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Low-Temperature Surface-Active Complex-Radical Oligodert.Alkylperoxidic Initiators

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Summary: Carbon-chain functional surface-active oligoperoxides (FSAP) with ditertiary peroxidic, carboxyl or hydroxyl groups form stable oligoperoxidic metal complexes (OMC) through their interaction with transition metal salts in organic solutions. The mole fraction and formation constants of OMC are interrelated with the microstructures of FSAP, first of all, with the disposition of complex forming groups. Increasing the set of FSAP conformational structures promotes the enhancement of the local concentrations of reactants in the reaction zone during complex formation, thereby increasing the probability that the reaction will proceed. The kinetic and thermodynamic characteristics of the decomposition of peroxide fragments of FSAP in the aqueous medium providing the formation of controlled amount of free radicals, thereby the initiation of emulsion polymerization processes were investigated. The realization of the process of decomposition of – O:O – bonds as a result of homolytic dissociation or/and Red-Ox reactions depending media polarity and OMC nature were assumed.

Introduction

FSAP with ditertiary peroxidic fragments are of great practical interest as high temperature radical initiators with multiple centers[1-3]. However, the temperature range of application of such substances can be greatly widened by decreasing activation energy of the homolysis of peroxidic groups. Effective decrease of the activation energy of decomposition of peroxidic derivatives can be reached by creating RedOx systems. It is known[4] that the stage of intermediate peroxide-containing Me^{n+} complex formation precedes the stage of mono-electronic transfer. But the creation of initiating RedOx systems with ditertiary alkyl peroxides, which produce free radicals in temperature range of 273 - 298K, is impossible due to the stereochemical hindrances to complex formation. At the same time we have shown[3, 5] the possibility of inclusion of ditertiary peroxidic fragments of FSAP into the coordinate sphere of transition metal cations as a result of the formation of complexes with FSAP functional groups. The experimental data described in our

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previous article[5] confirm the possibility of controlling the content and formation constants of stable OMC by varying structural characteristics of FSAP. The existence of two levels of FSAP molecule ordering such as their microstructure and structure of hydrogen bonded complexes (HBC) from FSAP molecules explains the cooperative mechanism and some peculiarities of the OMC formation.

The discussion of the results of the investigation of the synthesis and properties of OMC on the basis of oil-soluble Me^{n+} salt and FSAP is the aim of the report.

Experimental Part

Carbon chain FSAP derived from vinyl acetate (VA), maleic anhydride (MA), 2-tert.butylperoxy-2-methyl-5-hexen-3-yne (VEP) and butylacrylate (BA) or acrylic acid (AA) were obtained by solution copolymerization at 333K in ethyl acetate or dimethylformamide using azobisisobutyronitrile (AIBN) or benzoyle peroxide (BP) as initiator[1,6].

VA, AA and BA were purified by vacuum distillation after which their characteristics coincided with literature data[7]. MA was purified by vacuum sublimation and after purification its melting point was 325K (literature data: 325.9K[8]). AIBN and BP were purified by recrystallization from ethanol. The solvents were used without further purification.

Copolymerization was carried out in a three-necked glass reactor equipped with a stirrer and reflux condenser. Polymerization process kinetics was studied by both dilatometric and gravimetric methods. The polymerization process was carried out till approximately 50% conversion. At this conversion a sufficient quantity of the most reactive monomer (VEP), which is simultaneously the chain length regulator is left in the reaction system. As shown in our previous works[1,6], this provides the relative compositional and molecular-weight homogeneity of FSAP. FSAP were purified by precipitation and dried to a constant weight under vacuum.

The content of MA units in FSAP was determined by potentiometric titration of carboxylic groups, while that of VA units was determined by alkaline hydrolysis method[9]. The content of peroxidic fragments (VEP units) was determined by thermal decomposition of FSAP, at 483 K, followed by gas chromatographic analysis of the decomposition final product[10].

OMC synthesis on the basis of such FSAP was carried out in the following manner: 10% solution of the FSAP and then solution of the metal salt in ethanol were charged into a three-necked flask equipped with a stirrer and a reflux condenser. After stirring at 298K for a definite period of time the reaction mixture was precipitated into distilled water. OMC were carefully washed from metal cations by water and dried under vacuum to a constant weight. The content of metal cations was determined using elemental analysis and controlled by atom-adsorption spectroscopy.

IR spectra of films and dilute solutions of FSAP and OMC were recorded on a Hitachi spectrometer. The OMC structures were confirmed by UV - spectroscopy of FSAP and OMC in ethanol and ethyl acetate on a “Specord 40” device. Volt - ammetric characteristics of FSAP and OMC were investigated on a ECL device for electrochemilumenecsence and electrochemical investigations using glass-carbon and copper electrodes for measurement and AgCl electrode for comparison in 0.03 M solution of $(C_4H_9)_4NClO_4$ in dimethylformamid (DMF). The surface tension (σ) of water-alkaline solutions of FSAP and OMC was determined by the measurement of maximum bulb pressure after achievement of equilibrium state by technique described in ref[11].

The values of FSAP and OMC adsorption at aqueous solution-air phase boundary as well as the values of their surface activity ($G = -d\sigma/dC$ at their concentration in solution $C \to 0$) were calculated from the experimental σ - C isotherms using Gibbs equation[12]. The values of $d\sigma/dC$ were determined from the slope angles of tangents to σ - C isotherm curves at $C \to 0$. Then the values of adsorption (A) at the phase boundary can be calculated by the substitution of known values of C and $d\sigma/dC$ in Gibbs equation. The values of limiting adsorption, A_m, FSAP and OMC molecules at the phase boundary were calculated from Langmuir equation after its transformation to form[13].

$$\frac{1}{A} = \frac{\alpha}{A_m C} + \frac{1}{A_m}$$

The content of FSAP and OMC sorbed on the γ-Fe_2O_3 particle surface as well as peroxidic fragment content in particle shell were determined via the thermal decomposition of peroxide containing fillers at 483K under argon, followed by gas chromatographic analysis of the decomposition final products as it was above shown. The samples were previously treated with solvent for FSAP and OMC. The average deviation between contents of FSAP or OMC on particle surface determined using above mentioned technique and elemental analysis is of 3 - 5% which does not exceed the systematic error of both methods.

Since we are interested only in stable OMC, we have earlier proposed[5] to characterize the ability of reactants to form stable complexes which can be separated from all possible complexes in solution by the γ and K_{st} values. γ is the mole fraction of stable OMC, which can be separated from overall amount of oligoperoxidic molecules and metal complexes existing in equilibrium state in solution.

$$\gamma = \frac{[P_n - Me^{n+}]_{st}}{[P_n]_0}.$$

Stable OMC formation constant

$$K_{st} = \frac{[P_n - Me^{n+}]_{st}}{[P_n]_0 [Me^{n+}]_0},$$

where $[P_n...Me^{n+}]_{st.}$, $[P_n]_0$, $[Me^{n+}]_0$ are the concentration of stable metal complexes, the initial concentration of FSAP hydrogen bonded complexes and the initial concentration of metal salt, respectively.

