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Heterogeneous Catalytic Initiation by Cu^0 Colloidal Particles of Water-Dispersion Polymerization

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Introduction. It is known that the strongest adhesion between the polymer chains and inorganic dispersed substrates can be achieved if the macromolecules are covalently bound to the surface.[1,2] One of the most promising approaches of obtaining polymer grafted to filler surface is utilization for polymerization initiation of radical-generating fragments immobilized on the surface. Polymerization initiated by peroxides (including surface-active oligoperoxides (OP)) immobilized on the surface of dispersed mineral fillers such as SiO_2, TiO_2, and other oxides is a prospective method for their tailored modification as well as for obtaining filled composites.[3−5] The experimental data described in previous papers[3,4] indicate significant decrease of activation energy of homolysis of ditertiary peroxide fragments as a result of their immobilization on a dispersed solid surface of these fillers. Homolysis of peroxide fragments localized on the filler surface at 333−353 K results in formation of free radicals initiating the polymerization. Moreover, it is known that free radicals can be formed by such peroxidic groups as a result of transfer reactions on them.[6,7] Ditertiary peroxidic groups immobilized on the surface of colloidal particles of copper or ferrous oxide obtained by the method of homogeneous nucleation in the presence of OP can participate in radical reactions during water-dispersion polymerization and provide polymer grafting onto a particle surface at 298 K.[8]

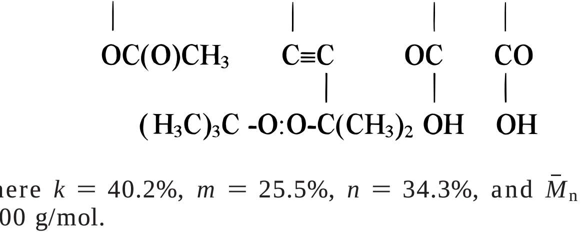
The method proposed in our previous works[8,9] allows to combine the stage of obtaining the colloidal particles of copper, nickel, silver, and ferrous oxide with the stage of their surface modification by OPs which are sorbed irreversibly. Copper particles formed by this method can be of spheric or octaedric shape depending on whether $Cu(OH)_2$ or Cu_2O is an intermediate product during reduction. Hydrophobic particles obtained by this method are reliably protected from oxidation and possess the necessary affinity to different polymeric matrices. The presence of reactive ditertiary peroxidic fragments on their surface results in their ability to form free radicals and participate in elementary stages of low-temperature radical polymerization.

We have noticed the phenomenon of catalysis of free radical formation by octaedric Cu^0 particles obtained by the above-mentioned method during investigation of cold (303 K) water-dispersion polymerization in alkaline media in the presence of modified or nonmodified copper particles. The polymerization with copper particle participation occurs even in the case when the peroxide fragments in the adsorption shell or other radical initiators in investigated systems are absent. A similar phenomenon of polymerization of methyl methacrylate in acidic water medium in the presence of copper and nickel particles was observed and very briefly described by other authors.[10]

The interrelation between the surface characteristics of colloidal copper particles and kinetic parameters of the process of "heterogeneous catalytic initiation" of water-dispersion polymerization in study is a matter of discussion in the present communication.

Experimental Section. The colloidal particles of zerovalent copper were obtained by chemical reduction of a complex of Cu^{2+} cation with potassium salt of citric acid with formaldehyde as reducing agent in alkaline medium (12% solution of caustic potash was used for obtaining alkaline water medium) at 298 K; then the powder was separated from reaction mixture and carefully washed by distilled water and dried until constant weight under vacuum. Metal particles containing oligoperoxide shell were obtained in the presence of surface-active oligoperoxides in solution being reduced.[9] The contents of copper oxides and Cu^0 in metal polymeric particles were determined by the method of added standards using an X-ray structure analysis with a diffractometer DRON-30 (Cu Kα radiation). The content of zerovalent copper was 99.5 ± 0.1%. The particle size was determined using method of scanning electronic microscopy with further statistical treatment of micrographs. The length of the octahedral basis edge was taken for calculations of surface area of octahedral copper particles. The content of OP sorbed on particle surface as well as peroxidic fragment content in a shell of particles was determined via the thermal decomposition of peroxide containing CCPs at 483 K under argon, followed by gas chromatographic analysis of the decomposition final products.[11] The CCP samples were previously treated with solvent in which OPs are solving. The average deviation between contents of OP on a copper particle surface determined using the above-mentioned technique and elemental analysis is of 3−5%, which does not exceed the systematic error of both methods. Copper colloidal particles were extracted after water-dispersion polymerization of styrene, washed previously by distilled water and then by organic solvent from polymer, and dried under vacuum until constant weight. Such copper colloidal particles contain 0.3% of grafted polystyrene. Its content was determined by elemental analysis. This powder was used for the secondary initiation.

