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SYNTHESIS AND PROPERTIES OF SILICA NANOPARTICLES WITH FUNCTIONAL POLYMER SHELL

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Silica nanoparticles with functional polymer shell based on reactive peroxide-containing copolymers were synthesized via sol-gel method. Unimodal nanoparticles of spherical shell with the size of 190–350 nm and low polydispersity index were obtained. The influence of copolymer nature and concentration, catalyst concentration, onto process kinetics and nanoparticle size was studied. The formation of functional polymeric shell on the surface of silica nanoparticles was proved using the methods of gas-liquid chromatography and complex thermal analysis.

Key words: nanoparticles, silica, Shtober process, reactive copolymers, radical copolymerization, adsorption.

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СИНТЕЗ ТА ВЛАСТИВОСТІ НАНОЧАСТИНОК ДІОКСИДУ СИЛІЦІЮ З ФУНКЦІОНАЛЬНОЮ ПОЛІМЕРНОЮ ОБОЛОНКОЮ

Наночастинки діоксиду силіцію з функціональною полімерною оболонкою на основі реакційноздатних пероксидовмісних кополімерів синтезовано з використанням золь-гель методу. Отримано унімодальні наночастинки сферичної форми розміром 190–350 нм з низьким коефіцієнтом полідисперсності. Досліджено вплив природи та концентрації кополімеру, концентрації каталізатора, температури на кінетику росту та розмір наночастинок. Формування функціональної пероксидної полімерної оболонки на поверхні наночастинок діоксиду силіцію підтверджено методами газорідинної хроматографії та комплексного термічного аналізу.

Ключові слова: наночастинки, діоксид силіцію, метод Штобера, реакційноздатні кополімери, радикальна кополімеризація, адсорбція.

Introduction

Organic-inorganic nanocomposites (NC) are functional materials consisting of immiscible organic and inorganic components in which at least one phase possesses the size of nanometer range (1–100 nm). These highly effective materials demonstrate unusual combinations of properties and unique design possibilities. It is known that with the size decrease to nanometer range at constant composition materials reveal the sharp change of properties: conductivity, elasticity, strength, optical properties and reactivity which are not demonstrated at macro level. Besides, with such decrease in size interfacial surface and consequently interactions at phase boundary increase drastically as well [1, 2].

In recent years composition materials based on nanosized silica have attracted increasing attantion. Silica nanoparticles (NP) are the promising material as the fillers for composites that can be applied for creation of coatings, flame-retardant materials, optical devices, photo-resistant materials photoluminescent conductive films, in catalysis, biotechnology packing materials due to their high physical properties and ability to functionalization by diverse organic substances [3].

Silicon alkoxydes (tetraetoxysilane (TEOS) or tetramethoxysilanes (TMOS)) and alkoxysilane-containing polymers are the most frequently used precursors of SiO_2 nanoparticles [4, 5]. At present two main groups of methods are applied to synthesize SiO_2 NPs: sol-gel synthesis and microemulsion method.

Table 1

Synthesis, composition and characteristics of used peroxide-containing copolymers

RC	Monomer mixture composition, % mol.				Copolymer composition, % mol.				Conversion, %	Wpol·10^3, %/c	Intrinsic viscos. in acetone, m^3/kg	$M_w \cdot 10^{-3}$, g/mole
	AkAm	PM	BMA	MA	AkAm	PM	BMA	MA				
1	–	10	50	40	–	9.7	48.3	42.0	78.0	5.0	0.014	
2	–	20	40	40	–	17.7	40.0	42.3	76.1	4.7	0.007	28.9
3	20	20	20	40	25.6	19.5	14.8	40.1	82.1	4.9	0.007	10.6

Synthesis of nanosized monodisperse silica particles via controlled hydrolysis of TEOS in microemulsion with the use of non-ionic emulsifier was described in [6]. In 1968, Stober and Fink reported the simple method of the sinthesis of monodisperse SiO_2 NP via hydrolysis of diluted TEOS solution in ethanol at high pH values [7]. Using this technique, they formed amorphous SiO_2 spheres with the size of 10nm - 2μm depending on reagent concentrations. Later, Stober method was improved and now it is one of the simplest and most effective methods of the synthesis of monodisperse SiO_2 NP.