It is apparent that the oligoperoxide HBC concentrations are directly interrelated to the concentrations of initial FSAP and metal-containing oligoperoxidic molecules and they can be replaced by the corresponding $[FSAP]_0$ and $[OMC]_{st}$ values, which can be easily determined from the experimental data.

The processes of water-dispersion polymerization in the presence of FSAP or OMC (no conventional radical initiator for polymerization initiation was used) were carried out in water alkaline media at 273 - 353K. Monomer to water phase ratio was 1:3 (v/v). Water phase pH was 9. Polymerization kinetics was studied by both dilatometric methods in described in the literature[14] collapsible emulsion dilatometers with magnetic stirrer and gravimetric method in 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 biphenyl verdazyl.

Results and Discussion

1 THE BASIC PRINCIPLES AND PECULIARITIES OF OMC SYNTHESIS

It is known that the nature of metal cations and ligands predominantly influences complex stability[15,16]. It can be seen from Diagram 1 data that the values of K_{st} and γ depend on the nature of bonded metal cations. The series in which K_{st} and γ diminish coincides with the series in which the values of cation atomic number increase. It is obvious that the decrease of complex stability and their fraction in this series is caused by the change of occupation of cation valent orbital and enlargement of their atomic nuclei charge. The latter results in the enlargement of electrostatic repulsion, which hinders the binding of the metal cations with the neighboring complex forming functional fragments of FSAP. The ability of the Cu^{2+} cation to participate in the formation of relatively high fraction of stable metal coordinated complexes with its d-electron contributing to bond formation with the vacant p - orbital of the FSAP complex forming groups determines its separate position in this series. Although as it seen from Diagram this cation also possesses the same regularities of complex formation with oligoperoxidic ligands.

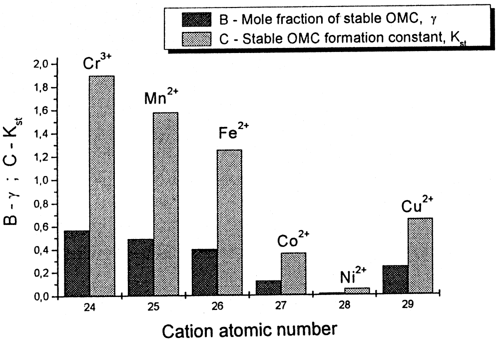


Diagram 1: Characteristics of OMC on the basis of FSAP VA - VEP - MA (synthesis occurred at a temperature of 298K, with a FSAP/Me^{n+} mole ratio=1)

The data of Diagram 1 witness also about the cooperative mechanism of coordinate binding with cations which is common for all FSAP. This results in the formation of compositional nonhomogeneous products, which contain HBC from oligoperoxidic molecules and metal complexes with different constants of stable OMC formation. Calculations taking into account the maximal contents of transition metal cations in OMC and the number average molecular weights of oligomeric ligands in these complexes show that more than one FSAP molecule is necessary per one bound metal cation. At the same time it is evident that the probability of binding more than one metal cation by oligoperoxidic molecule is not very large. Such cooperative mechanism of complex formation is characteristic for polar oligoperoxidic molecules

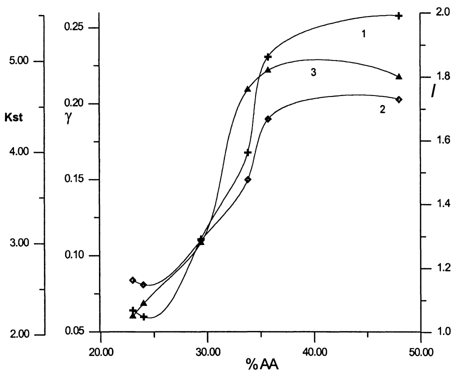


Fig.1: The dependence of stable OMC mole fraction (γ) (1), constant of stable OMC formation (K_{st}) (2) and AA unit block length (l) (3) on their content in FSAP on the basis of VA - VEP - AA copolymer

with low molecular weights and low content of accessible complex forming fragments. Therefore as it shown in Fig.1 and Fig.2 the nature and microstructure characteristics of initial FSAP, which provide their ability to form definite conformational and supermolecular structures with enlarged local concentration of accessible carboxylic groups are the predominant factors influencing the probability, mole fraction and stable OMC formation constants. The extremal dependences of stable OMC content and their formation constants on the AA unit content in the oligomer (Fig.1) can be explained, in our opinion, by the microstructure of initial FSAP. Such a character of the dependence on AA unit content is caused by the change in length and amount of carboxylic monomer unit blocks on changing its content in the oligoperoxide. It is obvious that the character of observed dependences is the similar to the character of the dependence of the length of AA unit blocks calculated from the experimental data on the total content of this monomer units in the oligomer (Fig.1). Upon complex formation with FSAP, in which two neighboring carboxylic groups are introduced with the MA units, the monotonous increase of stable OMC fraction and constants of their formation with content of MA units in FSAP chain is observed (Fig.2). The maximal content of bound metal cations corresponds to the maximal content of MA units in the oligoperoxidic ligand. Such dependence is caused, in our opinion, by the increase of local concentration of accessible complex forming carboxylic groups in oligoperoxidic molecules of HBC and corresponding increase of the probability of their coordination with metal cations.

However, the dependences of stable OMC formation constants $(K^*_{st} = \frac{[Me^{n+}]_{OMC}}{[COOH]_0[Me^{n+}]_0})$, calculated from the initial overall concentration of carboxylic groups of FSAP (but not from the initial overall concentration of oligoperoxide molecules), which does not take into account the oligomeric chain length, differ for OMC on the basis of FSAP of different nature (Fig.3). In

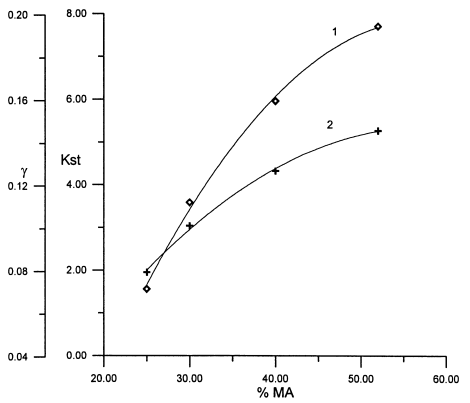


Fig.2: The dependence of mole fraction of stable OMC (γ) (1); constants of stable OMC formation (K_{st}) (2) on the MA unit amount. (OMC on the basis of FSAP VA - VEP - MA)

contrast to K_{st}* for complexes of VA - VEP - AA based FSAP the values of K_{st}^* corresponding to copolymer with MA units remain the same, irrespective of its unit content in FSAP. The similar dependence characterizes the change of structure and stability of OMC on the basis of FSAP of different nature when the content and position of complex forming carboxylic groups in FSAP structure are altered. In contrast to VA - VEP - AA FSAP, the microstructures of which greatly depend on content of AA units, the microstructures of the oligoperoxides with MA units are invariable in the studied range of their unit contents. This causes the predominated inclusion of the cations in the coordinate complex as a result of their interaction with two neighboring carboxylic groups of MA fragments, which regularly alternate with VA and VEP units.