Surface-active oligoperoxidic modifier (OP) of copper particle surface had the following structure:



$$-[CH_2-\underset{\underset{\displaystyle OC(O)CH_3}{|}}{CH}]_k-[CH_2-\underset{\underset{\underset{\underset{\displaystyle (H_3C)_3C-O{:}O-C(CH_3)_2}{|}}{C\equiv C}}{|}}{CH}]_m-[\underset{\underset{\underset{\underset{\displaystyle OH}{|}}{OC}}{|}}{CH}-\underset{\underset{\underset{\underset{\displaystyle OH}{|}}{CO}}{|}}{CH}]_n-$$

where $k = 40.2\%$, $m = 25.5\%$, $n = 34.3\%$, and $\bar{M}_n = 4500$ g/mol.

Carbon-chain OP on the basis of vinyl acetate (VA), maleic anhydride (MA), and 2-*tert*-butylperoxy-2-methyl-5- hexen-3-yne (VEP) was obtained by polymerization at 333 K in ethyl acetate using azobis(isobutyronitrile) (AIBN) as initiator. Copolymerization was carried out both in calibrated dilatometers and in a three-necked

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glass reactor equipped with stirrer and condenser. Polymerization process kinetics was studied by dilatometric and gravimetric methods. The polymerization process was carried out until approximately 50% conversion. At this conversion a sufficient amount of the most reactive monomer (VEP), which is simultaneously the chain length regulator, remains in the reaction system. As is shown in our previous works, such synthesis provides the relative compositional and molecular weight homogeneity of OPs.[6,7,12] OP was purified by reprecipitation and dried until constant weight under vacuum.

The MA unit content in OP was determined using a potentiometric titration of carboxylic groups; the VA unit content was determined by the alkaline hydrolysis method. The peroxidic fragment content (VEP units) was determined using the above-mentioned technique. The results of analysis reveal the predominant linear structure of cooligomer.

The processes of water-dispersion polymerization in the presence of CCPs (no conventional radical initiator for polymerization initiation was used) were carried out in water alkaline media at 303 K. The monomer-to-water phase ratio was 1:3 (v/v). The water phase pH was 10. Polymerization kinetics was studied by both dilatometric methods in described in the literature:[13] collapsible emulsion dilatometers with magnetic stirrer and the gravimetric method in a three-necked vessel for additional checking. The polymerization rate was determined from the section of the kinetic curves with the stationary rate when the amount of growing polymer–monomer particles (PMP) was constant. The overall initiation rates were determined from the induction periods observed in the presence of different amounts of oil-soluble inhibitor diphenylverdazyl (DPV).

The monomers—styrene (St), methyl methacrylate (MMA), vinyl acetate (VA), and *N*-vinylpyrrolidone (N-VP)—were purified by triple vacuum distillation, and their constants were found to be in agreement with the literature data.[14] MA was purified by vacuum sublimation, and after purification, its melting point was 325 K (literature datum:[15] 325.9 K). The peroxidic monomer VEP was purified by vacuum distillation and had the following characteristics: $d_4^{20} = 0.867$; $n_D^{20} = 1.4480$; active oxygen content = 8.79% (calcd 8.75%). AIBN was purified by recrystallization from ethanol. The solvent was used without further purification.

Sodium pentadecyl sulfonate (SPS) was used as emulsifier.

The water phase for emulsion polymerization was boiled for 4 h in the presence of ammonium bicarbonate, after which the pH reached 10, and then it was carefully purged with argon before charge. No additional alkaline agent was used. After completion of water-dispersion polymerization in the presence of CCPs the pH of reaction medium was 9.5–9.7.