Significant difference in the properties of polymer and SiO_2 NP may cause phase separation. Therefore, interphase interaction between two phases of nanocomposite is the crucial factor influencing the properies of obtained materials. The modification of nanoparticle surface is the most widely used method for improving the compatibility of hydrophilic SiO_2 NP and hydrophobic polymers. This technique allows to enhance NP dispersion degree in polymer matrix and as a result to improve physico-mechanical properties of composite. Physical methods of surface modification consist in the adsorption of molecules surface-active substances or polymers. Physical adsorption proceeds due to electrostatic interactions. They provide the attenuation of interactions between NP inside agglomerates and modified in such a way nanoparticles can easily incorporate into polymer matrix. For example, in [8] SiO_2 NP were modified by n-hexadecyl trimethylammonium bromide. Also it was reported about SiO_2 NP modification by stearic or oleic acid that improve dispersion degree of nanoparticles and their adhesion to matrix polymer [9, 10]. Chemical modification of SiO_2 NP is widely used as well because in this case very strong bonds between organic and mineral phases are formed [11].

But at the same time the elaboration of methods of obtaining SiO_2 NP with controlled size and reactive polymer shell which can provide the control of interactions on phase boundary at composite material formation is an actual task of polymer chemistry.

The main goal of this work was to study the processes of sol-gel synthesis of SiO_2 NP with functional polymer shell and to determine the influence of reactive copolymer nature and concentration onto process kinetics and properties of synthesized nanoparticles.

Materials and methods

Synthesis of peroxide-containing reactive copolymers (RC) of butyl methacrylate (BMA), acryl amide (AcAm) maleic anhydride (MA) and peroxidic monomer 5-tert-butylperoxy-5-methyl-1-hexene-3-yne (PM) with different content of monomer links was carried out via radical copolymerization of the aforementioned monomers in ethyl acetate at their diverse ratios (total monomer concentration was 3.5 mole/l) at 333 K in the presence of lauroyl peroxide as initiator as described elsewhere [12]. RC were purified by double precipitation from ethyl acetate solution into hexane and dried under vacuum to constant weight. Composition and some chemical characteristics of RC are shown in Table 1.

Modification of peroxide-containg copolymer performed via interaction of dimethyl aminoethanol (DMAE) hydroxyl groups with MA subunits of copolymer at mole ratio of [DMAE]:[MA subunits] = 1:2 in ethyl acetate at total solution concentration of 10 % at 333 K during 5 hours (Table 2). Total solution concentration was 10 %.

The content of peroxide groups in RC was determined from the results of gas chromatographic analysis of the final decomposition products obtained at the RC thermolysis at 483 K under argon with the use of gas-liquid chromatograph SELMICHROM-1(Selmi, Ukraine) [13]. The content of MA subunit in RC was determined using a reverse potentiometric titration of carboxylic groups. The content of AcAm and DMAE subunits was estimated from the results of elemental [C, H, N] analysis. Intrinsic viscosity [η] of RC solutions was measured using Bishoff viscosimeter in acetone at 298 K [14]. Molecular weight of copolymers was determined by gel-permeation chromatography using Polymer Standard Service system (PSS, Mainz, Germany, MDS RI detector).

Table 2

Composition and some characteristics of peroxidic amino-containing copolymer based on RC-2

RC	[N], %		[MA-DMAE], % mol	Intrinsic viscos. in acetone, m^3/kg	$M_w \cdot 10^{-3}$, g/mol
	theor.	pract.			
2a	2.0	1.99	21.1	0.0014	29.1

Synthesis of SiO_2 NP was carried out in accordance with Stober method in the presence of reactive copolymers in two-necked reactor at constant stirring (400 rpm) in water bath. Firstly, RC was dissolved in water-ethanol solution containing water ammonia. Prepared solution was placed in water bath. After reaching synthesis temperature tetraetoxysilane was added to the solution (C_{TEOS} = 0.14 mole/l, water concentration was 20–30 mole/l, ammonia concentration – 2.5–5.0 mole/l). Synthesis temperature was 293–303 K. TEOS conversion was determined gravimetrically.

In order to study kinetics of SiO_2 NP growth, 0.1 ml probes of the reaction mixture were taken at certain periods of time and diluted in 2 ml ethanole to stop the reaction. Particle size was determined by dynamic light scattering (DLS) with the use of DynaPro NanoStar dynamic light scattering detector (Wyatt Technology Co., USA). In addition, number-average and weight average sizes of SiO_2 NP were calculated from from micrographs obtained using a REM-106I scanning electron microscope (“SELMI”, Ukraine). Content of irreversibly adsorbed RC was determined by elemental (C, H, N) analysis and using the results of gas chromatographic analysis of the final decomposition products of RC thermolysis at 483 K with the use of gas-liquid chromatograph SELMICHROM-1 [13].

Results and Discussion

SiO_2 nanoparticles with functional polymer shell were synthesized using sol-gel method in water-alkaline solution of functional surface-active copolymers in the presence of water ammonia as a catalyst (Fig. 1).

