The Complexes of Macromolecules and Metal Nanoparticles: Pseudo-template Synthesis and Behavior

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Summary: Metal sols composed of metal nanoparticles (1 - 10 nm in diameter) protected with polymer molecules may be regarded as dispersions of polymer-metal complexes formed due to cooperative non-covalent (e.g., hydrophobic, coulombic) interaction of polymer chains with the surface of metal naoparticles. The sols are commonly prepared by reducing of metal ions in solutions of appropriate polymers.
The interactions between macromolecules and nanoparticles are reversible. In the case of long polymer chains and minute particles, the equilibrium constant of the reaction exponentially depends on the surface area of the particle. The probability of mutual "recognition" (complex formation) of growing particle and a macromolecule rapidly increases from practically zero to practically unity in narrow interval of the particle's diameters. The recognition is followed with the shadowing of the particles and the stop of their growths. Such kind of processes was termed "pseudo-template". In frame of the concept of pseudo-template processes can be estimated: (1) the conditions at which sol particles of desirable size can be prepared, (2) the influence of temperature, polymer concentration, nanoparticles size, and other conditions on the stability of polymer - particle complex having been prepared, and (3) the conditions at which stable sol does not exist and can not be prepared at all.
The interactions between metal nanoparticles and macromolecules are highly selective regard to the structure of polymer chains. The property can be effectively used for the control the size characteristics of metal nanoparticles (in course of their formation) and the stability of metal sols.
The selectivity provides high conversions in catalytic chemical modification reactions in which a macromolecule is the substrate and a component of the catalyst in the same time. As an example, the hydrolysis of lactame groups in monomer unites of poly(N-vinyl pyrrolidone) catalyzed with copper sols is discussed.

Keywords: catalyze; macromolecules; metal sols; molecular recognition

Introduction

The sols of metal nanoparticles protected with polymer molecules are commonly prepared by the reducing of metal ions in water or water-alcohol solutions of appropriate polymers. Besides other applications, the sols are known to be active and selective catalysts of various chemical reactions.[1,2] The activity and the selectivity of the catalysts are considerably dependent not only on the nature of the metal and the structure of protective polymer but also

on the size of the nanoparticles. For this reason, the control of the size of metal nanoparticles both in course of sol preparation and in course of application turns out very important.

Metal sols may be regarded as dispersions of micelles representing polymer-metal complexes formed due to cooperative non-covalent interaction between macromolecules and the surface of metal nanoparticles

$$\text{Macromolecule} + \text{Nanoparticle} \Leftrightarrow \text{Complex} \qquad\qquad (1)$$
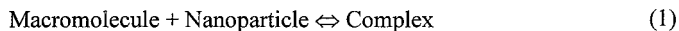
Polymer chains "envelope" (shield) metal nanoparticles thus lyophilizing and protecting them from aggregation (and from oxidation, if any). However, regardless of long history of the investigations of metal sols, the nature of the interactions and the structure of the polymer – metal complexes remain practically unexplored. It is supposed generally that hydrophobic interaction between a macromolecule and hydrophobic surface of metal particle plays an essential role in the shielding.[1] This point of view was supported a few years ago: the sign of the enthalpy and the entropy of the interaction between copper nanoparticles and poly(N-vinyl caprolactame) (PVC) in water medium was found to be positive.[3] On the other hand, it was reported recently that in the case of charged macromolecules, coulomb interaction between oppositely charged metal nanoparticle and polymer chain can play decisive role in stabilization of respective polymer - particle complex.[4]

The structure of sol particles is usually represented schematically as it is shown in Fig. 1.
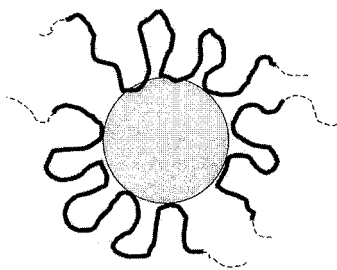

Fig. 1. Schematic representation of metal sol particle's structure (commonly used but unacceptable in the case of nanoparticles with a few nm in diameter).

Being more or less reasonable for relatively big particles, this scheme seems to be inappropriate for the particles the diameter of which is of about 1nm in magnitude. The "thickness" of common polymer chains is commensurable with the diameter of such a particle. In the scale of 1nm, the fragments of polymer chains are rigid thus making

impossible the formation of loops as in Fig 1. Regardless of fine points of the structure, it is evident that sol particles represent micelles. Recently Hirai and Yakura[5] published the results of accurate measurements of the thickness of polymer adsorbed layers in palladium sol particles protected with poly(N-vinyl pyrrolidone) **(PVP)**, and estimated the density of monomer unites in the layers.

