of the active groups is attained during bifunctional catalysis [8].

In both polymer catalysis and low-molecular compound catalysis the order in catalyst is close to 1/2, *i.e.*, according to literature and experimental data bifunctional catalysis is hardly possible during tetralin oxidation. It is common knowledge [9, 10] that catalyst complex (com) activates oxygen molecules reacting with tetralin (RH) and forming free radicals capable of further transformations in the chain process. The scheme of the reaction is as follows:

$$\mathrm{Com} + \mathrm{O_2} \longrightarrow \mathrm{Com} \ldots \mathrm{O_2}$$
$$\mathrm{Com} \ldots \mathrm{O_2} + \mathrm{RH} \longrightarrow \mathrm{Com} \ldots \mathrm{O_2H} + \mathrm{R}\cdot$$
$$\mathrm{R}\cdot + \mathrm{O_2} \longrightarrow \mathrm{RO_2}\cdot$$
$$\mathrm{RO_2}\cdot + \mathrm{RH} \longrightarrow \mathrm{ROOH} + \mathrm{R}\cdot$$

The experiments on inhibiting oxidation with ionol additives were conducted in order to determine the stage of the chain oxidation process that is affected by the chain length [4]. It was established that the addition of ionol in amounts of $2-4 \times 10^{-2}$ mol/l of inhibitor completely terminates the process. By measuring the rate of ionol consumption per metal atom in the induction process it was shown that ACA and the initial rate of oxygen absorption in the uninhibited process increases with increasing *M*.

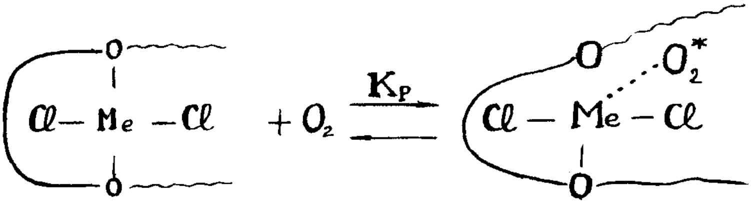
As follows from Table I, the rate of oxygen absorption in the uninhibited oxidation exceeds the absorption rate of ionol (JnH) during

TABLE I The dependence of the initial rates of oxygen consumption and absorption of *M*

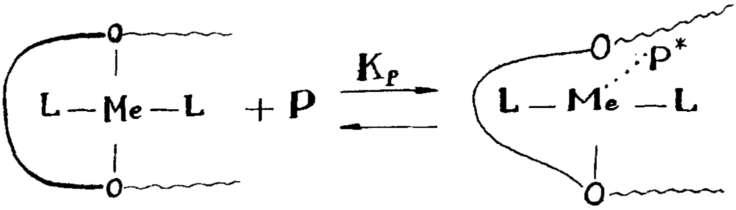
M_{PEG}	$W_1 \cdot 10^{24}$ *g-mol JnH/min g-atom Co/II/*	$W_2 \cdot 10^{22}$ *g-mol* O_2*/min g-atom Co/II/*	W_2/W_1
4000	0.5	0.6	120
20000	2.4	2.9	121
40000	4.8	5.8	121

the induction period (W_1) 120 times. As W_1 is proportional to the initiation rate, the $MeCl_2$/PEG complexes may be considered to be initiators. Radicals generated on the complex appear in the volume and initiate independent oxidation.

On the basis of the above and literature data the initial stage of the process may be assumed to be:

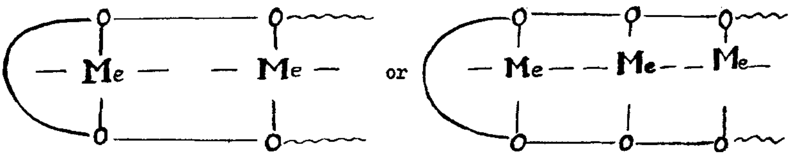


As is seen, the mechanism of bifunction catalysis is not involved in the given process. Similar conclusions were drawn for other investigated reactions: the first stage for all processes involves the complex formation:



which propagates the reaction.