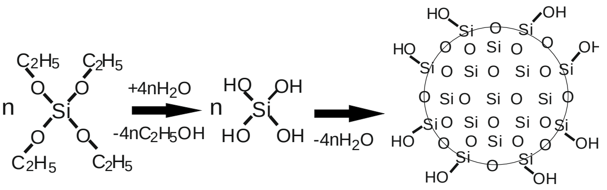

Fig. 1. Scheme of SiO_2 NP synthesis using Stober method

One can see that used technique provides the formation of spherical nanoparticles with predominantly unimodal size distribution and low polydispersity index (Fig. 2).

The influence of diverse parameters (reagent ratio, temperature, RC nature) onto nanoparticle growth kinetics and size was studied. The rate of particle growth is very high. After 5–10 min the curves of dependence of particle size on time reaches the plateau and after that particle size does not change (Fig. 4, 5). Particle size diminishes with the increase in water concentration. It can be explained as follows. Synthesis of SiO_2 NP consists of two stages: i) induction period of seed formation and ii) their growth due to condensation reaction of hydrolysis products. During the induction period the concentration of SiO_2 seeds growths. The rate of TEOS hydrolysis reaction increases with the increase in H_2O concentration causing the rise of quantity nanoparticle seeds during induction period and as a result the decrease in NP size.

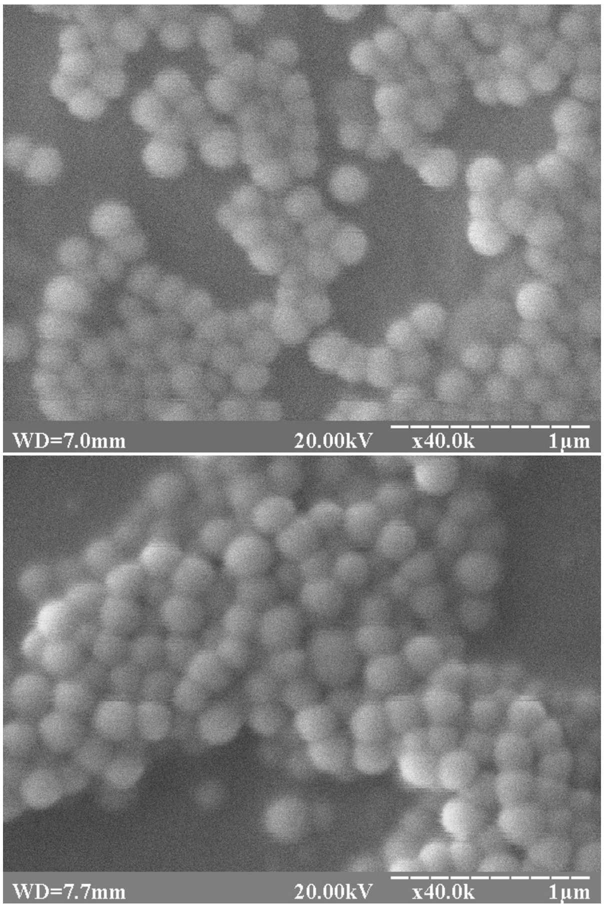

Fig. 2. SEM micrographs of SiO_2 NP obtained in presence of 5 % (a) and 50 % (b) RC-3 with respect to SiO_2 weight (T=303 K, C_{H2O}=25 mole/l, C_{NH4OH}=5 mole/l)

The increase in ammonia concentration leads to the rise of SiO_2 NP size (Fig. 5) that is in agreement with literature data [15]. Evidently in the case of high concentration, ammonia which is the catalyst TEOS hydrolysis reaction simultaneously accelerates the process of of particle growth due to condensation reactions. As a result of these processes the final particle size increases.

The rise of temperature causes the diminishing of particle size (Table 3) because in this case the rate of TEOS hydrolysis accelerates sharply and the number of seeds increases.

The study of dependence of particle size on RC concentration witnesses that with the increase in RC content in reaction mixture from 5 % to 20 % with respect to calculated SiO_2 weight the size of nanoparticles rises 20–50 % depending on copolymer nature (Fig. 5, Table 3). Such dependence evidently is explained by the increase (with increase in RC concentration) in size of micelle-like structures formed by RC that can serve as nanoreactors in which NP synthesis is carried out.