Viscosity-average molecular weights (M_η) of polystyrene were determined from intrinsic viscosities of their solutions using the values $K = 2.7 \times 10^{-4}$ and $\alpha = 0.66$ (benzene, 298 K).[16] The polymer–monomer particle size (r_{PMP}) was determined by a light-scattering method at wavelengths from 420 to 620 nm.

The sorption of the 2,2′,6,6′-tetramethyl-1-piperidinyloxy (TEMPO) stable radicals on the surface of peroxide-containing and unmodified copper particles was studied using the EPR technique in situ (spectrometer AE 4700, "Micropribor", Lviv, Ukraine). The concentration of TEMPO in solution was detected as a function of time starting from the moment when the sample of CCP was dispersed in the solution. The experiments were performed at the temperature of 303 K, using xylene as a solvent in the weight ratio of 0.3–0.4:1 to the solid phase.

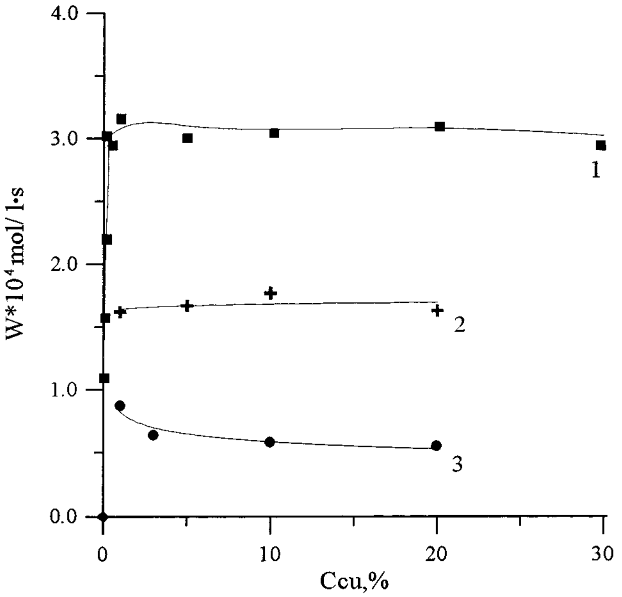


Figure 1. Dependence of St emulsion polymerization rate upon CCP concentration (1, copper particles obtained without OP; 2, 3, copper particles obtained in the presence of OP; SPS concentration in water solution: 1, 2, 0.5%; 3, 0.1%).

Results and Discussion. It is evident from the plots presented in Figure 1 that the water-dispersion polymerization of styrene occurs in the presence of CCPs obtained by the above-mentioned method. The polymerization rate depends on the concentrations of CCPs, the level of surface modification of CCPs, and the concentration of SPS emulsifier. The dependences of the kinetic parameters of emulsion polymerization upon the concentrations of CCPs as well as upon the level of sorption modification of their surface suggest the participation of CCPs in the processes of free radical formation. The decrease of the overall uncovered surface of copper particles due to their adsorption modification by the surface-active OP molecules results in lowering the process rate (Table 1). These facts can be explained from the assumption of the catalytic participation of the CCP uncovered surface in free radical formation, as a result of the activation of monomer molecules sorbed on their active sites, in accordance with the classical sorption–desorption scheme (Scheme 1).[17]

We determined the value of the apparent activation energy of the polymerization from kinetic investigations of the process in the temperature range 293–313 K. It is equal to 30.6 kJ/mol. This value is typical for catalytic processes and agrees with known literature data[18] (Figure 2).

The existence of active sorptive sites on copper particle surface is proved by the EPR investigations of TEMPO stable radical sorption on the CCP surface from the solution. The process of TEMPO sorption on sites of uncovered or occupied by OP molecules copper particle surface is accompanied by disappearance of the signal characterizing the stable radical in the EPR spectrum. The values of particle surface area per oligoperoxide chain (S_{surf}) suggest the conformational

Table 1. Dependence of Rate (*W*) of St Emulsion Polymerization Initiated by Colloidal Copper upon the Monomer Nature and Method of Obtaining Copper Powder

	$W \times 10^3$ (%/s)			
means of obtaining copper powder	St	MMA	VA	N-VP
conventional technique without OP	9.5	4.4	1.4	do not proceed
precipitated and washed after polymerization	8.8			
conventional technique in the presence of OP	5.5			
with OP after thermal decomposition at 473 K	6.3			
conventional technique in the presence of OP[a]	0.33	0.25	0.28	

[a] Polymerization processes were carried out in ethanol at 343 K.