On the Thermodynamic Stability of Polymer-Nanoparticle Complexes

As a rule, the reduction of metal ions in polymer solutions results in formation of metal nanoparticles with narrow size distribution and the mean size from 1 to less then 10 nm. The common point of view is that the shielding of growing metal nanoparticle with a macromolecule (i.e., the formation of polymer-particle complex) is followed with the growths stop.[1] In other words, the size distribution and mean size of the particles in resulting sol has to be defined by the dependence of the probability of the complex formation on the size of growing metal particle. Such kind of processes was termed "pseudo-template".[6,7] (In template processes, e.g., in template polymerization, after the formation of a complex between macromolecular template and growing specie, the specie continues its growth under template's control). The probability was assumed to be defined by thermodynamic stability of corresponding complex.[6,7] Papisov and Litmanovich[6,8] suggested that the interactions between very small particles and long macromolecules are similar to those between oligomers and polymers, and by this reason both can be treated using one and the same model of adsorption of small species on long polymer chain. In assumption that the nanoparticles are spheres with the diameter D, and the polymer is taken in large excess with regard to the nanoparticles, in equilibrium state

$$p_D = \frac{m_0 K_D}{1 + m_0 K_D}$$

(2)

where p_D is the fraction of particles included in the complex, m_0 is ground-mol fraction of polymer in reaction medium, and K_D is the equilibrium constant of the reaction (1) which is dependent on free energy ΔG_1 of polymer-particle interaction referred to a unit of particles surface as

$$K_D = exp \ (-\pi D^2 \Delta G_1 / kT)$$

(3)

The Eq. (2) can be rewritten as

$$K_D = K_1{}^{D^2}$$ (4)

where $K_1 = exp\,(-\pi \Delta G_1/kT)$ is referred to a unit of the surface.

At least three consequences of Eqs (2) – (4) seem to be very essential:[8]

1. At low concentrations of protective polymer and the diameter of nanoparticles from 1 to 10 nm, high stability of polymer – nanoparticle complexes can be provided with ΔG_1 values of order 10^{-4} J m^{-2} in magnitude. The values make up portions of per cent of specific surface energy values of common solids.

2. The stability of polymer – nanoparticle complexes must be strongly dependent on the size of the nanoparticles.

3. The interactions between macromolecules and nanoparticles may be very selective with regard to both the structure of macromolecules and the size of the particles.

The conclusions enumerated offer the opportunity to explain or to predict characteristic features of new phase formation processes taking place in polymer solutions.

Pseudo-template Synthesis of Metal Sols

The sols of non-protected metal nanoparticles cannot be obtained due to their instability. By this reason, in particular case of metal nanoparticles, reversible reaction (1) cannot be studied using classical methods. However, it was shown experimentally that the size of a particle at which its growth is terminated in course of the reduction of metal ions corresponds to that at which the complex of the particle and a macromolecule turns out sufficiently stable.[4,9] This is possible if the rate of polymer-particle complex formation is commensurable with (or higher than) the growth rate of free metal particles in course of the reduction of correspondent metal ions. In other words, the probability of the growth termination of a particle on a given step of the particle's growth is equal to the probability of mutual polymer - particle recognition p_D. The last is equal to the equilibrium portion of particles included in the complex (see Eq. (2)) on respective step.

Fig. 2 shows typical theoretical dependencies of p_D (i.e. that of the probability of growth termination) on the diameter of growing nanoparticle estimated using different values of K_1 and the value of m_0 corresponding to about 1% solutions of common polymers. For given value of K_1, the value of p_D is seen to increase very rapidly in certain narrow interval of the particle's size. This stands for rapid deceleration of the particle's growth in the same interval