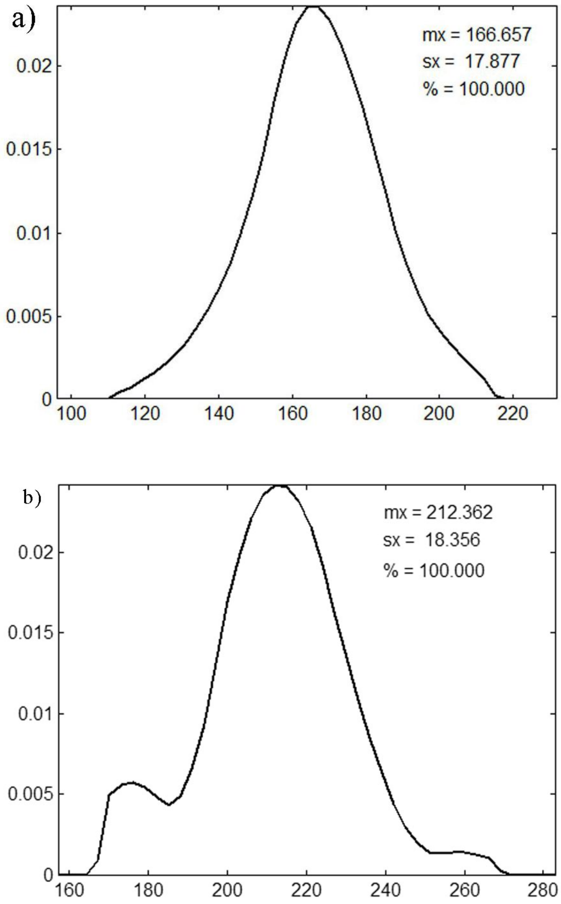

Fig. 3. Curves of size distribution of SiO_2 NP obtained in the presence of 5 % (a) and 50 % (b) RC-3 with respect to SiO_2 weight (T=303 K, C_{H2O}=25 mole/l, C_{NH4OH}=5 mole/l)

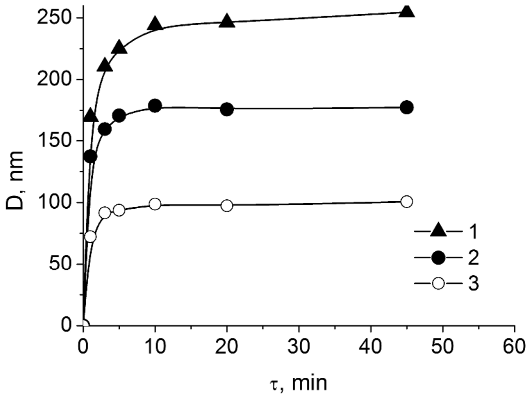

Fig. 4. Kinetics of SiO_2 NP growth in presence of 5 % RC-4 depending on H_2O concentration: C_{H2O}=20 mole/l (1), 25 mole/l (2), 30 mole/l (3) (T=303 K, C_{NH4OH}=2,5 mole/l)

Table 3

Synthesis conditions and characteristics of SiO_2 NP with polymer

№	RC composition	C_{PK}, % per SiO_2	C_{NH_4OH}, mole/l	T, K	Conversion, %	Dp, nm	RC adsorption onto SiO_2 surface			
							Elemental analysis		Chromatographic analysis	
							[C], %	A_{RC}, mg/g	$C_{O\text{-}O}$, %	A_{RC}, mg/g
1	–	–	2.5	303	95	198				
2	RC-1	5	2.5	303	96	200				
3	-"-	10	2.5	303	80	197				
4	-"-	50	2.5	303	81	277				
5	RC-2	5	2.5	303	93	203	1.1	18.7		
6	-"-	10	2.5	303	82	205	1.6	26.5		
7	-"-	50	2.5	303	81	291	2.0	34.1		
8	RC-3	5	5.0	303	96	215				
9	-"-	5	5.0	293	98	338				
10	-"-	50	5.0	303	88	275	2.3	39.2	0.087	41.2
11	-"-	50	2.5	303	86	215	2.5	42.8	0.101	48.4
12	RC-2a	50	2.5	303	81	197	2.3	39.9		

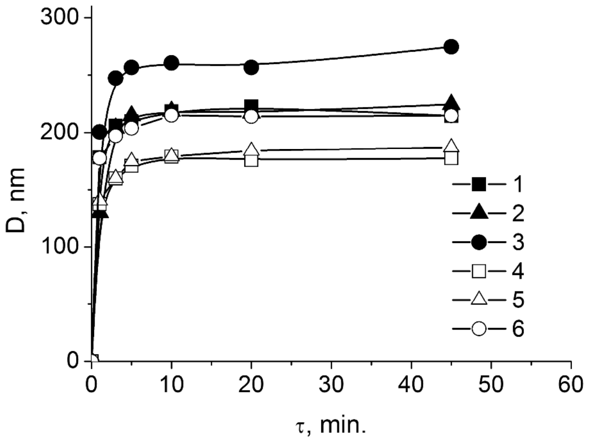

Fig. 5. Kinetics of SiO_2 NP growth in the presence of RC-4 at C_{NH4OH}=5 mole/l (1–3) and 2.5 mole/l (4–6): C_{RC}=5 % (1, 4), 10 % (2, 5), 50 % (3, 6) with respect to SiO_2 weight (C_{H2O}=25 mole/l, T=303 K)