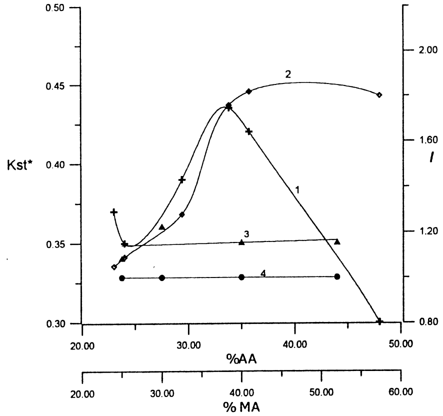


Fig.3: The dependence of unit block length (l): FSAP VA-VEP- MA (4); FSAP VA - VEP - AA - (2), - and constants of stable OMC formation K^*_{st} OMC of oligomers with MA - (3) and AA - (1) units on unsaturated acid unit content.

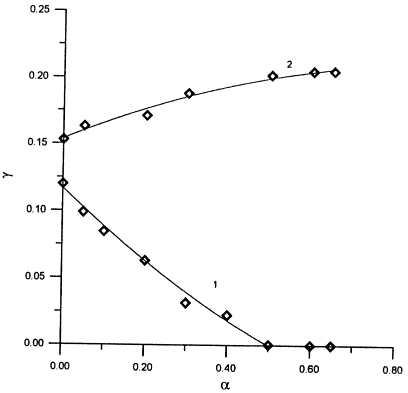


Fig.4: Stable OMC fraction (γ) vs level of carboxylic group ionization (α): 1 - OMC with ligand on VA - VEP - MA based FSAP; 2 - OMC with ligand on VAl* - VEP - MA based FSAP. *VAl - units of vinyl alcohol

This is confirmed by the dependence of the content of OMC, formed by such oligoperoxides on the level of ionization of FSAP carboxylic groups (Fig.4). It is evident that the amount of coordinated cations diminishes as the level of ionization (α) increases and attains a minimum at $\alpha = 0.5$, when only half of complex forming carboxylic groups is in the acid form. At the same time for hydrolyzed FSAP, which, besides the carboxylic groups, contains hydroxy groups liable to complex formation, the content of cations coordinated with ligand increases. This can be explained by the increase of the local concentration of complex forming hydroxyl groups due to the straightening of oligomeric molecules under electrostatic repulsion of ionized carboxylic groups.

The coincidence of fraction and constants of stable OMC formation of OMC on the basis of FSAP of different nature (but with the same unit sequence distribution in their chain) is a clear evidence of the interrelation between the FSAP microstructure and structure of OMC formed (Table 1). It can be concluded also that FSAP of the same microstructure form the similar supermolecular ordered structures in solution.

Table 1. Characteristics of OMC on the basis of FSAP with the similar microstructure

FSAP composition, % mole.				Block length			Content of bound metal cations in OMC, %	Mole fraction of OMC	Stable OMC formation constants
VA	VEP	AA	MA	l_1	l_2	l_3*		γ	K_{st}
22	49	29		1.03	1.11	1.85	0.87	0.23	0.61
22	48	-	30	1	1	1	0.85	0.24	0.65

*-The third comonomer unit (AA or MA) block length.

A number of factors favoring complex formation (quantity and arrangement of complex forming groups[5], as well as the chain length and flexibility) determine the conformational structures of FSAP in supermolecular ordered structures of HBC. Increasing the set of these structures promotes the enhancement of the local concentrations of reactants in the reaction zone (which are outside as well as inside of HBC), thereby increasing the probability that the reaction will proceed. It is shown that the content and stable OMC formation constants differ (at constant content of copper cations in OMC) in the series of polymeric homologues with similar macro- and microstructures but different chain length (Table 2).

Table 2. Characteristics of OMC on the basis of FSAP VA - VEP - BA - MA with different molecular weights

#	Initial FSAP composition, % mole				$CuCl_2$: FSAP ratio during synthesis	FSAP mole. weight	$[\eta]\cdot 10$, m^3/kg, in acetone, 298K	Content of coordinated Cu^{2+} cations	γ	K_{st}
	VA	VEP	BA	MA						
1*	15.5	38.0	14.1	32.4	1:1	5200	0.28	1.42	1.15	3.3
2**	15.0	37.4	15.0	32.6	1:1	3300	0.20	1.42	0.73	2.0
3**	15.2	37.8	15.0	32.0	1:1	2200	0.15	1.40	0.48	1.3
4***	15.0	38.0	14.5	32.5	1:1	1400	0.11	1.38	0.30	0.82
5	15.5	38.0	14.1	32.4	1:2	5200	0.28	0.96	0.78	4.46
6	15.0	37.4	15.0	32.6	1:2	3300	0.20	0.97	0.50	2.85
7	15.2	37.8	15.0	32.0	1:2	2200	0.15	0.94	0.32	1.85
8	15.0	38.0	14.5	32.5	1:2	1400	0.11	0.94	0.21	1.18

* Number average molecular weight of FSAP #1 was determined by the method of gel - permeation chromatography (the data are given by the Sherwin-Williams Co);

** Viscosity average molecular weights of FSAP #2 and #3 were determined from their intrinsic viscosity's using the values: $K=6.33\cdot 10^{-4}$ and $\alpha = 0.71$ (acetone, 298K), - found by us from independent investigations of molecular weights of FSAP in this series;

*** Number average molecular weights of FSAP #4 were determined by the isopiestic method[12] in acetone after preliminary blocking of the FSAP polar carboxylic groups by means of esterification.

These values rise with increasing FSAP chain length. As a result all oligoperoxidic molecules contain coordinated copper cations at sufficient copper salt concentration and attainment of the definite chain length of oligomers. In our opinion, this does not contradict the earlier proposed[5] probable cooperative mechanism of complex formation of FSAP molecules with Cu^{2+} cations but can be explained by the rise of this reaction probability as a result of the increase in length and flexibility of oligomeric ligand chains, which provide the enhancement of the set of FSAP conformational structures with accessible carboxylic groups in HBC.

Also, the probability of complex formation increases with the increase of copper salt concentration. The extremity on the curve of the dependence of stable OMC formation constants on the initial concentration of metal salt in solution (Fig.5) confirms the probable cooperative mechanism of formation of coordinate complexes of Me^{n+} with oligoperoxidic molecules and witnesses about compositional nonhomogeneity of the products of complex formation. The maximal value of K_{st} for metal coordinated complexes of FSAP can be explained by the attainment of the optimal conformations of the oligomeric ligands, which provide enhanced local concentration and favorable disposition of the complex forming fragments at the corresponding salt concentration. The swift increase of the fraction of the metal complexes in this range of copper salt concentration and the following leveling off at further increase of salt concentration confirms this supposition. It is known[17] that further increase of Cu^{2+} cation concentration suppresses the straightening oligomeric chains and diminishes the local concentration of accessible carboxylic groups. The complex forming fragments of other FSAP molecules in the HBC are inaccessible for instantaneous interaction with copper cations due to their participation in hydrogen bond formation in these ordered structures. The diffusion of Cu^{2+} cations inside of HBC is also restricted by the already bound Cu^{2+} cations of the same charge, which hinder their movement to the reaction zone. This results in the decrease of the formation constants of stable OMC and their mole fraction is independent of the salt concentration.