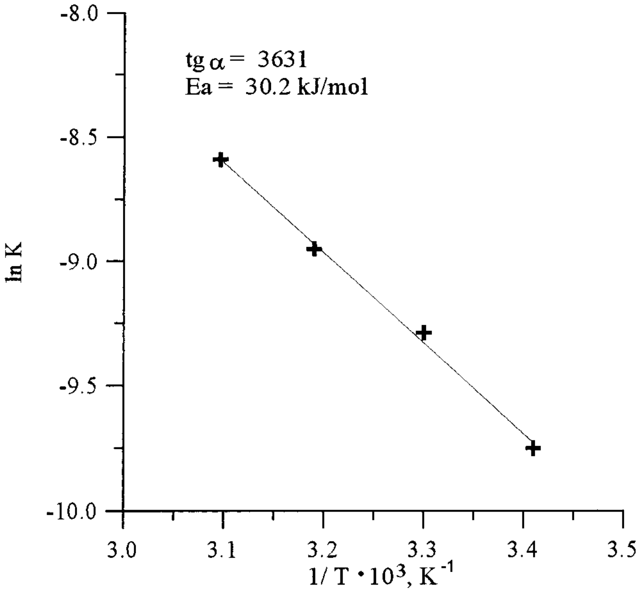
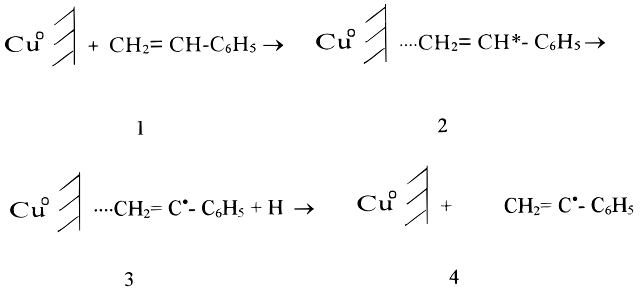


Figure 2. Dependence of logarithm of St emulsion polymerization rate constant vs 1/*T*.

Scheme 1. Assumed Scheme of Radical Formation on the Copper Particle Surface



structure for the sorbed molecules that is intermediate to a completely extended conformation and one that is flat on the surface (Table 2). Therefore, there are uncovered parts on the particle surface accessible for sorption of radicals or monomer molecules. It is evident from the data shown in Figure 3 that TEMPO stable radicals are sorbed (as a result of interaction with free electrons of copper particles) on this part of surface in a trice. But after instantaneous sorption of TEMPO stable radicals (A_R) on the surface of nonmodified CCPs (or CCPs thermotreated in toluene under argon at 473 K for full decomposition of peroxidic fragments), the TEMPO concentration in solution remains constant. It is evident from the data characterizing TEMPO concentration decrease in solution as a function of time as a result of its sorption on modified CCP surface (Figure 4, Table 2) that TEMPO sorption on the particle surface occupied by OP molecules occurs slowly. Lower rates of interaction of TEMPO stable radicals can be caused by slow radical formation by ditertiary peroxidic fragments immobilized on CCP surface at 303 K. The kinetic plots of Figure 4 correspond, in our opinion, to the recombination of the stable radicals with the radicals formed by peroxidic fragments of the modifying shell. The increase of the immobilized peroxidic fragment concentration in investigated systems ($[\mathrm{VEP}]_{\mathrm{sol}}$) results in the increase of initiation rates determined using this technique (Table 2). This proves the interaction of TEMPO with the radicals formed by modifying the shell. It is evident also from Table 2 that the initiation rates which are interrelated to the amount of radicals formed by peroxidic fragments and calculated from TEMPO concentration decrease in solution from the kinetic curves of Figure 4 is not sufficient (as is known[19]) for realization of water-dispersive St polymerization with the observed rates. Proceeding from the assumption that the amount of TEMPO radicals sorbed by the active sites of the uncovered surface of copper particles is equal to the amount of radicals formed from monomer molecules as a result of one sorption−desorption act, we suggest that just these radicals determine the initiation and overall polymerization rates. Thus, we have suggested also that the initiation rates found from the investigations of induction periods of polymerization in the presence of inhibitior are detemined by the amount of these radicals produced as a result of catalysis by uncovered surface of CCPs. Exactly these initiation rates allow to provide the formation of a sufficient amount of growing PMPs and consequently determine observed polymerization rates (Table 2). The experimentally observed values of rates of initiation by the uncovered CCP surface and total polymerization rates correlate satisfactorily with the values of specific areas of copper particles (Ssp).