up to practically full stop at $p(D) \approx 1$. As a consequence, the size distributions of sol particles formed in pseudo-template process have to be narrow. Almost all published experimental data concerning metal sols formed in polymer solutions confirm this conclusion. However, if the value of K_1 is changing in course of the reduction process, the final distribution may be wide or even bimodal. The formation of copper sol in the presence of polycation [poly(1,2-dimethyl-5-vinyl-pyridinium methylsulfate) (**PCat**)] may be taken as an example.[4] In this particular case, the change of the reaction medium (namely, the change in concentrations of copper and hydrogen ions) in course of sol formation is followed with the change of relative roles of hydrophobic and coulombic interactions in stabilization of polymer-particle complex thus resulting in respective change in K_1 value.
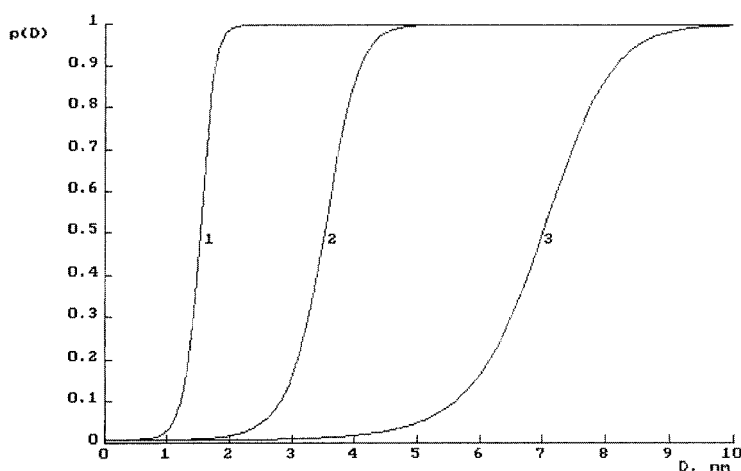

Fig. 2. Theoretical (Eq. (2)) dependencies of the probability of polymer-nanoparticle recognition (that of the probability of the nanoparticle's growth termination) on the diameter of the nanoparticle. K_1: 34 (1), 2.41 (2), and 1.18 (3). At 20°C the values of K_1 correspond to $\Delta G_1 \times 10^4$, J m^{-2}: -46.1 (1), -11.6 (2), and -2.2 (3). (c_0 corresponds to about 1% concentration of common polymers).

The mean size of metal particles in a sol formed by pseudo-template mechanism is determined with the position of the interval in which the value of $p(D)$ rapidly increases with the increase of growing particle's diameter. The position, in its tour, is defined with the values of K_1 (which depends on metal, polymer, reaction medium, and temperature) and polymer concentration. Numerous examples of the influence of the nature of metal, polymer, and the medium on the size of metal sol particles are collected in.[1] Experimental data concerning the

dependence of the size on polymer concentration and temperature were published in[5] and,[4,9,10] respectively.

The position of the interval and, then, the size of metal particles formed at certain conditions, on qualitative level characterize the stability of polymer-particle complex (or, what is the same, that of protective polymer shields on the surface of metal particles) at the conditions of metal ions reduction. The higher is the stability, the smaller particles are formed. Then, the influence of some condition (for example, that of the composition of dispersion medium, temperature, etc) on the stability of a given polymer-particle complex can be simply elucidated by the comparison of size characteristics of sols formed in respective conditions. This offers the opportunity to predict the behavior of respective metal sol if certain condition is to be changed after the sol having been prepared.
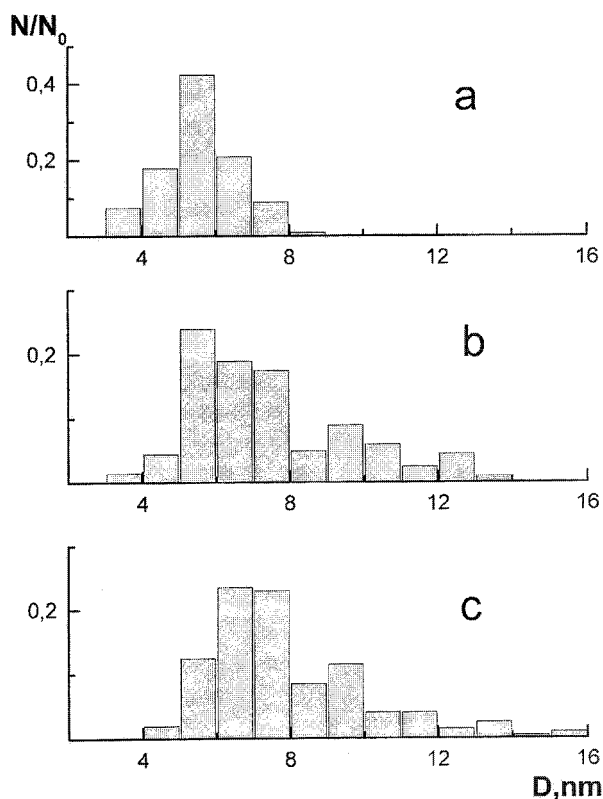