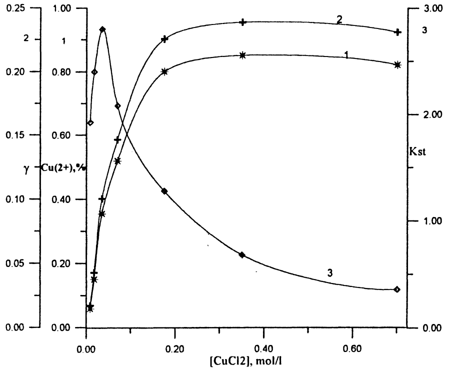


Fig.5: The dependence of the stable OMC mole fraction (γ) (1), Cu^{2+} cation content (2) and stable OMC formation constants (K_{st}) (3) on the copper salt concentration in solution during synthesis of OMC on the basis of FSAP VA - VEP - MA

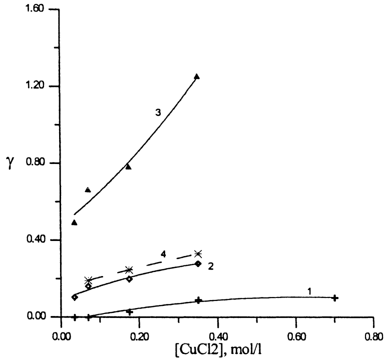


Fig.6: The dependences of mole fraction of OMC on the basis of FSAP VEP -MA (60:40; M_n=1600 mole/g) (1); VA - VEP - MA (22:48:30; M_n=1800 mole/g) (2); VA - VEP - BA- MA (15:38:14,5:32,5; M_n=5200 mole/g) (3); VA - VEP - BA- MA (15:38:14,5:32,5; M_n=1400 mole/g) (4) on copper salt concentration in solution at complex formation

From the dependences of OMC maximal content on copper salt concentration in the initial solution it is evident that (in spite of the higher content of MA link in binary FSAP structure) the maximal content of cations coordinated with such ligands is lesser than in OMC on the basis of tertiary and quadruple oligoperoxides, respectively (Fig.6). This is caused by the capability of the binary FSAP to form the firmer HBC due to their micro- and conformational structures in solution and infers the occurrence of the interaction between Cu^{2+} cations and carboxylic groups of FSAP molecules associated in HBC.

2 OMC CHARACTERISTICS AND STRUCTURES

Conformational changes of oligoperoxidic molecules, which take place as a result of the interaction with the copper salt and FSAP molecules associated in HBC are confirmed by the dependence's of scaled viscosity (η_s) of FSAP VA - VEP - MA solutions on the concentration of the latter's during dilution with methanol solutions of salts with different ability to complex formation (Fig.7). It is evident from Fig.7 that the addition of salt solutions leads to significant increase of the scaled viscosity of FSAP. The scaled viscosity's of FSAP solutions increase with the increase of the concentration of salt solution. The increase of viscosity's is explained, in our opinion, by the ionization of FSAP carboxylic groups and subsequent “polyelectrolytic swelling” of FSAP in HBC. In the case of dilution with the solution of KCl this results in the disintegration of HBC, uncoiling of oligomeric molecules and swift increase of η_s values. However, such a phenomenon was not observed during dilution of solution of FSAP with the solution of copper salt, which possesses complex forming ability. Extremal decrease of the scaled viscosity of the solution takes place upon dilution to a definite concentration which evidently provides maximal concentration of the accessible complex forming carboxylic groups of FSAP in the given point.

The falling of η_s value is explained by the formation of more compactly packed metal-containing oligoperoxidic molecules as a result of cations having coordination bonds with FSAP. Both the significant change of the intrinsic viscosity values of OMC on the basis of tertiary and quadruple FSAP with increase of cation contents and the slope angles on the dependences characterizing the level of these changes (Fig.8) indicate relatively high chain flexibility, which results in the formation of the higher amount of compactly coiled up OMC. In our opinion, this testifies also to the disintegration of HBC as a result of coordinate metal complex formation and following coiling up of OMC.

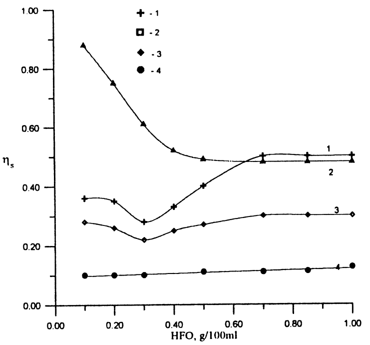


Fig.7: The dependence of scaled viscosity η_S of FSAP on their concentration during dilution by 1% (1, 2) and 0,5 % (3) solutions of $Cu(NO_3)_2$(1,3) and KCl (2) and pure methanol (4) .

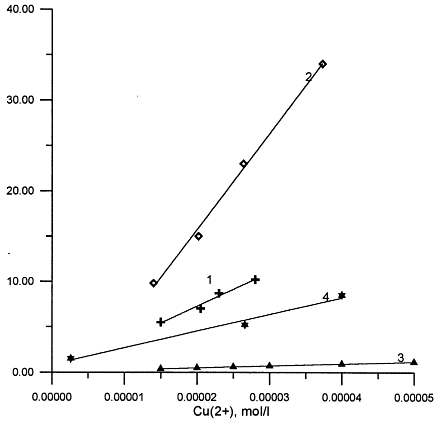


Fig.9: Electronic spectra of solutions in methanol with the following concentrations and contents: 1 - [FSAP]=1×10^{-4} kg/m^3; 2 - [OMC]= 1×10^{-4} kg/m^3, ([Cu^{2+}]=0.4% in OMC), 3 - [OMC]= 1×10^{-4} kg/m^3, ([Cu^{2+}]=0.85% in OMC), 4 - $Cu(NO_3)_2$=1.2×10^{-3}kg/m^3

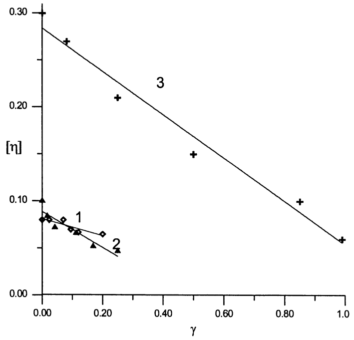


Fig.8: The dependence of intrinsic viscosity of copper OMC on the basis of FSAP VEP - MA (1); VA - VEP - MA (2); VA - VEP - BA - MA (3) in acetone at 298K on stable OMC mole fraction.