The impossibility of polymer formation in the absence of CCPs as well as in the presence of solution of copper acetate, CuO, Ag, Fe_2O_3, and Fe_3O_4 colloidal particles and other mineral fillers under the above-mentioned conditions of polymerization witnesses in favor of the proposed heterogeneous catalytic mechanism of the radical initiation of latex polymerization by particles zerovalent copper. The possibility of reiterative initiation of latex polymerization by CCPs extracted after the previous polymerization process substantiates the sorption−desorption mechanism of heterogeneous catalysis of free radical formation by active sites on their surface. At the same time, a small decrease of polymerization rate in the case of initiation by the secondary copper particles is obviously caused by gradual deactivation of CCP active sites due to the sorption of polystyrene molecules on them (Table 1). The content of irreversibly sorbed polystyrene on the surface of the secondary CCPs was about 0.3%. The slight change in the rate of polymerization initiated by OP-modified copper particles after thermal decomposition of the peroxidic fragments

Table 2. Surface Characteristics and Initiative Activity of Copper Colloidal Particles Modified by OP

	characteristic of OP sorption (A_{OP}) and peroxidic shell formed on copper colloidal particles surface					characteristic of TEMPO sorption (A_R) on particle surface		characteristic of termination of TEMPO radical by peroxidic shell		kinetic parameters of polymerization process	
	Ssp of particles (m^2/g)	$A_{OP} \times 10^7$ (mol/m^2)	S_{surf} per OP chain (Å^2)	[VEP] × 10^6 (mol/m^2)	S_{surf} per VEP link (Å^2)	$A_R \times 10^7$ (mol/m^2)	S_{surf} per TEMPO radical (Å^2)	$[VEP]_{sol} \times 10^3$ (mol/L_{solut})	$W_{in}{}^a \times 10^{10}$ (mol/L·s)	$W_{in}{}^b \times 10^7$ (mol/L·s)	$W_{pol} \times 10^4$ (mol/L·s)
1	0.51	0	0	0	0					4.7	3.3
2	0.48	7.0	238	5.0	33	4.8	345	6.3	4.3	2.2	2.0
3	0.47	8.0	208	5.7	29	5.2	321	6.0	3.6	2.0	1.8
4	0.76	6.0	276	4.3	38	3.7	451	7.0	5.6	3.5	2.6
5	0.85	5.9	286	4.2	40	3.8	438	8.5	8.3	3.6	2.7

[a] The rate of initiation by peroxidic fragments of OP calculated from data of EPR analysis. [b] The overall initiation rate determined from the induction periods of polymerization in the presence of inhibitor

Table 3. Characteristics of Styrene Emulsion Polymerization Initiated by Nonmodified and Modified CCP

	SPS concn (% per water phase)	CCP concn (% per monomer)	$W_{pol} \times 10^3$, %/s	polyst grafting, mg/g_{CCP}	$M_\eta \times 10^{-6}$	r_{PMP}, μm	PMP no. × 10^{-17}, L^{-1}
1[a]	0	10	0.19	3.8			
2[a]	0.1	10	2.5	2.6	0.26	89	0.45
3[a]	0.25	10	6.4	2.2	0.34	66	1.39
4[a]	0.5	10	9.5	2.0	0.77	37	7.94
5[a]	1	10	17.5	1.7	1.12	36	8.32
6[b]	0.5	1	5.0	3.5	3.4	55	2.15
7[b]	0.5	5	5.2	4.3	3.1	50	2.92
8[b]	0.5	10	5.5	5.8	3.0	51	2.80
9[b]	0.5	20	5.1	6.2	2.7	52	2.53
10[b]	0.1	1	2.7	3.9	0.38	92	0.40
11[b]	0.1	10	1.8	7.2	0.3	99	0.32

[a] Nonmodified CCP. [b] CCP modified by OP.