Fig. 3. The histograms of Cu sol particles obtained by the reduction of copper(II) ions with hydrazine borane at 6 (1) and 30°C (2). (3) – the histogram of the particles obtained at 6°C and exposed at 30°C (3 hours).Initial concentrations: $[Cu^{+2}]$=0.01 mole/l, $[N_2H_4.BH_3]$=0.03 mole/l, [PVP]=0.02 base-mole/l.

For example, Fig. 3a,c show that the size of copper particles in sols prepared in PVP solutions increases with the increase in temperature of sol synthesis indicating that the stability of respective polymer - particle complex decreases at heating. It is logical to prognosticate that in the sol having been prepared at low temperature, the fraction of less stable complex (i.e. that formed with the participation of smallest particles) should disappear after heating due to deshielding of the particles. Bigger particles formed due to their aggregation can be shielded anew. The data of Fig. 3b agree with this assumption. The change in some condition providing sharp falling in polymer – particle complex stability can be followed with rapid deshielding and aggregation (and oxidation, if any) of metal nanoparticles. Such behavior was observed after addition of low molecular salt to copper sol having been prepared in presence of PCat. Being stabilized with coulombic interactions, respective polymer-particle complex rapidly loses its stability with the increase in ionic strength of dispersion medium.[4]

Quantitative approach to the analysis of experimental data with the use of the equilibrium (1) is a matter of some difficulty by two reasons. The first is bound up with high instability of bare metal nanoparticles. The second is that very low interaction energy needed to provide polymer-nanoparticle complex stability cannot be measured with the use of common methods. However, the approximate value of ΔG_l can be estimated from the size of metal nanoparticles formed at given conditions in assumption that the mean size correspond to some definite value of $p(D)$. Taking into account narrow size distributions of metal particles formed in the processes under consideration, it may be assumed that the mean size D_{av} correspond to $p(D)=0.5$.[6,8] In this case
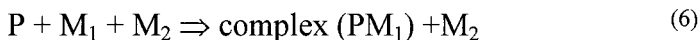
$$\Delta G_l = kT \ln m_0 / \pi D_{av}^2 \qquad (5)$$

The enthalpy (ΔH_l) and the entropy (ΔS_l) can be find from temperature dependence of ΔG_l as usual. The examples of respective estimations were given in.[3,9,10] In particular, it was found that, dependently on the structure of protective polymer, for copper nanoparticles in water medium the value of ΔH_l may be negative (PVP), positive (PVC)), or equal zero (PCat, at [Cu^{+2}] →0). The use of the values offers the opportunity to estimate: (1) the conditions at which sol particles of desirable size can be prepared, (2) the influence of temperature, polymer concentration, nanoparticles size, and other conditions on the stability of polymer-particle complex having been prepared, and (3) the conditions at which stable sol does not exist and can not be prepared at all. Estimated values of ΔH_l and ΔS_l allowed to predict the existence of limiting temperature $T_{lim} = \Delta H_l / \Delta S_l$ higher (as it is in the case of PVP) or lower (as it is in the case of PVC) of which correspondent sols are not stable at any size of copper

particles and, then, stable sols cannot be prepared. The prediction was experimentally proved in.[12] (Higher 60°C both ΔH_1 and ΔS_1 turn out positive and higher this temperature the sols can be prepared anew).
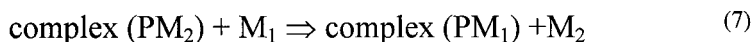
It is noteworthy that thermodynamic stability of polymer-particle complex is dependent on the particle's surface area (i.e. that on D^2) only in condition that polymer chain is able to shield the entire surface of the particle. If either the chain is too short or the particle is too big so that only a part of the surface area can be shielded with the chain, then the stability of correspondent complex is dependent on the chain's length. In this particular case, the higher is polymerization degree (d.p.) of the chain, the higher is the stability of the complex. At a given d.p., the probability of complex formation (that of the growth's stop) in the course of the growth of a particle increases up to the particle's size which corresponds to the limit of shielding ability of the chain. Further growth of the particle does not affect the value of the probability because the chain covers only the portion of particle's surface area corresponding to the d.p. of the chain. This is the reason why stable polymer-particle complex, and then, stable metal sol, cannot be formed in the process of reduction of given metal ions in presence of given polymer if the d.p. is lower than some "critical" value corresponding to given conditions (reaction medium, temperature) of the reduction process.[11] The change in the conditions results in respective change of "critical" d.p. value. For example, the stability of PVP-copper complex decreases with the increase of temperature. For this reason, in sols formed in presence of PVP the size of copper particles increases with the increase of temperature of reduction process. As soon as the shielding of bigger particle requires longer chain, "critical" d.p. of PVP which is needed to obtain stable sol increases with the increase of temperature, and at $T_{lim} \approx 50°C$ stable sol cannot be formed at any length of PVP chains.[12]