The significant shift and increase of the absorption intensity of OMC corresponding peaks in their UV-spectra in comparison with the absorption peaks of the initial copper salt and its mixture with FSAP at the same Cu^{2+} cation concentration is a convincing proof of coordinated metal complex formation (Fig.9). The linear correlation between values of absorption peak intensity ε of the reaction products and coordinated cation content in them also testify to coordinated metal complex formation. Evident from the absorption maximal intensity on cation concentration dependence is the fact that the absorption intensity in UV- spectra at the same cation content is essentially higher for separated stable OMC than for solutions of copper salt or its mixture with the FSAP (Fig.9).

The data of electrochemical investigations (Table 3) conform with UV-spectra confirming the interaction of Cu^{2+} cations with functional groups of FSAP, which lead to the formation of corresponding metal complexes. Analysis of the volt-ammetric diagrams illustrating successive transformations of the reacting system (FSAP, $CuCl_2$, OMC) with time demonstrated that even in diluted solutions (0.01kmole/m^3) under the conditions of cathodic polarization, the complex formation process occurs at a noticeable rate. The decrease of reduction values $-E_{1/2}$ (-0.82V-0.73V) as well as the limited cathodic currents of free Cu^{2+} ions characterizes their binding in complex.

Table 3. Volt- ammetric characteristics of the components of the system (FSAP*, $CuCl_2$, and OMC on glass-carbon and copper electrodes) in 0.03 M solution of $(C_4H_9)_4NClO_4$ in DMF.

System	I		II		III		IV		V	
	$-E_{1/2}$ V	h, cm	$-E_{1/2}$ V	h, cm	$-E_{1/2}$ V	h, cm	$-E_{1/2}$ V	h, cm	$-E_{1/2}$ V	h, cm
FSAP	-	-	1.21	2.50	1.75	4.2	-	-	-	-
FSAP + $CuCl_2$ (0 min)	0.82	1.20	1.17	4.20	1.70	1.75	2.13	1.25	2.38	1.25
FSAP+ $CuCl_2$ (30 min.)	0.73	0.15	1.05	3.10	1.48	1.40	1.83	1.62	2.34	0.61
OMC	0.70	0.20	1.05	2.20	1.53	4.80	2.02	1.60	2.48	1.05

FSAP VA -VEP -MA.

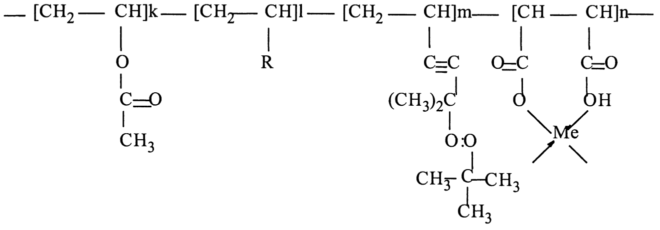
Comparison of IR spectra of initial FSAP and derived OMC shows the differences in their structures. Relatively broad FSAP peak centered at 1730 cm^{-1} overlaps two absorption bands at 1720 and 1742 cm^{-1} belonging, in our opinion, to carbonyls of MA and VA units, respectively. This coincides with a literature data[18]. The metal complex formation leads to fission of this band and shift of absorption peak, which we attribute to carboxylic carbonyl. However, disposition of absorption band VA carbonyl does not change. This confirms that only carboxylic groups of oligomeric ligand form firm bonds with the coordinated metal cations.

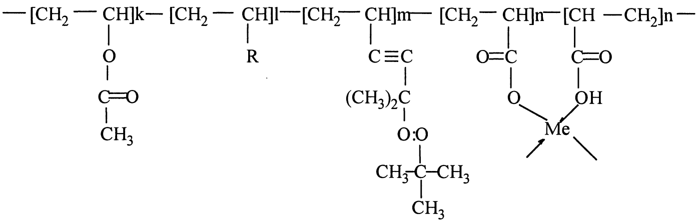
The noticeable shift of absorption peaks from 1720 to 1710 cm^{-1} and from 1660 to 1640 cm^{-1} attributing to valent oscillations of carbonyls of maleic acid units in IR-spectra of OMC (Table 4) substantiates as it is known[19] the participation of carboxylic groups predominantly in formation of stable coordinate complexes. The increase of the value $\Delta\nu$ of these adsorption peaks upon increase of coordinated Cu^{2+} cation content in OMC infers he probable mechanism of complex formation with investigated oligoperoxidic ligands. Such dependence of carbonyl absorption band disposition on metal cation content can be explained by the formation of nonhomogeneous OMC with different constants of stable complex formation as a result of different FSAP conformational and supermolecular structures in solution. These data are in a good accordance with the results of volt-ammetry and UV-spectroscopy presented above.

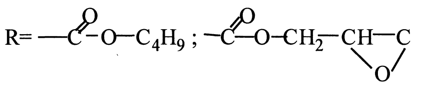
Table 4. FSAP and derived OMC IR-spectral characteristics

Absorption bands of MA unit carbonyls (ν, см$^{-1}$)			
FSAP VA-VEP-MA based	OMC with $[Cu^{2+}]=0.35\%$, ($\gamma=0.1$)	OMC with $[Cu^{2+}]=0.6\%$, ($\gamma=0.17$)	OMC with $[Cu^{2+}]=0.85\%$, ($\gamma=0.24$)
1720	1716	1712	1710
1660	1650	1640	1640

Supposed on the basis of the experimental results of the synthesis and analysis spectra data of metal-containing complex radical oligoditert.alkylperoxidic initiators are presented as follows:







; where k = 0÷20%; l = 0÷20%; m = 15÷50%; n=15÷50%; Mm = 1500÷5200 g/mole

Chemical and physicochemical methods of analysis have witnessed about structural entrance of metal cations into oligoperoxidic molecules. Appearance of paramagnetic properties, which are characteristic for complex derivatives, confirms also the coordinate bond of cations with the oligoperoxidic ligands. OMC are soluble in water and/or polar or low polar solvents, forming intensively colored solutions.

The investigations of colloidal-chemical properties of OMC aqueous solutions showed that the formation of coordinated bonds of copper cations with the oligomeric ligands leads to the enhancement of their surface tension (σ) and its increase with the increase of OMC mole fraction (Fig.10).

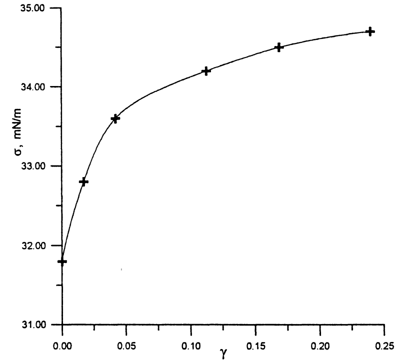


Fig.10: Surface tension (σ) dependence vs stable OMC mole fraction (γ).

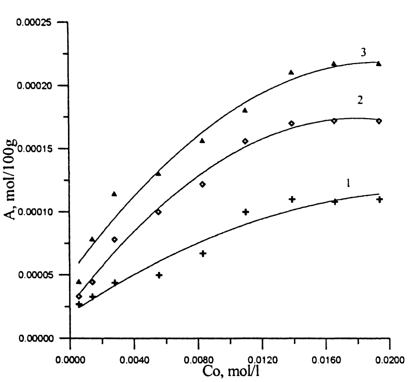


Fig.11: The dependence of FSAP (1) and OMC (2,3) irreversible sorption on surface of dispersed γ-Fe_2O_3 fillers on their concentration in initial solution at OMC mole fraction γ 0.11 (2) and 0.17 (3).

