Macromol. Symp. **2004**, *210,* 193-202

Inorganic, Polymeric and Hybrid Colloidal Carriers with Multi-Layer Reactive Shell

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Summary: Main experimental approaches for obtaining polymer, inorganic and hybrid colloidal particles as well as the tailored functionalization of their surface by oligoperoxide surfactants (OPS) and metal complexes (OMC) on their basis are discussed in the paper. The methods proposed enable to combine the stage of the formation of colloidal polymer, siliceous, metal and metal-oxide particles with the stage of their surface modification by functional surface-active oligoperoxides, which are sorbed irreversibly. Novel functional particles are studied by chemical, colloidal-chemical, rheological methods and scanning electronic microscopy. The occurrence of metal and metal oxide particle formation in distinct zones correlates well with the particle size distribution. The availability of reactive ditertiary peroxidic fragments on the particle surface as a result of OPS or OMC sorption causes their reliable protection, hydrophobity and ability to form free radicals and participate in elementary stages of radical processes.

Keywords: “core-shell” polymerization; functional colloidal particles; kinetics; metal complexes; oligoperoxide surfactants; radical emulsion polymerization

Introduction

Last decade, investigation of the methods of functional particle synthesis with the reactive polymeric shell providing their sedimentation stability, compatibility with various matrixes, reactivity and variety of specifically targeted properties is of a significant interest for obtaining carriers of biomedical application and active fillers for microelectronics [1-4]. The creation of theoretical and experimental bases of the synthesis of novel surface-active oligoperoxides and metal complexes on their basis causes the possibility of obtaining new functional polymeric, inorganic and hybrid colloidal particles [5,6]. Modification of dispersed filler surface by the technique of homogeneous nucleation in the presence of such oligoperoxides provides increased adsorption value due to high activity of the newly formed surface as well as the control of filler particle size and size distribution. New functional surface-active water- soluble OPS and OMC are sorbed onto the surface of dispersed polymer and mineral fillers causing localization of the necessary quantity of hydrophobic or hydrophilic peroxide-containing fragments. Such radical-

DOI: 10.1002/masy.200450622

forming sites cause the possibility of the initiation of polymerization from the surface of solid phase [7-9], which is a prospective technique for obtaining filled polymer composites. The study of the principal approaches for the formation of active functional particles is the aim of the work.

Experimental

Oligoperoxide surfactants (OPS) on the basis of vinyl acetate (VA), maleic anhydride (MA), and 5-tert.butylperoxy-5-methyl-1-hexene-3-yne (VEP) were synthesized by polymerization at 333K in ethyl acetate using azobisisobutyronitrile (AIBN) as initiator. Surface-active oligoperoxidic metal complexes (OMC) were obtained by interaction of corresponding OPS with copper cations in organic medium at room temperature.

The monomers – styrene (St), methylmethacrylate (MMA), N-vinylpyrrolidone (N-VP), butyl acrylate (BA), acrylic acid (AA), VA were purified by double vacuum distillation. MA was purified by vacuum sublimation and after purification, its melting point was 325K (literature datum[10]: 325.9K). The peroxidic monomer VEP was purified by vacuum distillation (active oxygen content = 8.79% (calcd 8.75%)). AIBN was purified by recrystallization from ethanol. Other monomers and solvents (Merck) as well as metal salts were used as received.

Discussion

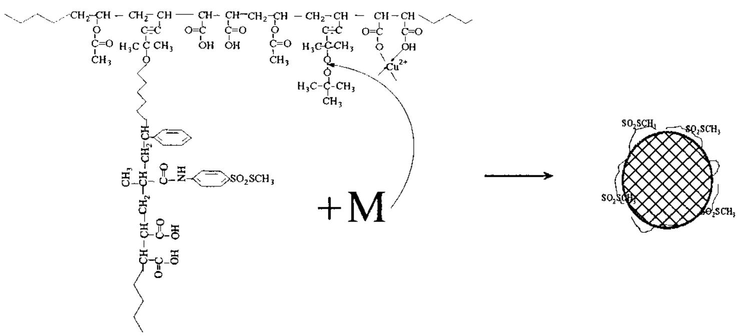
The formation of primary reactive polymer particles with functional shell

Among the variety of the methods for obtaining functional polymer particle the methods using OPS and OMC as universal and convenient tool are, in our opinion, the most prospective for the formation of reactive polymer particles of tailored size and functionality.