An increase in the number of atoms in polymer chain leads to the reduction in ACA (Fig. 3). It follows from Figure 3 that the sharpest ACA reduction is observed in the most active complex $CoCl_2$/PEG. The intrinsic viscosity displays the same trend. Taking into account the solubility of the resultant complexes and spectral data, one may assume their structure;



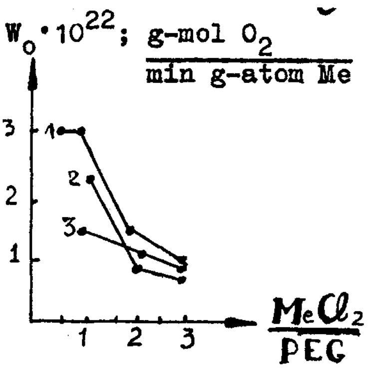
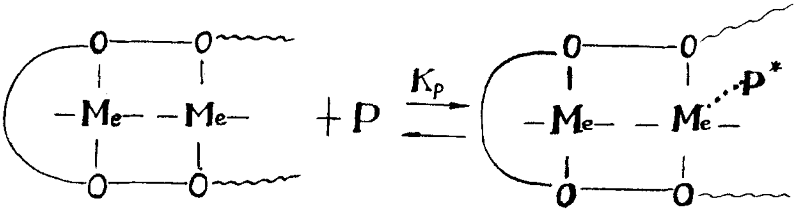


FIGURE 3 The dependence of ACA on $MeCl_2$/PEG ratio (M = 20000); 1-$CoCl_2$/PEG (80°); 2-$MnCl_2$/PEG (97°); 3-$CuCl_2$/PEG (80°).

The reaction mechanism in that case is the same, but apparently, only the part of the chain is involved. For example:



When the chain-bonded metal atoms increase in number, the chain coils and the initial rates of the processes become close. It may be assumed that the main effect in the process is chain-conditioned. For all complex compositions, tetralin hydroperoxide is the main product. The temperature dependence of the reaction rate is given in Figure 4. For all complex compositions and regardless of M, the activation energy in the processes is determined only by the nature of metal. For the complexes with $CoCl_2$, $CuCl_2$ and $MnCl_2$ the activation energy is 46.0; 39.8; and 64.8 kJ/mol, respectively.

The fact that the activation energy is independent of M and complex composition makes it possible to conclude that the differences in activity are related to changes in the pre-exponent in the Arrhenius equation, *i.e.*, are due to entropy.

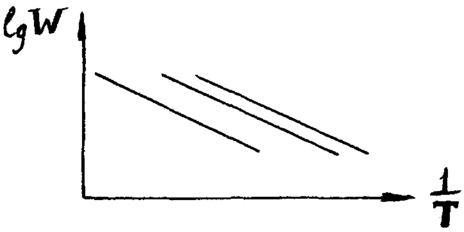


FIGURE 4 The dependence of lg W_0 on I/T for various M of polyethylene glycol.

Thus, on the basis of the experiment it may be concluded-that in polymer catalysis and, in particular, in catalysis by metal complexes, the influence of the chain on the process is mainly entropy related.

Evidently, the observed phenomenon can not be accounted for by the principle of the equal reactivity of units [11] in the infinitely long chains (polymers). In the relatively short chains (so called, oligomers) the reactivities of chain groups are unequal [12].

When considering a chemical reaction in the field of oligomers, one should take into account not only the chemical act itself but a change in the average distance between chain ends. This specific feature of oligomer reactions will be discussed in detail for equilibrium processes. The direction of the process can be neglected in thermodynamic analysis since all free energy constituents are assumed to be additive. Hence, the reaction should be conducted in two stages: at first the chain stretches (coils) until it reaches the size which is attained when one molecule of the low-molecular compound is introduced and then the chemical reaction is performed. Since the same addition is considered under the same conditions, a change in free energy (ΔGx) due to chemical act may be assumed constant in a first approximation, and the dependence of total change in free energy in the process (ΔG) will be determined by a change in the average distance (usually a change in mean square distance is considered) between chain ends.

Therefore:

$$\Delta G = \Delta Gx + A$$

where A is the work for stretching the chain. This expression does not take into account the term determined by the number of rearrangements of the reacted site in the chain because it is small as compared to $(\Delta Gx + A)$.

A mean square distance $(\bar{R}^2)$ between the ends of a finite length chain is present by the Landau–Lifshitz model [13]. It may be calculated from other models applicable to the chains of the limited size [14]. Although possible, the measuring of this value for short chains is too complicated. For the cases when molecules of low-molecular compounds are fit on the chain the culculation of $\bar{R}^2$ is given in [12]. $\Delta\bar{R}^2$ on M dependence is shown in Figure 5.