Surface activity values of these substances calculated from experimental σ - C isotherms (Fig.10) witness yet that they do not depend on Me^{n+} cation content. The surface activity value for FSAP and OMC in investigated range of OMC mole fraction from 0 to 0.25 is - 0.003 J·m/mole. It is evident that this value is too small and characteristic for molecules with high content of polar groups. This phenomenon is explained by the decrease of sorbed OMC molecule size, which results in the distribution of their higher quantity at the interface due to their compactly packed conformations in comparison with conformations of FSAP. The increase of OMC maximum sorption on water solution - air phase boundary as well as onto the surface of dispersed γ-Fe_2O_3 fillers with the enhancement of stable OMC mole fraction infers this (Fig.11).

3 FREE RADICAL FORMATION BY OMC IN ALKALINE AQUEOUS MEDIUM.

The characteristic feature of OMC is their ability to low temperature formation of free radicals through decomposition of ditertiary peroxide fragments in the media of different polarity, especially in alkaline aqueous solutions. This can be explained by catalytic influence of transitional metal cation, which is included in oligoperoxide structure. The essential decrease of the temperature range of ditertiary peroxidic group decomposition in such substances is caused, in our opinion, both by polarizing influence of Cu^{+2} cations on -O:O- bond, which weakens it and facilitates the homolytic dissociation, and the possibility of RedOx interaction between the metal cations and peroxidic groups. The first assumption can be confirmed by the values of activation energy decomposition for metal complexes with Al^{+3} and Fe^{+3} cations, which are not able to RedOx interaction with peroxidic groups, presented on Diagram 2. The decrease of these values in the series, which coincides with the lowering flexibility of oligoperoxide chains as it was shown above also witnesses about polarizing influence of included metal cations. The corresponding alteration of the values of the entropy of activation in the same series infers this assumption as well. The essential acceleration of the decomposition of OMC containing transition metal cations witnesses also about the possibility of realization of free radical formation as a result of intra or intermolecular RedOx reactions. The RedOx interaction causes the formation of oligomeric radicals predominantly.

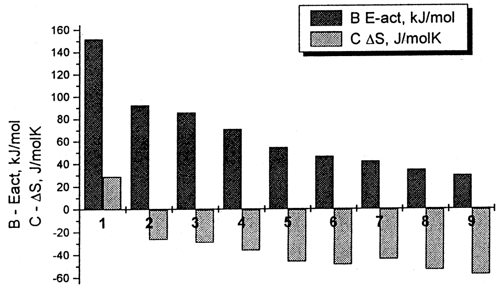
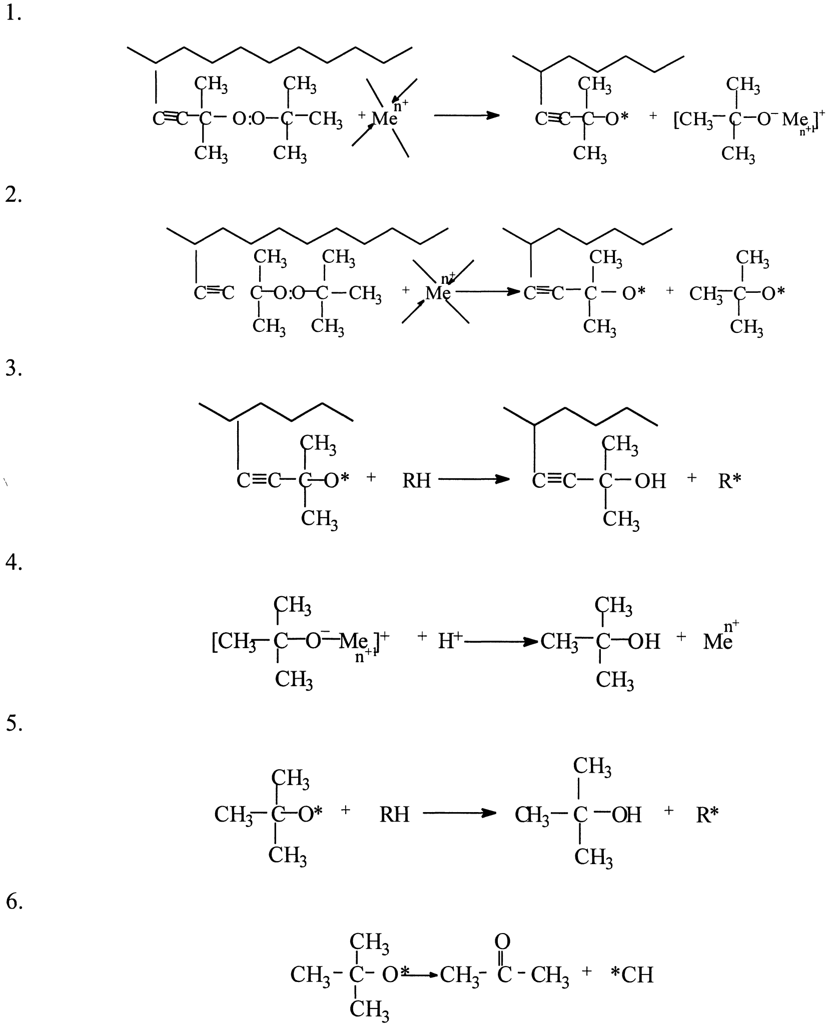


Diagram 2: The thermodynamic characteristics of decomposition of FSAP and OMC peroxide fragments. 1- FSAP in naphthalene; 2 - FSAP VA-VEP-BA-MA in 5% aqueous solution of ammonia; 3- FSAP VA-VEP-MA in 5% aqueous solution of ammonia; 4 - FSAP VEP-MA in 5% aqueous solution of ammonia; 5- OMC on a basis VA- VEP-MA $[Fe^{3+}]$=1,0% in 5% aqueous solution of ammonia; 6 - OMC on a basis VA-VEP-MA $[Al^{3+}]$=1,04% in 5% aqueous solution of ammonia; 7 - OMC on a basis VA- VEP-BA-MA $[Cu^{2+}]$=1,12% in 5% aqueous solution of ammonia; 8 - OMC on a basis VA- VEP-MA $[Cu^{2+}]$=0,85% in 5% aqueous solution of ammonia; 9- OMC on a basis VEP-MA $[Cu^{2+}]$=0,45% in 5%.