For example, the study of dependence of hydrodynamic radius of micelle-like structures formed by RC-4 on concentration shown essential growth of their size (from 460 nm to 680 nm) with the increase in RC concentration from 5 % to 50 % with respect to SiO_2 weight. Besides, RC macromolecules adsorbed on the initial clusters of nanoparticles can facilitate their aggregation causing the increase in NP size.

It should be noted that the nature of RC has a significant influence on the size of SiO_2 NP. So, for nanoparticles synthesized in the presence of three-component RC-1 and RC-2 which slightly differ by the nature the particle size differs negligibly (Table 3, samples 2–4 and 5–7). But when we use four-component RC containing hydrophilic AcAm links, the size of SiO_2 nanoparticles decreased by 40 % (Table 3, sample 11). In the case of RC-2a containing tertiary amine groups (sample 12) which has basic properties and can interact with acidic groups on the surface of SiO_2 NP restricting their growth the particle size decreases even more noticeable. In these cases with the rise of RC concentration nanoparticle size increased as well. This proves our assumption that RC macromolecules can facilitate aggregation of primary clusters of silicon dioxide.

The RC adsorption value was determined by elemental ([C]) analysis and the presence of peroxide fragments in adsorption shell was proved by gas-chromatographic analysis of decomposition products of peroxide group immobilized on the nanoparticle surface (Table 3). Obtained results witness about rather high adsorption values on NP surface that can be explained by small size of nanoparticles and respectively high values of specific surface. The fact that with the decrease of NP size the value of RC adsorption increases (Table 3, samples 10 and 11) testifies this assumption.

Besides, the presence of peroxide-containing polymer shell on the NP sutface was proved by complex thermal analysis. In the derivatograms of synthesized SiO_2 nanoparticles the endothermic peak is observed on the DTA curve in the range of 330–400 K with simultaneous decrease of sample weight (Fig. 6) that is explained by the elimination of bonded water. With further temperature rise the exothermic peak appears on DTA curve at 465 K with simultaneous decrease of sample weight. This effect evidently corresponds to the decomposition of adsorbed peroxidic fragments.

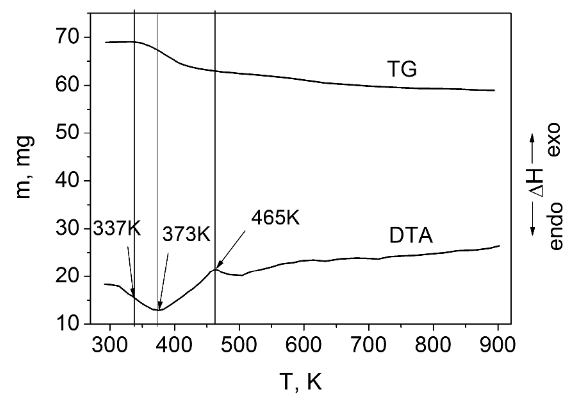

Fig. 6. Derivatogram of the sample of SiO_2 NP with peroxide-containing shell synthesized in the presence of 50 % RC

Conclusions

Spherical nanoparticles of silicon dioxide with the size of 190–350 nm and functional polymer shell were synthesized by nucleation from solution in the presence of reactive peroxide-containing copolymers. The kinetics of nanoparticle growth was studied and dependencies of SiO_2 NP size on copolymer nature and concentration and process parameters were established. Particle size increases with increase in concentration of catalyst (water ammonia) and reactive copolymers as well as with the decrease in temperature and water concentration that is caused by different effect of these factors onto process elemental stages – TEOS hydrolysis, nucleation and growth of particles. It was shown that the nature of RC has a significant influence on the size of synthesized SiO_2 NP. When four-component RC containing hydrophilic AcAm links was used the size of SiO_2 nanoparticles decreased by 40 %, while in the case of RC containing tertiary amine groups which had basic properties and could interact with acidic groups on the surface of SiO_2 NP restricting their growth the particle size decreased more noticeable. The presence on the SiO_2 NP surface of peroxide-containing polymer shell was proved by the methods of elemental analysis, complex thermal analysis, gas-liquid chromatography. The value of RC adsorption is rather high that is explained by small size of nanoparticles and respectively high values of specific surface.

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