Both reacted and unreacted short chains represent a "rigid stick" (low-molecular compounds), while in the infinitely long chains (polymers) the contribution from more rigid (flexible) reacted section to $\bar{R}^2$ will be very small. Only in oligomers its contribution to $\bar{R}^2$ value becomes appreciable. Therefore, the dependence of the observed equilibrium constant (K_p) on the chain length has an extreme. The typical $K_p - M$ dependences are illustrated in Figure 6.

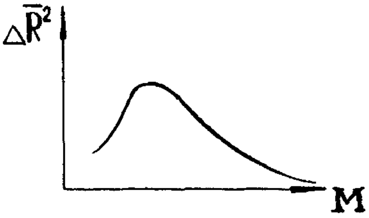


FIGURE 5 $\Delta\bar{R}^2$ *versus* M for the fit of one low-molecular compound on the chain.

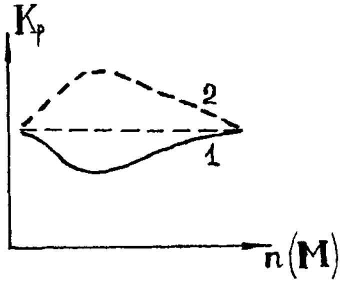


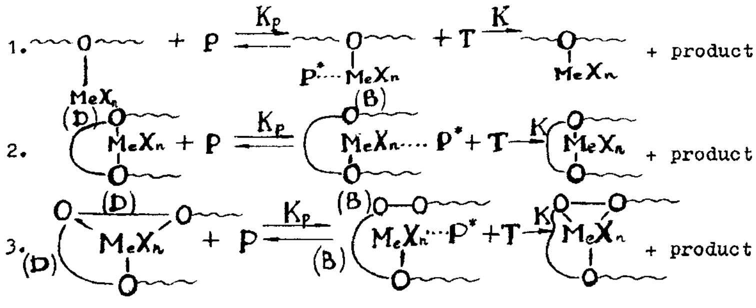
FIGURE 6 K_p *versus* M; 1-reacted section is more rigid than the section of the initial chain; 2-reacted section is more flexible than the section of the initial chain.

It may be seen from Figure 6 that if the reacted section is more rigid, then the $K_p = K_p(M)$ dependence has a minimum; if it was more flexible, the curve has a maximum. In fact, at first the flexibility of the chain increases with the growth of its length and the influence of the reacted section becomes stronger; on reaching a certain length the chain becomes flexible and, starting from this moment, the contribution of the reacted section goes down, tending to zero. Other specific features of the chain processes are not taken into account in this consideration.

Therefore, at the beginning of the process (L is small) and at high lengths A tends to zero; the values of K_p are equal in both cases which serves the basis of the Flory principle of the equal reactivity of chain units. In this case all groups of similar chemical structure in the chain, with the exception of several and groups, possess experimentally independent constants. Naturally, the range where this dependence/independence/ of the reactivity or K_p on M is observed is determined by the experimental conditions and methods of evaluating the constants.

It follows from K_p *versus* M dependence that in case of metal coordination with the formation of several chain-ligand bonds the complex formation with various molecules takes place mainly in shorter chains ("rigid stick" is hard to fold), and complexes remain insoluble. Thus, $CoCl_2$/PEG complexes of 1:1 ratio remain insoluble up to $M = 4000$. At greater M the intramolecular cyclization prevails because the entropy losses in the chain are small (a small change of $\bar{R}^2$ in the reaction).

Let us now consider how the chain length affects the catalysis for various types of metal coordination on the chain molecule (one fit on the chain). The reactions run according to the scheme:



In all cases the reaction rate can be written as:

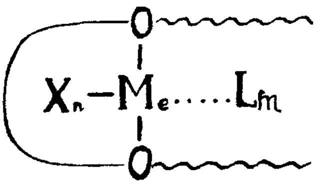
$$W = K[B][T],$$

where $B = K_p[p][D]$ (local equilibrium).

The value of B compound is not an equilibrium one but a stationary one, because a complete equilibrium requires the chain to reach a certain equilibrium value of $\bar{R}^2$. Consequently, if the reaction rate exceeds that of attaining the equilibrium, the B possesses an excess free energy that increases the observed reaction rate. This excess free energy is equal to the difference between free energies of the formation of equilibrium state and state B. It is determined by the work for stretching (compressing) the chain from equilibrium state to state B.