The Selectivity in Interactions between Metal Nanoparticles and Macromolecules. Additional Stabilization of Metal Sols

High selectivity with regard to the structure of polymer chains is a fundamental property of non-covalent interactions between nanoparticles and macromolecules.[8] The selectivity manifests itself either in recognition of optimal macromolecular partner by a nanoparticle in a mixture of polymers (Eq. (6)), or in substitution of protective polymer chain in the shield of sol particle with a chain of another polymer (Eq. (7)):

$$P + M_1 + M_2 \Rightarrow \text{complex (PM}_1) + M_2 \qquad (6)$$

$$complex\ (PM_2) + M_1 \Rightarrow complex\ (PM_1) + M_2 \qquad (7)$$

where P is the nanoparticle, M_1 and M_2 are macromolecules of different structure.

First information giving the evidence of the existence of the selectivity in polymer-nanoparticle interactions was published in.[13] Systematical investigations concerning recognition and substitution were carried out recently by O. Litmanovich, G. Marmusov, E. Eliseeva, A. Litmanovich, and I. Papisov (see below).

In the case of metal nanoparticles, the recognition can show its worth in course of metal sol formation taking place in presence of two polymers competing for complex-formation with growing particle. The competition should result in preferential shielding of growing particles with the polymer which is "stronger" as pseudo-template (complex-former). (In frame of the concept of pseudo-template processes, the "stronger" is a polymer as complex-former, the smaller sol particles are formed in result of the reduction of metal ions in presence of the polymer).

It was shown by the comparison of respective histograms that in water at $30^{\circ}C$ PVP is "weaker" pseudo-template than PVC (with regard to growing copper nanoparticles). As a result, in simultaneous presence of PVP and PVC the size of copper particles formed at $30^{\circ}C$ is similar to that formed in presence of PVC. In contrary, at lower temperature $(6-10^{\circ}C)$ the role of "stronger" pseudo-template plays PVP (due to opposite signs of complex-formation enthalpy, the "force" of PVC and PVP oppositely change with variation of temperature). This indicates that in simultaneous presence of two pseudo-templates the formation of metal sol is controlled by the "strongest" one.

As mentioned above, the "force" of polymeric pseudo-templates might be dependent on conditions. For example, in the processes of copper sol synthesis the "force" of PVP insignificantly depends on ionic strength of the reaction medium. In contrary, the "force" of PCat rapidly decreases with the increase in concentration of low molecular salt. At $20^{\circ}C$ and in the absence of NaCl the "force" of PVP and PCat is commensurable as soon as the sizes of copper particles formed in presence of each of the polymers are similar. When the formation of copper sol takes place in presence of the mixture of both polymers, then, with the increase in concentration of NaCl, the role of "stronger" pseudo-template progressively pass to PVP, see Fig. 4.

In accordance with relative force of polymers as complex-formers, the addition of the "stronger" polymer to a sol stabilized by "weaker" one results in substitution of the latter by the former in accordance with Eq.(7). The change of protective shield of metal particles is