We haven't noticed the dependence of decomposition rate on the concentrations of studied OMC in presented above conditions. Evidently, induced decomposition of ditertiary peroxidic fragments of OMC in alkaline aqueous media doesn't take place. The dependences of the ratio of the OMC decomposition main products upon temperature, decomposition duration, and OMC nature (Fig.12, 13) testify to existence of different mechanisms of their low temperature decomposition: homolytic dissociation and RedOx interaction, - leading to formation of the final product mixture enriched by acetone or tert. butyl alcohol, respectively in accordance with the proposed scheme:

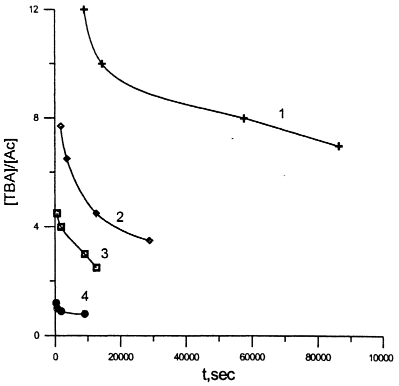


$$[CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O^{-}Me_{n+1}]^{+} + H^{+} \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH + Me^{n+}$$

$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O^{*} + RH \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH + R^{*}$$

$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O^{*} \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + {}^{*}CH$$

The formation of acetone is provided by the reaction of tert. butoxy radical β-scission (6), which is characterized the more value of activation energy than the formation of tert.butyl alcohol in a result of interaction of tert. butoxy radical with substances containing moveable hydrogen atom (5) or through intermediate formation of metal cation containing adduct and its further transformation (4) as it was known from literature[20]. This explains the formation of enhanced amount of acetone at the higher temperature or duration of decomposition. In contrary the tert.butyl alcohol formation is the more preferable at low temperature wherein the portion of RedOx reaction with peroxide group participation increases (Fig. 12, 13).



decomposition ratio (tert-butyl alcohol and acetone) on time decomposition of OMC on the basis of VA- VEP-MA, [Cu]=0,85% in temperature range: 1 –277K; 2 – 298K; 3-313K; 4 –343K

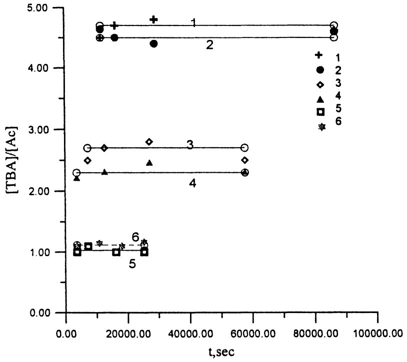


Fig.13: The dependence of a product decomposition ratio (tert-butyl alcohol and acetone) on time decomposition of OMC with Al^{3+} (1,3,5) and Fe^{3+} (2,4,6) cations on the basis of VA- VEP-MA in temperature range: 1,2 – 298K, 3,4 –313K; 5,6 – 343K.

Both the independence of tert. butyl alcohol/acetone ratio from decomposition duration and decrease of the ratio with the temperature enhancement (Fig.13) witness, in our opinion, in favor of this assumption. In spite of impossibility of peroxidic groups of corresponding OMC to RedOx intra-molecular interaction with Al^{+3} or Fe^{+3} cations in their molecules and formation of free radicals via homolytic dissociation it is evident the predominant formation of the alcohol at low temperature in a result of formation of intermediate metal containing adduct.

Proceeding from the assumption of simultaneous realization of decomposition of OMC peroxidic fragments through both above-mentioned mechanisms and additivity of the total rate of decomposition process the equation (1) and its further transformations can be presented as follow:

$$W_{\Sigma} = K_H [VEP] + K_{efR} [VEP][Me^{n+}] \quad (1)$$

$$d[VEP]/dt = [VEP](K_H + K_{ef\,R}\,[Me^{n+}]^x) \qquad (2)$$

$$d[VEP]/[VEP] = (K_H + K_{ef\,R}\,[Me^{n+}]^x)dt \qquad (3)$$

$$d[VEP]/[VEP] = K_{ef}dt \qquad (4)$$

$$K_{ef\Sigma} = K_H + K_{ef\,R}\,[Me^{n+}] \qquad (5)$$

It is obvious (Fig. 14) that the experimental data coordinate perfectly with plots of equation (5).

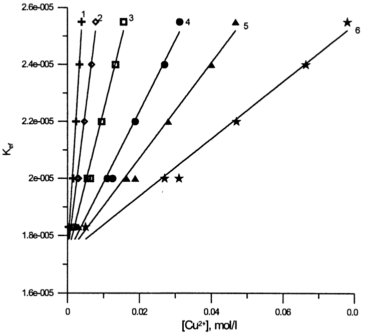


Fig.14: The dependence of effective decomposition constant ($K_{ef\,\Sigma}$) of peroxidic groups in OMC on content of coordinated copper cations at OMC concentration in water: 1-[OMC]=0,014 mole/l; 2-[OMC]=0,028 mole/l; 3 -[OMC]=0,056 mole/l; 4 - [OMC]=0,11mole/l; 5 -[OMC]=0,17mole/l; 6 - [OMC]=0,28 mole/l

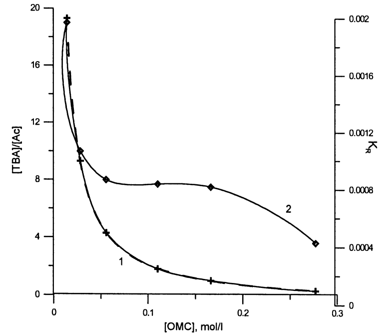


Fig.15: The dependence of effective constant of decomposition as a result of Red-Ox reaction (K_{efR}) (1) and of a product decomposition ratio (tert-butyl alcohol and acetone) (2) on OMC concentration in aqueous solution.

From the Fig. 14 it is clear that K_H is the true constant of homolytic dissociation of peroxide groups in OMC in this series. Its value can be easily determined from experimental data. However, the value of $K_{ef\,R}$ (constant of the rate of radical formation in a result of mono-electronic transfer $Me^{n+} \xrightarrow{e^-} -O:O-$) depends on OMC concentration as it is shown on Fig. 15. Therefore, it is an effective constant defining the radical formation in a result of RedOx intra- or/and intermolecular interactions.

This dependence is described by the equation (6): $K_{ef\,R} = K_R\,[OMC]^{-1}$ (6)

, - thereby the value of the true constant K_R of the rate of RedOx reaction between Me^{+n} cation and peroxidic group of OMC can be determined by the solution of equation (6) describing the experimental dependence shown on Fig. 15. The independence of K_H value on OMC and Cu^{2+} on cation concentrations in this series is explained by only polarizing influence of Me^{n+} cation included in OMC molecule, which is independent from OMC conformational state. At the same time the conformational state of OMC molecules in the solution depending from their concentration defines the possibility of realization of RedOx interaction Me^{+n} cations and peroxidic fragments of OMC because this reaction is feasible only at achievement of such mutual arrangement of metal cation and peroxy-containing fragment, which provides the interaction between them. The convincing proof of this is the enhancement of *tert.*butyl alcohol amount in the decomposition products with the increase of OMC concentration in solution. The calculated from experimental data values of $K_H = 1.5 \cdot 10^{-5}$ c^{-1} and $K_R = 2.8 \cdot 10^{-5}$ c^{-1} for the investigated series of OMC at 298K testify to acceleration of decomposition of their ditertiary peroxide fragments in alkaline aqueous media in comparison with known from ref[10] data of decomposition of FSAP in hydrocarbon media.