1. Water dispersion polymerization initiated by OMC

Earlier [11,12] we have studied the formation of primary reactive polymer particles with functional shell by the technique of homogeneous nucleation during water dispersion polymerization initiated by OMC. The main regularities of controlled radical polymerization initiated by oligoperoxide Me^{n+}-containing surfactants witness about the possibility of obtaining polymer water dispersions with unimodal particle size distribution and reactive functional shell liable to radical, condensation and other reactions [12].

The special case of the formation of primary reactive colloidal polymer particles-carriers with antibacterial properties by this technique is water dispersion polymerization initiated by OMC - graft –poly (styrene—maleic acid —4-methacrylamid-1-methylsulfonate) (Scheme 1).



Scheme 1. The scheme of the synthesis of colloidal polymer particles with antibacterial properties by water dispersion polymerization initiated by OMC on the basis of peroxide-containing graft copolymer

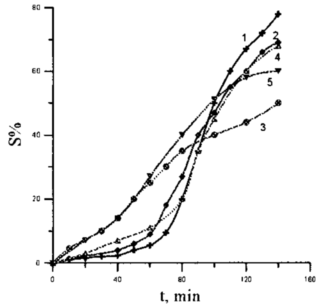
2. Dispersion of condensation resin melts or solutions in water in the presence of OPS or OMC

Another prospective method for obtaining polymer colloidal particles with reactive functional shell is provided by mechanical dispersion of unsaturated polyester, alkyd or epoxy resin melts or solutions in water with OMC acting simultaneously as surfactant, stabilizer and modifier. As a result highly stable artificial water dispersions of the colloidal particles with the resin core and oligoperoxide shell are formed (Table 1).

Table 1. Characteristic of artificial water dispersions of polycondensation resins

Resin	%, OPS	additional surfactant	additional surfactant content per H_2O, %	pH	Water dispersion solid content, %	Latex particle size, μм
polyester PN-15	1.0	Rycinox-80 (oxyethylated rycinolyc acid)	10.0	6,5-7,5	45.0	0.22
	2.5				44.5	0.14
	5.0				46.0	0.1
Alkyd GF-188	1.0	Tinoram (N'-alkyl-N'N''-(3-aminopropyl)-amine)	7.5	3.5-4.0	40.0	0.16
	2.5				39.0	0.13
	5.0				39.5	0.1
Epoxy ED-16	1.0	Rycinox-80	7.5	6,5-7,5	33.0	0.20
	2.5				33.0	0.15
	5.0				32.0	0.12

The particle size is in the range of 0.1–0.4μm depending on the oligoperoxide surfactant concentration (Table 1). Water dispersion polymerization of the solutions of polycondensation resins in acrylic monomers (Fig. 1) enables to obtain particles with "core-shell" morphology and stable film forming colloidal systems on their basis combining the properties of these resins and polyacrylic polymers.



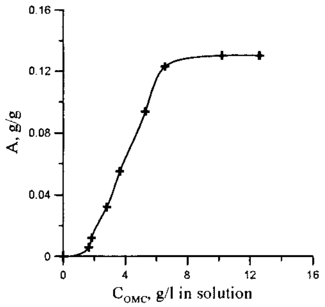


Fig. 1. BA—St—AA mixture conversion vs. emulsion polymerization time at the content of alkyd (**2, 3**) and epoxy (**4, 5**) resins: **1**- without resin, **2, 4** - 10% of resin per monomer mixture; **3, 5** - 40% of resin per monomer mixture

Fig. 2. Characteristics of OMC adsorption onto particles of Rhoplex acrylic latex

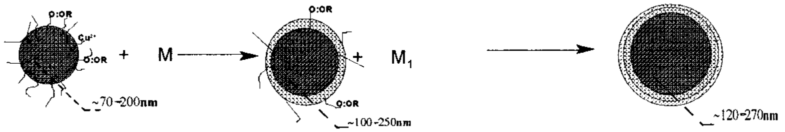
3. Sorption modification of industrial latexes by OPS or OMC

The sorption functionalization of the particles of industrial latexes by pre-determined amount of OMC is an interesting and practically feasible approach for obtaining primary reactive functional polymer particles. The investigation of OMC adsorption (Fig. 2) onto particle surface of industrial polyacrylic latex Rhoplex shows the achievement of the saturation of the surface at definite OMC concentration in solution as well as the decrease of the particle size, which is apparently due to the disaggregation of existing particles at the same time.