The greatest gain in rate is expected for the pathway 2, since the maximum difference between free energies of equilibrium states and state B can be reached during transition from D to B. In tetralin oxidation reaction the pathway 2 is observed in reactions with $CoCl_2$ and $MnCl_2$ complexes. That is why the acceleration of their reaction rates is approximately identical in the same range of M. In pathway 1 both the gain and loss of free energy in free state are possible; however in general it is less than in pathway 2. In pathway 3 the breaking of one or several chain-metal bonds leads either to an incomplete cycle opening (breaking of one bond) or to the formation of the more stable complex (breaking of two coordination bonds) which results in slower acceleration of the catalytic reaction as compared with the pathway 2. Actually, a catalyst containing $CuCl_2$ doubles the reaction rate in the same range of M (M changes from 4000 to 20000) with catalysts with $CoCl_2$ and $MnCl_2$ increase the rate ten times.

Thus, while selecting metal-polymer catalysts it is expedient to use compounds working according to Scheme 2 and having an optimum chain length. If metal can coordinate with the chain through more than two bonds it becomes reasonable to introduce additional ligands into the system, *i.e.*, to prepare more complicated complexes to the type:



where L is a low-molecular ligand, and m is its number (m is equal to coordination number of metal minus 2).

Unfortunately, at present the optimum length of the chain molecule for catalysis can not be evaluated as there is no rigorous theories on oligomeric chain length of irregular chain structure in a given solvent at a given temperature. However, evaluating the difference in $\bar{R}^2$ of the complexes and initial polymers, the range of M where the reaction rate should be the highest (maximum difference in $\bar{R}^2$) can be estimated. It is obvious that in comparing $\bar{R}^2$ of the chains containing the catalyst and intermediate complexes it should be borne in mind that $\bar{R}^2$ for the uncomplexed chain and equilibrium chain of the 

type are not equal because "the local rigidity" (characteristics of bending strength) at the reaction site and in the initial chain differ. That is why the optimum value of M should be experimentally verified.

The intrinsic viscosity, being an easily determined characteristics, is the most suitable for selecting the optimum value of M. Figure 7 illustrates the dependence of ACA on the difference between intrinsic viscosities in the initial and complexed chain for the $CoCl_2$/PEG complex of 1:1 composition. It should be noted that the extreme in the dependence of the rate constant on M is well defined. Therefore the narrowest possible fractions are to be used for the catalysis. In this work the polymers with $M_w/M_n = 1.08$ were taken.

The work for stretching is mainly accounted for by changes in entropy of the system. A change in entropy of the system is illustrated by simple example (Fig. 8). Let one end on a molecule be positioned in zero coordinates. Then the second chain end (the chain is assumed to represent a "rigid stick") circumscribes a circle with a diameter $2L$

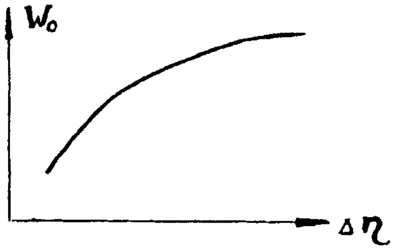


FIGURE 7 The dependence of ACA on the difference in intrinsic viscosities of the initial and complexed chain of the $CoCl_2$/PEG (1:1) complex.

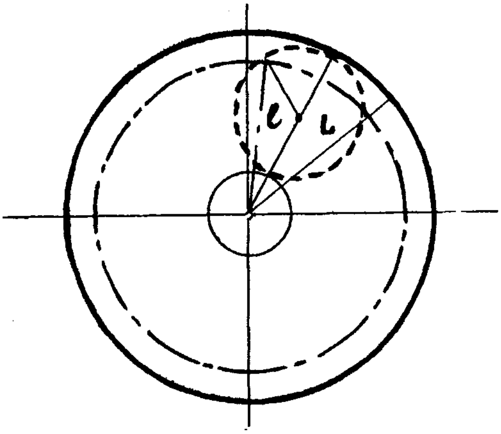


FIGURE 8 The scheme for determining the number of states in the "rigid stick" and in the "rigid stick" with a hinge.