followed with additional stabilization of the sol to aggregation and oxidation of metal particles. Such kind of effects was observed both in PVP+PVC+Cu and PVP+PCat+Cu systems. Moreover, in presence of two polymers, respective sols keep their stability in relatively wide intervals of temperature (both systems) and ionic strength (second system) due to reversible substitution of one polymer to another when the conditions are varied. Such sols can be prepared either by the reduction of copper ions in the presence of both polymers or by the addition of one polymer to the sol obtained in presence of the another.
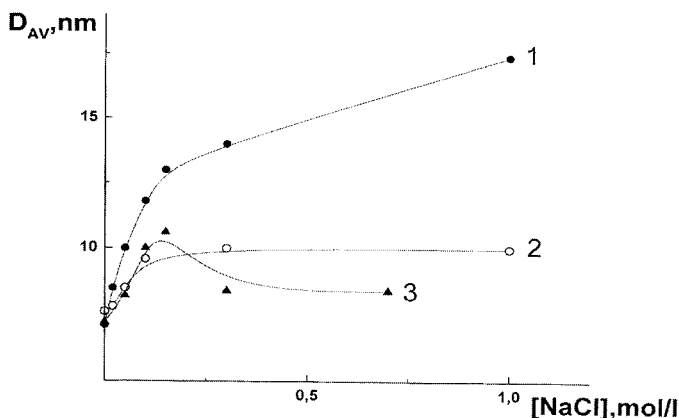

Fig. 4. The dependencies of mean square average diameter of copper particles on NaCl concentration. The sols were prepared at 20°C in presence of: PCat (1), PVP (2), and the mixture of PVP and PCat (3). Total polymer concentration 0.02 base-mole/l in each system, other conditions as in Fig. 3.

Experimental data are in good agreement with the results of theoretical analysis of selectivity phenomena in polymer-nanoparticle interactions published earlier.[8] While being all uniform with regard to the size, metal nanoparticles have a choice between macromolecules of two (or more) polymers of different structure, M_1 and M_2, then the degree of selection (recognition) may be characterized by the ratio N_1/N_2 where N_1 and N_2 are numbers of particles bound with M_1 and M_2, respectively. The recognition in such a system may be spoken about if the particles are in deficiency with regard to each of the polymers (otherwise, after saturation of the "strongest" polymer complex-former, the particles will bind "weaker" one). Assuming that each polymer is in large excess

$$N_1/N_2 = (c_1/c_2)\Psi \tag{8}$$

where c_1 and c_2 are concentrations of corresponding polymers, and

$$\Psi = (K_{1(1)} / K_{1(2)})^{D^2} = \exp[-\pi D^2 (\Delta G_{1(1)} - \Delta G_{1(2)}) / kT)] \qquad (9)$$

Ψ was termed "the factor of recognition" by the analogy with selective interpolymer interactions.[14]

It follows from the Eqs (8) and (9) that the preference in selection must be given to the polymer for which the value K_1 is higher. The selectivity increases rapidly with the increase both in the size of particles and the difference in interaction free energies $\Delta G_{1(1)}$ - $\Delta G_{1(2)}$ of the nanoparticles with macromolecules M_1 and M_2, respectively. In the case of relatively big nanoparticles, the selection may turn out remarkable even at very small value of $\Delta\Delta G$ = $(\Delta G_{1(1)}$ - $\Delta G_{1(2)})$.

The values of Ψ estimated for some of the systems studied are as follows (for particles with 10 nm in diameter).

$\Psi_{PVP/PVC}$: $\cong 10^{-3}$ at 30°C (perfect recognition of PVC)

$\cong 10^{-4}$ at 6°C (perfect recognition of PVP).

$\Psi_{PVP/Pcat}$: $\cong 10^{-9}$ at 30°C and [NaCl]=0 (perfect recognition of PCat),

$\cong 10^{-1}$ at 20°C and [NaCl]=0 (slight recognition of PCat),

$\cong 10^{-3}$ at the same temperature and [NaCl]=1 mole/l (perfect

recognition of PVP).

It is evident that the phenomenon of high selectivity of the interactions between nanoparticles and polymers can be effectively used for the control both the size characteristics of metal nanoparticles (in course of their formation) and the stability of metal sols (in course of their application).

The Features of Reactions Proceeding in Protective Polymer Chains and Catalyzed with Metal Sol Particles

Polymer protected metal sols are known to be active and selective catalysts of various chemical reactions.[1,2] For example, Hirai and co. used copper sols protected with PVP for selective hydration of acrylonitrile to produce acrylamide.[15,16] It was shown recently that lactame circles in monomer unites of PVP macromolecules themselves are undergoing hydrolysis in the sols mentioned:[17]
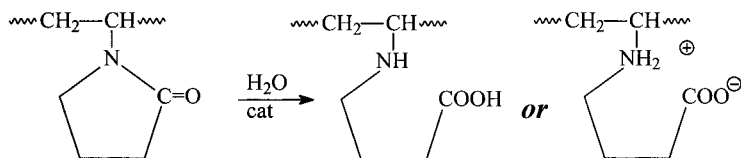
The conversion of the circles to amino acid groups reaches up to 50% or even more at temperatures from 5 to 30°C regardless of high stability of the circles to hydrolysis in common conditions.