Adsorption saturation of the particle surface and the availability of radical-forming groups on them are evident from the results of chemical analysis and study of colloidal-chemical characteristics of polymer colloidal systems modified by OMC. This provides the possibility of carrying out graft copolymerization initiated from the particle surface leading to the formation of new tethered polymer chains with tailored length, functionality and reactivity.

4. Seeded polymerization initiated from the surface of the particles modified by OMC

The experimental results of seeded low temperature polymerization initiated from the surface of primary polymer particles represented by the scheme below (Scheme 2) and in Table 2 display the formation of composite particles with "core –shell" morphology and the possibility of obtaining multi-layer reactive shell as a result. It is evident (Table 2 , Fig. 3,4) that various monomers and monomer systems can be used for the formation of the second and third functional polymer shell on the particles resulting in the change of particle hydrophobic-hydrophilic properties, functionality and enhancement of their size.



Scheme 2. The scheme of multi-stage seeded polymerization initiated from the particle surface

Table 2. Multi-stage seeded (co)polymerization initiated from the particle surface (293K)

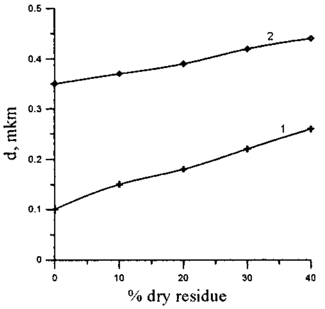
First stage			Second stage*				Third stage **			
Latex particle structure	Dry residue, %	Dpart., μm	Monomer for the second shell***	Dry residue, %	Dpart., μm	W. %/h	Monomer for the third shell	Dry residue, %	Dpart. ,μm	W. %/h
Core St-BA-VEP 53:32:15 Shell OMC	22.0	0.015	F-MA	27.0	0.020	7.2	-	-	-	-
			Si-MA	25.5	0.018	9.0	-	-	-	-
			BA-GMA 90:10	28.0	0.020	10.2	-	-	-	-
Core St-BA-AA 70:25:5 Shell - OMC	23.0	0.010	VEP-BA 50:50	29.0	0.014	9.0	Si-MA	33.0	0.016	7.2
							F-MA	32.2	0.016	9.0

* - the formation of the second shell was initiated by residual OMC in the particle shell;

** - the formation of the third shell was initiated by additional OMC sorbed onto particle surface (0.5% per monomers);

*** - F-MA–2,2,3,3-tetrafluoropropyl-2-methacrylate; Si-MA – (3-trimethoxysilyl)propyl-2-methacrylate; GMA – (2,3-epoxy propyl)-methacrylate

One can see from the results of the investigation of the latex dynamic viscosity (Fig. 4) that the formation of new shell as a result of St seeded polymerization altered the particle surface functionality and weakened interaction between the particles. Moreover, the dependences of seeded polymerization rate on the concentration of sodium pentadecylsulphonate (E-30) and particle-initiator content in the systems (Fig. 5) proves the occurrence of the polymerization exceptionally on the primary particle surface leading to particle size enhancement. No new particles is formed during seeded polymerization initiated by particles modified by OMC.



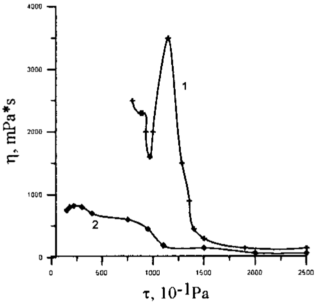
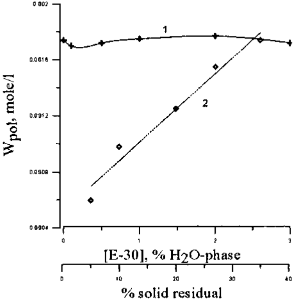


Fig. 3. "Core-shell" particle size vs. dry residue of initial dispersion (St seeded polymerization) 1 – unsaturated polyester dispersion, 2 – alkyd resin dispersion. (St conversion - 100%)

Fig. 4. Dynamic viscosity vs. shear stress for polyester dispersion modified by OMC (1) and after St polymerization initiated from surface (2) (dispersion solid content 27%)