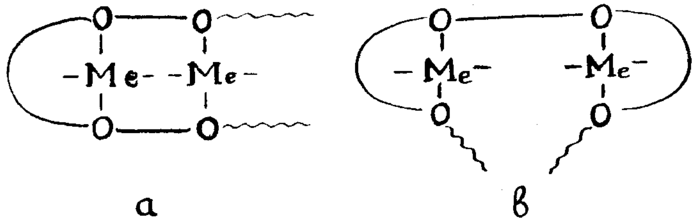
which determines the number of chain states. Clearly, the number of states is proportional to the chain length.

If a hinge is incorporated into the chain at "l" length from zero coordinates (it is assumed that a very flexible section was formed in the reaction), the number of states will sharply increase, although the energy of each state will remain unchanged. For the "rigid rod" with a hinge the number of states will be determined by the number of states of the "rigid rod" and the number of states of the bend "rigid rod". The maximum number of states is attained at $l = L/2$. Hence, both the certain chain length and optimum location of the reacting groups in the chain are responsible for the maximum effect in polymeric reactions (including polymeric catalysis). Unfortunately, the selected method of synthesis of metal complexes with homopolymers renders it impossible to prepare individual compounds due to a statistical character of the process. To prepare more productive catalyst it would be desirable to obtain copolymers with a certain arrangement of complex-forming groups (the number of these groups in the chain should be minimum).

In double-centre catalysis [2] the complex-forming groups should preferably be located at maximum distance from one another. The size limitations, of the maximum thermodynamically stable cycle and kinetics of its decomposition dictate, however, the limited cycle dimensions for the intermediate complex (*D*).

With increasing amount of the metal that participates in the reaction and has at least two bonds to the chain, $\bar{R}^2$ decreases; this finally leads to a decrease in the equilibrium constant of complexation with increasing conversion degree (Fig. 9). Since in the formation of the intermediate complex the gain in the system entropy is opposite in sign to the loss of entropy in the course of complexation, each subsequent metal in the chain is less catalytically active (Fig. 3). Consequently, the effect of the chain will reduce with increasing amount of metal and at large amounts may not be manifested at all.

The formation of cyclic compounds in the chain can follow two pathways:



The formation of "b"-complex apparently is more probable than that of "a" because of greater $\bar{R}^2$ in the former case. To design the optimum catalyst, the number of catalytic groups in the chain should, therefore, be minimal. For infinitely long chains (polymers) the number of catalytic groups in the chain may be greater since in this

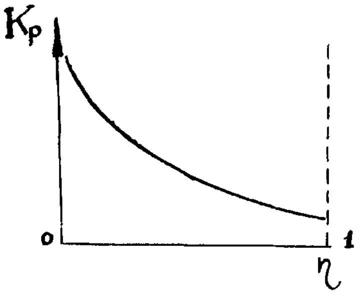


FIGURE 9 The dependence of the equilibrium constant of complex-formation on conversion degree (η).

case $\bar{R}^2$ is independent of the number of metal atoms bonded to the chain, *i.e.*, in accord with the Flory principle of the equal reactivity of chain groups, catalytic centres are independent of each other.

While selecting the chain for the synthesis of catalysts, one should take into account the influence of the chain flexibility on its entropy. The higher is the system flexibility, the smaller are M values required for the chain to start to behave like polymer. A minimum possible chain size will be the chain consisting of 3 units [15]. With an increase in "local rigidity" the cyclization ability of short chains will drop and the optimum catalyst length will rise. The longer is the catalyst, the greater is A value for the opening of the cycle and higher the rate of the catalytic reaction following the pathway 2. It should also be noted that the growth of "local rigidity" lowers the cyclization ability.

The influence of the "local rigidity" may well be observed in reactions with complexes containing two different metals in the chain one of which is inactive. The reaction of tetralin oxidation in the presence of PEG complexes with $CdCl_2$ and $MgCl_2$ was studied. The special experiments proved complexes $CdCl_2$ and $MgCl_2$ to be inactive. It was also established that the reaction rate grows with an increase in the chain flexibility (the intrinsic viscosity of the system goes down). The rates for the systems containing $CoCl_2$ and $CdCl_2$ or $CoCl_2$ and $MgCl_2$ complexes are compared in Figure 11. Thus, the use of double and even triple complexes may be recommended to increase the process rate if the inactive metal in the chain improves the chain flexibility. Such complexes increasing the flexibility of the chain have the structure: 

$\sim\sim\underset{\mathrm{MeX}_n}{\mathrm{O}}\sim\sim$

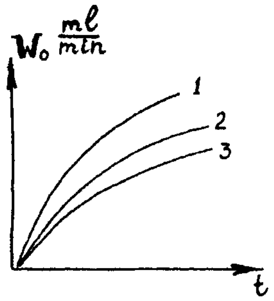


FIGURE 10 Oxygen absorption plotted against time: 1-catalyst with Mg and Co; 2-catalyst with Co; 3-catalyst with Cd and Co.