The reaction was studied in details by O. Litmanovich, A. Litmanovich, G. Marmusov, E. Eliseeva, and I. Papisov using the sols in which only a few per cent of PVP chains present in reaction system were bound with copper nanoparticles (diameter 3 – 7 nm in diameter); other chains (more than 95%) were free. The conversion was measured by titration of carboxylic groups in supernatant (the centrifugation of sol samples was used if necessary). In a given condition, after certain induction period, the accumulation of hydrolyzed lactame groups in the supernatant was observed, Fig. 5. The longer are polymer chains, the higher is the induction period. On reaching certain limit conversion, the destabilization of the sol was occurred. It was mentioned above that short-chain PVP is not able bind copper particles with formation of more or less stable polymer – particle complex. It is well seen from comparison of dependencies 1 and 2 on Fig 7 that low molecular PVP introduced in the reaction system (either on the step of sol synthesis or after its formation) does not participate in the hydrolysis.
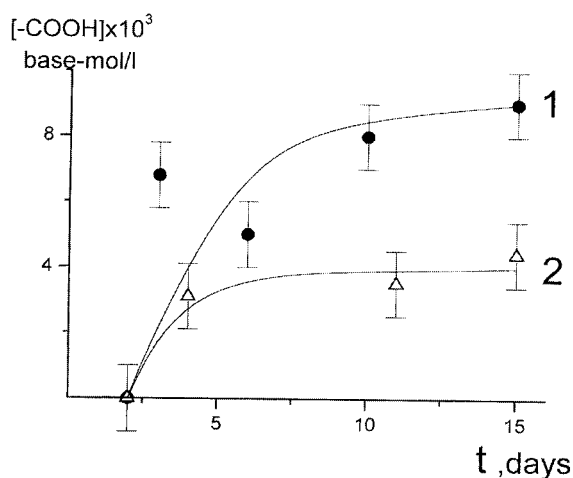

Fig. 5. The kinetics of the accumulation of hydrolyzed monomer unites of PVP in copper sols prepared in solutions of PVP: with M.W. 60,000 (0.02 base-mol/l) (1) and the mixture of polymers with M.W. 60,000 and 1700 (0.01 base-mole/l each) (2). 20°C, copper particles with D_{av}=7.2±0.5 nm.

This indicates that only the macromolecules formed protective shield around copper nanoparticles can participate in the reaction. Therefore, the appearance of hydrolyzed PVP

chains in supernatant and high overall conversion are the consequences of the substitution of hydrolyzed macromolecules in protective shields of copper nanoparticles with free non hydrolyzed (or less hydrolyzed, on late step of the reaction) polymer chains. The reason of the substitution seems to be the decrease in the polymer-particle complex stability with the increase in the degree of the hydrolysis of polymer chains. So to say, polymer chains are "pulled through" macromolecular shields of metal nanoparticles thus providing the participation of all or almost all chains present in reaction system in the hydrolysis. This suggestion is supported with the data concerning the existence of induction period and destabilization of copper sol after the limit conversion having been reached. It is noteworthy that the destabilization does not occur in presence of PCat. At $20^{o}C$ the "force" of this complex-former is commensurable with that of PVP (this follows from the comparison of the size distributions of copper particles formed in presence of each of the polymers as mentioned). By this reason, in simultaneous presence of PVP and PCat in reaction system, approximately a half of copper nanoparticles is bound with the latter polymer and, hence, does not participate in the catalysis resulting in the lowering of the reaction rate. As the "force" of PVP decreases with the increase in conversion, PCat progressively substitutes former polymer in protective shields. In course of the reaction, the portion of PCat-protected metal nanoparticles turns step by step increased thus keeping the sol stable after completion of the hydrolysis.

Therefore, high selectivity of polymer-particle interactions with regard to the structure of polymer molecules can provide high conversions in catalytic chemical modification reactions in which a macromolecule is the substrate and one of the components of the catalyst in the same time.

Acknowledgment

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