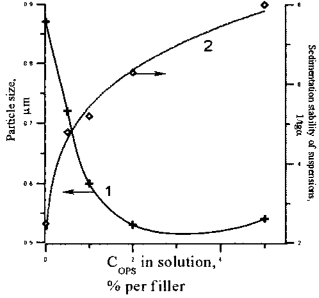


Fig. 5. St seeded polymerization rate vs. concentration of E-30 (1) and vs. dispersion solid residual (2) (initiator - OMC-3% with respect to monomer; 298K)

Fig. 6. Characteristics of Fe_3O_4 suspensions obtained via nucleation from the solution of the mixture of ferrous chlorides in the presence of OMC on the basis of N-VP-VEP-MA (the ratio [solid phase]:[H_2O] = 1:10, T=333K)

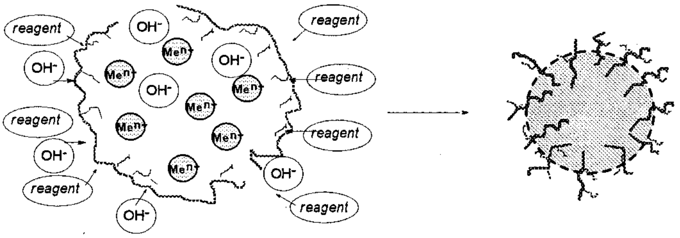
The formation of primary reactive inorganic particles with functional shell

It is clear that the methods of obtaining inorganic and hybrid colloidal particles with reactive functional shell on their surface are similar (in many aspects) to the above-mentioned methods of the formation of functional polymer particles.

1. Homogeneous nucleation from salt solutions in the presence of OPS or OMC

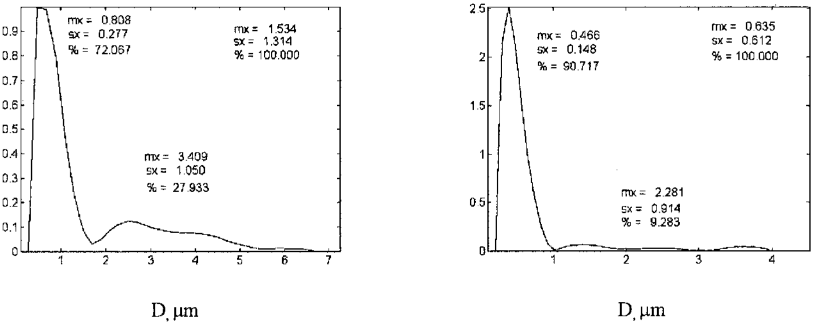
Using this technique primary reactive inorganic particles with functional shell are formed by homogeneous nucleation from the solutions of corresponding metal salts in the presence of OMC as illustrated in scheme 3.

The characteristics of water suspensions of ferrous oxide (Fig. 6) show that the increase of OMC concentration in the reaction mixture causes the decrease of particle size and simultaneous enhancement of the amount of sorbed OMC.



Scheme 3. The scheme of homogeneous nucleation of metal and metal oxide particles with functional OMC shell

The number average particle size distribution shows the tendency toward the formation of unimodal silver particles at their formation in the presence of OMC surfactant (Fig. 7). This can be explained as we have shown earlier [6] by the displacement of the reaction of particle nucleation into micelle-like structures formed by OMC, which are the exo-templates determining the particle size.

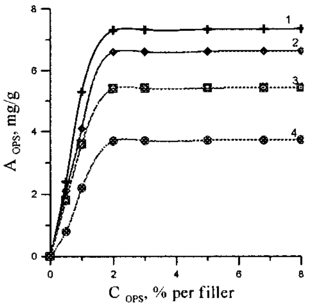


a) b)

Fig. 7. Number-average distribution of silver particles obtained via reduction. A) synthesis without OMC; b) 5% of OMC with respect to Ag^+ ions (0.09 % in solution).

2. The sorption modification of inorganic particle surface by OPS or OMC

The method of sorption modification of previously obtained inorganic particles by OMC also provides their tailored functionalization as a result of irreversible immobilization of ditertiary peroxide groups, hydroxyl, carboxy, epoxy and other functional fragments (Fig. 8).