4 WATER DISPERSION POLYMERIZATION IN THE PRESENCE OF OMC AS EMULSIFIER AND INITIATOR

In spite of high rate of radical formation by ditertiary peroxide groups of OMC in alkaline aqueous solution the rate of elementary stage of initiation of St water dispersion polymerization is comparatively low (Table 5). Kinetic characteristics of elementary stage of initiation by OMC witness, in our opinion, about the localization of radical formation and their interaction with monomer predominantly in polar water medium wherein the concentration of St is too small. This causes the peculiarities of topochemistry of polymer dispersion formation as well as low efficiency and rate of initiation reaction as it is shown in the Table 5.

Table 5. The kinetic characteristics of initiation stage of emulsion polymerization initiated by OMC VA- VEP-MA based ([Cu]=0,85%; T=298K; monomer: H_2O ratio 1:3, [OMC]= 0.5% in water-phase).

Monomers	Monomer solubility in water	Initiation rate, mole/l s	Initiation efficiency
Styrene	3.6×10^{-2}	1.8×10^{-8}	0.023
Butyl methacrylate	7.8×10^{-2}	3.0×10^{-8}	0.036
Methyl methacrylate	1.5	6.0×10^{-8}	0.041
Vinyl acetate *	2.5	2.5×10^{-8}	0.032

*Initiation with the ascorbic acid participation

It is evident that in a result of low rate of interaction of free radicals with monomer molecules in water phase this reaction limits and defines the general rate of initiation process. Surface-active oligoSt growing radicals grafted to OMC chains, which are the initiators of water dispersion polymerization process, form the polymer/monomer particles (PMP) in a result of homogeneous nucleation from aqueous solution at achievement of definite value of formed polySt molecular weight.

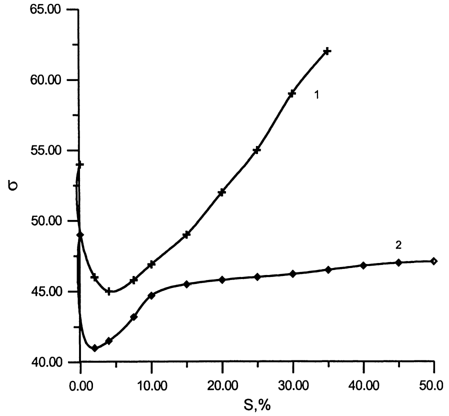


Fig.16: The dependence of surface tension of the St (1) and VA (2) water dispersions on their conversion during emulsion polymerization initiated by OMC (T=298K, [OMC]=0,0028 mole/l H_2O-phase).

PMP are also stabilized by these surface-active graft-cooligomers sorbed onto their surface. Afterwards the processes of initiation and chain propagation take a place predominantly in PMP or on their surface. It is evident from the curves of Fig. 16 the presence of the minimums on the dependences of surface tension of polymerizing systems upon monomer conversion explained by the formation of surface-active grafted oligomers firstly and their further participation in PMP nucleation and sorption onto particle surface. Sharp increase of surface tension (Fig. 16) after achievement of its extreme value witnesses about high efficiency of grafting, which causes significant lowering OMC and graft-copolymer concentrations in water solution as well as localization of all reactive sites and reactions with their participation in PMP nuclei or PMP surface.

Table 6. Kinetic characteristics of St water dispersion polymerization (298K, St:H_2O=1:3)

Initiator-emulsifier	OMC concentration in aqueous phase, %	Concentration OMC VEP links from monomer, mole/l 10^2	Decomposition rate of VEP links in OMC, mole/l s 10^6	The initiation rate of polymerization, mole/l s 10^8	Initiation efficiency	Polymerization rate, mole/l s 10^3
OMC	0.1	0.8	0.15	0.30	0.019	0.42
On the basis VA-VEP-MA	0.5	3.9	0.75	1.75	0.023	0.78
with content of Cu^{2+} cations	1.0	7.9	1.20	6.30	0.038	1.5
0.85%	7.5	59.3	13.00	71.00	0.060	4.0

The kinetic data of Table 6 witness about both the high rate of St water dispersion polymerization with OMC participation as initiator, emulsifier and stabilizer simultaneously providing formation of polySt latex's in a wide temperature range (273-333K) and also the possibility to influence on chain propagation and termination rates.

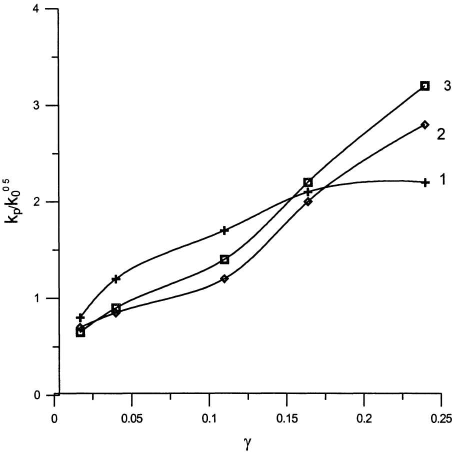


Fig.17: The dependence of $k_p/k_t^{0.5}$ ratio on γ (mole fraction of stable OMC) at polymerization of: 1– St; 2 - Butyl methacrylate; 3- Methyl methacrylate (T=298K)

This can be explained both by the ability of metal cation containing macroinitiators to coordination with monomers and formation oligomeric radicals predominantly, which provide steric and electronic control of polymer chain propagation and termination, and thereby sharp enhancement of molecular weight of latex's polySt. The increase of $k_p/k_t^{0.5}$ the enhancement of mole fraction of metal containing molecules γ in OMC initiating St and acrylates water dispersion polymerization infers the explanation (Fig. 17). This feature is the more peculiar for the more polar acrylates inclined to coordination with the metal cations. The highly stable latex's on the basis of monomers of different nature with controlled particle size and particle size distribution (0.1–1.0 μm), coefficient of polydispersity close to 1 are formed as a result of water dispersion polymerization initiated by metal containing surface-active oligoperoxides. The presence of the definite amount of active peroxidic fragments immobilized on the surface of the latex's colloidal particles causes their ability to secondary initiation providing formation of new composite latex's with the particle structure "core –shell'.

Conclusions

Carbon-chain functional oligomers with ditertiary peroxy, hydroxy or carboxy groups form stable oligoperoxide metal complexes through their interaction with transitional metal salts in organic solutions. The mole fraction and formation constants of OMC are interrelated with the microstructures of FSAP, first of all, with the disposition of complex forming groups, length and flexibility of oligoperoxide chains. The thermodynamic and kinetic characteristics of FSAP and OMC decomposition proved their ability to form free radicals as a result of decomposition of peroxide fragments in a wide temperature range. As a consequence of their specific structure and reactivity, OMC are the objects of increased interest as initiators, emulsifiers and stabilizers for tailored synthesis of stable latex's with narrow size distribution and composite latex's with the particle structure "core-shell" in the result of low temperature water dispersion polymerization.

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