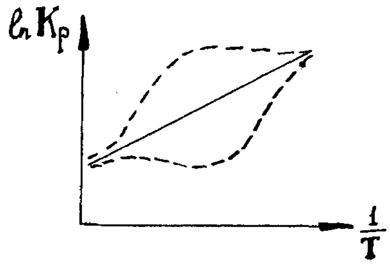


FIGURE 11 Equilibrium constant *versus* temperature (the influence of "the local rigidity" on the process).

"The observed local rigidity" of the chain in the solution is determined by the chain itself as well as by temperature, solvent and intramolecular interaction.

"The local rigidity" falls as the temperature rises, and at sufficiently high temperatures the units in the chain become statistically independent of each other (the chain behaves like a polymer). At low temperatures the chain behaves as a "the rigid rod", *i.e.*, its ability to complexation with the formation of cycles decreases. Hence, the maximum contribution of the chain to catalysis is observed within a certain temperature range. Therefore, the temperature dependences of catalytic processes with the participation of polymer chains should be analyzed with great care. Since the temperature dependence of "the local rigidity" is non-linear, the temperature dependence of the chain entropy is also non-linear. A change pattern of "the local rigidity" with temperature is best illustrated by the temperature dependence of the equilibrium constant [16] given in Figure 11. The curve is plotted for the case when other specific features of the processes in the chains can be neglected. When studying the temperature dependences of tetralin oxidation rate, we chose, the temperature range within which conformation changes occur neither in PEG nor in its complexes (conformation transition occurs at $T = 335$ K). The slight decrease in the apparent activation energy of the process as compared to the case using low-molecular analogs may be related either to the energy for rendering the chain more rigid or to a change in flexibility with temperature (see Fig. 11).

Evaluating the effect of the solvent on the process, its influence on both the chemical act itself and $\bar{R}^2$ should be taken into account. With decreasing interaction between the chain and the solvent the observed flexibility of the chain rises which results in a shorter optimum length of the catalyst. In the majority of cases $\bar{R}^2$ in the solvent is greater than in the isolated state. In addition, the solvent may change the optimal cyclization sites. Unfortunately, only very few publications are devoted to the influence of the solvent on the catalysis in non-aqueous solutions by chain molecules and therefore we restrict our selves to a general consideration of the problem.

The formation of the intermediate complex is accompanied by a considerable gain in free energy that at first rises with M and then decreases. This additional free energy may initiate catalytic reactions unknown with their low-molecular analogs. However, these reactions can only occur in a certain range of M values. In some catalytic reactions it may lead to the loosening of the chain molecules or even to their absence. Thus, under certain conditions it becomes possible to create such catalysts that will initiate new catalytic reactions including the ones not yet described in literature. Obviously, the rate of such reactions is slow.

In this research we used special methods to show that association of the chain molecules can be disregarded, because only individual molecules take part in the reaction. Generally speaking, the association increases the "observed rigidity" of the chain if an associate with a regular tertiary structure is formed. However the study of the synthesis of polymers with tertiary structure is still at the initial stage of the development (2).

One of the specific features of the catalytic reactions involving the chains is a high selectivity of the processes. The selectivity of the process is apparently due to the orientation of the low-molecular reagent T near the chain. The orientation is due either to local interaction between the chain and reagent or to excessive combinatoric entropy of mixing the molecules differing in size. It appears that the reaction runs primarily with the oriented molecules of T, that is probably one of the reasons for the acceleration of the process. Parallel to that the molecules inside the coil also take part in the reaction ("cage effect"). In this case the high rate of the process ensures its high selectivity. In other words, both the structure of the reaction site and the chain structure determine the selectivity of the process. To verify this assumption, the reactions of cobalt complexes with PEG and polyurethanes were conducted. As is known [9], the fluctuations of the selectivity remain negligible independent of the type of the low-molecular donor. Tetralin oxidation by the low-molecular catalysts produces both ketone and alcohol. Under certain conditions it becomes possible to produce practically only ketone by using polyurethane as a donor. For PEG complexes hydroperoxide was the reaction product whose decomposition yielded alcohol. The dependence of the selectivity on *M* is similar to the dependence of the process rate. The amount of metal in the chain does not change the selectivity but considerably affects the process rate (Fig. 3).