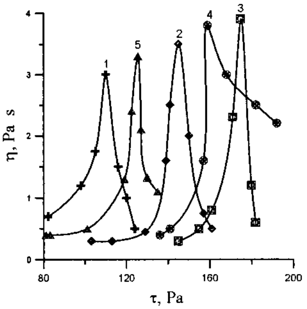


Fig. 8. Isotherms of OMC N-VP-VEP-MA sorption onto the surface of -Fe_2O_3 (1, 2) and Fe_3O_4 (3, 4). 1, 3 – before sample washing, 2,4 - after sample washing

Fig. 9. The dynamic viscosity of Fe_3O_4 suspensions modified by OMC N-VP-VEP-MA vs. shear stress. (C_{OMC}= 0%(1), 1% (2), 2% (3), 3% (4), 5% (5)

The dependence of dynamic viscosity of ferrous oxide suspension modified by various amount of OMC on shear stress (Fig. 9) witnesses, in our opinion, about the formation of multi-layer functional shell with different orientation of polar functional groups.

Table 3. Characteristics of the decomposition of OMC peroxide groups sorbed on colloidal Ni particle surface

Ditertiary peroxide fragments	Activation energy E, kJ/mole	lgA	$\Delta S^{\neq}$ J/mole K
OMC on Ni particle surface	37,0	2,0	-50,0
OMC in solution	42,0	2,5	-44,4

The experimental results of the investigation of the decay of ditertiary peroxide fragments immobilized on the particle surface (Table 3) show the significant difference between the activation parameters of the decomposition of peroxide groups on the surface and in solution, which is apparently due to the decrease of the degree of freedom of sorbed OMC molecules in comparison with the OMC molecules in solution.

3. Seeded polymerization initiated from inorganic particle surface modified by OMC

The presence of radical-forming sites on the particle surface causes the possibility of low temperature radical formation by the immobilized ditertiary peroxide groups as well as grafting of polymer chains to the surface with the formation of new functional shell at a given distance from the surface (Fig.10 and Table 4).

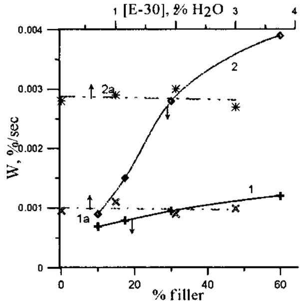


Fig.10. Water dispersion polymerization rate of VEP-GMA-St mixture vs. filler content (1,2) and concentration of emulsifier E-30 (1b, 2b). Initiation from the OMC modified filler surface: g-Fe_2O_3 ([OMC] =0,7%) (1, 1b) colloidal Ni particles ([OMC] =0,45%) (2, 2b); 291K

Table 4. Characteristics of copolymer GMA-VEP-St grafted to the surface of inorganic fillers (291K; monomers:H_2O=1:5; GMA-VEP-St 2:1:1)

Filler	Filler content, % wt	Content of copolymer grafted, %	Composition of copolymer grafted , %		
			GMA	VEP	St
γ-Fe_2O_3, [OMC]=0,7%	17,4	1,6	50,0	25,0	25,0
	30	2,5	60,0	19,0	21,0
	60	5,0	75,0	16,0	9,0
Colloidal Ni [OMC]=0,45%	17,4	0,8	65,0	5,5	29,5
	30	1,1	55,0	6,0	39,0
	60	2,5	50,0	10,0	40,0

One can see (Fig.10) that seeded polymerization initiated from the surface of inorganic particles obeys the same regularities peculiar to the polymerization initiated from the polymer particle surface, including the independence of the polymerization rate on the concentration of the additional emulsifier. This proves the occurrence of graft polymerization only on the particle surface and the impossibility of particle formation in the solution. The polymerization rate and conversion depend on the modified filler nature and content in the reaction system. The study of the particles after seeded polymerization witnesses about the increase of their size and tailored formation of grafted chains containing a definite amount of active epoxide and peroxide groups.

Conclusions

Various approaches of OMC and OPS use for the activation of colloidal particles providing polymer grafting onto their surface have been demonstrated in the work;·This allows the formation of "core-shell" particle structure with fragments providing their tailored compatibility, functionality and reactivity.

Functional particles including magnetic ones contain spacers with functional groups, which are liable to radical and polymer-analogous transformations.

Acknowledgement

The authors express their thanks to Science and Technology Center in Ukraine for financial support of this work, Project # 1447.

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