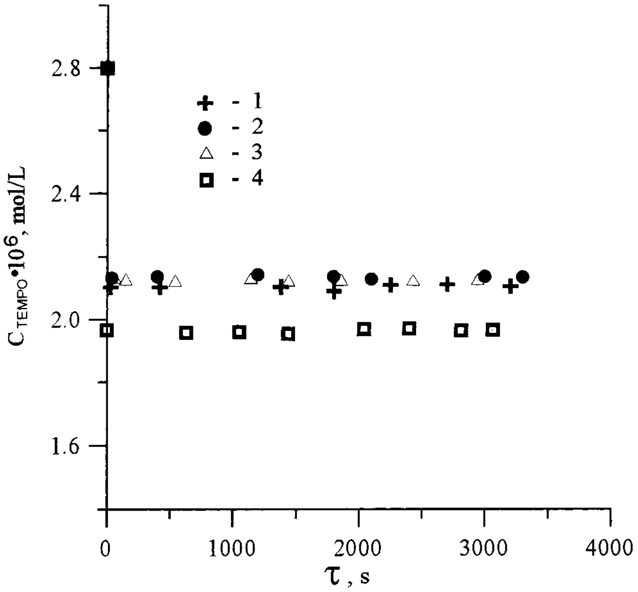


Figure 3. Dependence of TEMPO concentration in solution containing CCP modified by OP and thermotreated at 473 K on time: 1, sample 2; 2, sample 3; 3, sample 4; 4, sample 5 (see Table 2).

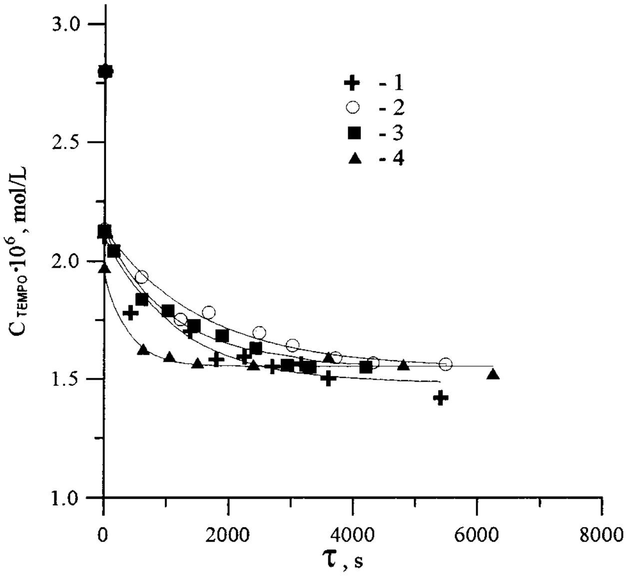


Figure 4. Dependence of TEMPO concentration in solution containing CCP modified by OP on time: 1, sample 2; 2, sample 3; 3, sample 4; 4, sample 5 (see Table 2).

of polymeric shell proves that the initiation of the polymerization process occurs mainly via the radicals formed as a result of heterogeneous catalysis by the uncovered surface of copper particles. It can also be concluded that the contribution of radicals formed by peroxidic fragments of the modifying shell of CCPs into total initiation process is too small. However, their participation in reactions of growing chain transfer with formation of macroradicals fixed on the CCP surface provides a noticeable increase of grafting (Table 3). In our opinion, it is caused mainly by the recombination of macroradicals produced by sorbed OP molecules with growing polystyrene chains. The increase of polymer grafting with the decrease of emulsifier SPS concentration witnesses in favor of this assumption. The probability of chain transfer reactions and grafting enhances with the increase of the initiation rates.