Additions of PEG in the process of cyclohexenyl hydroperoxide decomposition and cyclohexene oxidation catalysed by vanadil acetylacetonate exhibit an extreme in dependence of the selectivity on the amount of PEG (Fig. 12).

At a low PEG content the amount of the product formed on the low-molecular catalyst is smaller than that on the polymer complex (in this case there is more than one vanadil molecule on the chain.) At a high PEG content in the system the chain activity reaches its peak and the amount of the unbonded vanadil reduces. In the simplest case of the reaction occurring on two types of catalysts (one of which is bonded into the complex) the dependence of the selectivity on the amount of the added complexing reagent will smoothly grow or fall. The growth is observed in the case of higher selectivity of the reaction on the complex catalyst.

In conclusion we want to note the relation between polymer catalysis and enzymatic reactions in which, as was recently proposed,

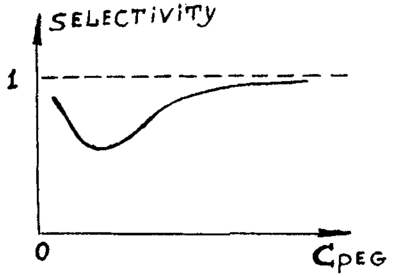


FIGURE 12 The dependence of the selectivity on the amount of the added PEG for the reaction of cyclohexenyl hydroperoxide decomposition.

the contribution of the mechanical constituent to the process should be taken into account [18]. In the present paper we did not consider the problems of catalysis in aqueous medium which are now intensively studied both by the Russian and foreign authors.

References

[1] Collection of articles "Catalysts with applied complexes", Novosibirsk, Institute of CO catalysis, Academy of Sciences of the USSR, 1997.

[2] Bekturov, E. A., Bimendina, L. A. and Kudajbergenov, S. (1982). "Polymer complexes and catalysts", *Alma-Ata*, Nauka.

[3] Seleznev, V. A., Vainstein, E. F., Artemov, A. V. *et al.* (1978). *Abstract for the All-union conference on the mechanism of catalytic reactions*, Nauka, M. **1**, 115.

[4] Seleznev, V. A., Tjulenin, Yu. P., Vainstein, E. F. *et al.* (1983). "Kinetics and catalysis", Vol. XXIV, issue 5.

[5] Tishenko, A. I., Volfson, N. S. and Brodsky, M. C. (1971). *Petroleum Chemistry*, **11**(3), 422.

[6] Overberger, C. G. and Okamoto, G. (1972). *Macromolecules*, **5**, 363.

[7] Overberger, C. G. and Chen, C. M. (1971). *Biorg. Chem.*, **1**, 1.

[8] Topchieva, I. I. (1972). "Polymer catalysis", In: "Encyclopedia of polymers", M., **1**, 93.

[9] Emanuel, N. M., Denisov, E. T. and Maisus, Z. K. (1965). Chain reactions of hydrocarbons oxidation in the liquid phase, M., 6, Nauka.

[10] Savitsky, A. V. and Nelubin, V. N. (1975). *Progress in Chemistry*, **44**(2), 214.

[11] Flory, P. (1953). Principles of polymer chemistry, Ithaka, N.7, Cornell Univ. press.

[12] Vainstein, E. F. (1981). Study of the complex-formation of chain molecules and their specific features in diluted mediums. *Doctoral Thesis*, M., Institute of Chemical Physics, Academic of Sciences of the USSR.

[13] Landau, L. D. and Lifshitz, E. M. (1964). Statistical Physics, Nauka, M.

[14] Flory, P. (1971). Statistical mechanics of chain molecules, Mir, M.

[15] Volkenstein, M. V. (1959). Configurational statistics of polymer chains, M., Acad. of Sciences of the USSR.

[16] Klochkova, L. V. (1983). The effect of "the change in flexibility" and its influence on the process of weak complex-formation. *Candidate Thesis*, Int. of Chemical Physics, Academy of Sciences of the USSR.

[17] Desennes, P. (1982). Problems of scaling in the physics of polymers, M., Mir.

[18] Bloomfeld, L. A. (1974). Problems of biophysics, M., Nauka.