All these facts as well as complete suppression of radical processes of the polymerization in the presence of CCPs by the inhibitors (such as oxygen or verdasyl) under such conditions confirm the radical nature of processes that occurred. The dependence of polymerization rate on overall area of particle surface was

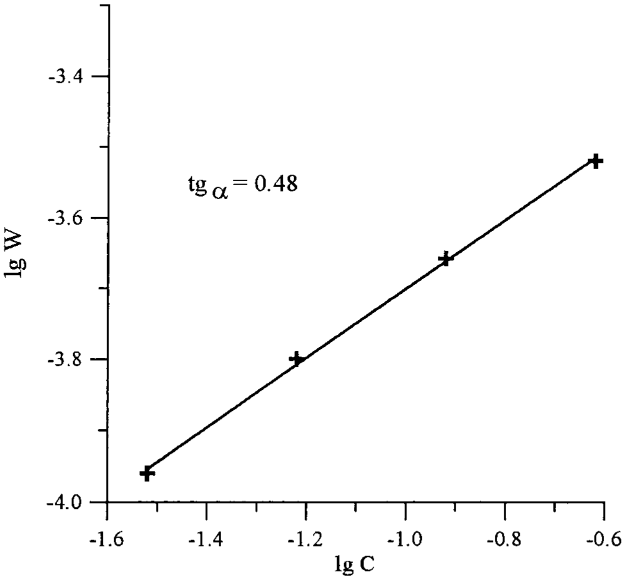


Figure 5. Dependence of St emulsion polymerization rate upon CCP concentration in logarithmic coordinates.

observed only at such CCP concentrations when the concentration of growing PMPs did not attain a constant value yet. The linear dependence of the polymerization rate upon the square root of the mass concentration of CCPs (which is directly proportional to their surface area) was established (Figure 5). Such a dependence in this range of CCP concentrations can be explained by mixed character of water-dispersion polymerization which consists of realization of elementary stages of water-dispersion polymerization both in adsorptive emulsifier layers saturated by styrene in the vicinity of the copper particle surface and in PMPs. The presence of adsorptive emulsifier layers saturated by styrene and formation of prime oil-soluble styrene radicals by CCP surface promote the localization of the initiation process in this zone. Growing polystyrene radicals attaining the definite length form PMPs which are stabilized by the SPS emulsifier molecules. The following stages of chain propagation and termination occur in PMPs. On reaching the PMP stationary concentration which corresponds to given concentration of emulsifier and CCPs, the polymerization rate no longer depends on overall particle surface. The dependences of particle number and size as well as polystyrene molecular weights on emulsifier concentration confirm this (Table 3). Such topochemistry of water-dispersion polymerization is peculiar for water-dispersion polymerization initiated by oil-soluble initiators and explains the existence of rate vs initiator square root dependence according to Medvedev−Sheinker additions for Smith−Ewart theory.[19,20] It is described by the equation proposed in ref 19:

$$R_p \propto [I]^{1/2}$$

The presence of SPS emulsifier is not a prerequisite for realizing the heterogeneous catalytic initiation mechanism (Table 3) but only facilitates the formation of the necessary amount of PMPs for latex polymerization and stabilization of monomer emulsion and latex. It is also possible that it promotes the desorption and further stabilization of growing polystyrene radicals. As shown in Figure 1 and Table 3, the decrease of SPS concentration leads to lowering the polymerization process rates. The features of the emulsion polymerization topochemistry related with the partial transfer of the polymerization process from PMPs formed with SPS participation to monomer drops sorbed on the copper particle surface are the most likely explanation for this.[21] The realization of the latex process polymerization initiated from colloidal particle surface in nonaqueous media (Table 1) (but with lower rates) as well as in the absence of SPS emulsifier points to that. The dependences of both the polymerization rates and final conversions upon the monomer nature, which determines their different solubility in water (Table 1), indicate the existence of different zones of polymerization: PMPs, adsorptive layers in vinicity of colloidal particles surface and monomer solution. The existence of these zones is explained by the different polarity of the growing radicals and determines the overall process rate.

Conclusions. It is concluded that the described phenomenon of heterogeneous catalytic initiation of the latex polymerization is of a great practical value relevant to the possibility of obtaining stable latexes including latexes filled during polymerization in technologically available conditions. At the same time the extremely high catalytic activity of the CCP surface not only provides the significant rates of free radical formation and polymerization as a result of heterogeneous catalysis but also greatly promotes the decomposition and/or chain transfer reactions with the participation of peroxidic fragments of the adsorption shell. This may be of a great interest for tailored modification of colloidal particle surface by grafting.

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