# Synthesis of $SiO_2$ Nanoparticles with Functional Polymer Shell

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***Abstract* – Silica nanoparticles with functional polymer shell based on reactive peroxide-containing copolymers were synthesized via sol-gel method. The influence of copolymer content and process parameters onto process kinetics and nanoparticle size was studied. The formation of functional shell on the surface of silica nanoparticles was proved by gas-chromatography and derivatography.***

Keywords – radical copolymerization, functional copolymers, sol-gel process, nanoparticles, kinetics.

## Introduction

Silicon dioxide nanoparticles (NP) are promising for different applications owing to their remarcable physical properties and ability to be functionalized with a range of molecules and polymers [1]. At present time there are three general methods for the preparation of polymer/silica nanocomposites: blending, sol-gel processes, and in situ polymerization [2]. Sol-gel synthesis of amorphous nano$SiO_2$ via hydrolisis of diluted solution of tetraethoxy silane elaborated by Stober and Fitch is one of the simplest and most effective approach of silica nanoparticle formation. During last years, composite materials based on nanosized silicon dioxide have attracted increasing attention of many research groups [3]. But there is a sufficient difference between the surface energy of the dispersed $SiO_2$ and that of the dispersive medium in such systems. This causes poor wettability of the polar surface of $SiO_2$ particles by low polar matrix polymer leading to aggregation of mineral filler in composite. In this case the phase compatibilization can be achieved by means of the formation on the filler surface of polymer encapsulating shell with definite chemical and physical properties. Besides, the modification of the surface of fine mineral fillers with reactive copolymers allows to localize there diverse functional groups that makes possible to design the compatibilizing polymer layers with determined thickness and functionality at the phase boundary.

This work is devoted to the study of the process of sol-gel synthesis of silica nanoparticles with functional polymer shell and to determination of the influence of reactive copolymer content and nature on the process kinetics and properties of synthesized nanoparticles.

## Experimental

Reactive peroxide-containing copolymers (RC) were synthesized via radical copolymerization of acryl amide (AcAm), 5-tert-butylperoxy-5-methyl-1-hexene-3-yne (PM), butyl methacrylate (BMA) and maleic anhydride MA at overall monomer concentration 3 mole/l in the presence of lauroyl peroxide as an initiator (initiator concentration $2 \cdot 10^{-2}$ mole/l) in solutions of ethyl acetate. The synthesized copolymers were purified by double reprecipitation in hexane and dried to constant weight. The conversion of monomers was determined by dilatometric methods and controlled by gas-liquid chromatography and gravimetrically. The composition and some characteristics of synthesized RC are presented in Table 1.

The content of peroxide fragments in RC was determined via their thermal decomposition at 483K under argon, followed by gas chromatographic analysis of the main final decomposition products. The content of maleic anhydride links was determined by a reverse potentiometric titration of carboxylic groups. The AcAm subunit content was estimated from the results of elemental [N] analysis by the Dumas' method.

*Table 1*

Synthesis and some characteristics of peroxide-containing copolymers

| RC | Monomer mixture composition, %mol. | | | | Copolymer composition, %мол. | | | | Conversion*, % | | Wpol·$10^3$, %/s | Intr. viscosity in acetone, dl/g |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | AcAm | PM | BMA | MA | AcAm | PM | BMA | MA | D.r. | Dil. | | |
| 1 | - | 10 | 50 | 40 | - | 9.5 | 48.5 | 42.0 | 78.0 | 88.4 | 5.0 | 0.14 |
| 2 | - | 20 | 20 | 40 | - | 17.6 | 40.0 | 42.3 | 76.1 | 77.8 | 4.7 | 0.07 |
| 3 | 20 | 20 | 20 | 40 | 25.6 | 19.5 | 14.8 | 40.1 | 82.1 | 76.6 | 4.4 | 0.10 |

* - D.r. – dry residue method, Dil. – dilatometry method

Synthesis of $SiO_2$ NP was performed using sol-gel Stober method in the presence of reactive copolymers in two-neck reactor equipped with magnetic stirrer and reflux condenser at 303K. Firstly the solution of RC in ethanol/water/ammonia mixture was prepared ($C_{H2O}$=25mole/l, $C_{NH4OH}$=2.5-5.0mole/l). After complete dissolving RC in the solvent mixture tetraethoxy silane ($C_{TEOS}$=0.14mole/l) was added to reaction mixture at vigorous stirring.

The size of $SiO_2$ NP was measured via Dynamic light scattering method using DynaPro NanoStar dynamic light scattering detector (Wyatt Technology Co., USA). The formation of adsorbed polymer shell was proved by gas-chromatografic analysis and derivatography.

## Results and discussion

The copolymerization process proceeds with high enough rates and up to high conversion level (Fig. 1). As it was expected the increase in peroxidic monomer content in reaction mixture causes the decrease in copolymerization rate that is explained by the action of PM as weak polymerization inhibitor because it generates low-active radicals.

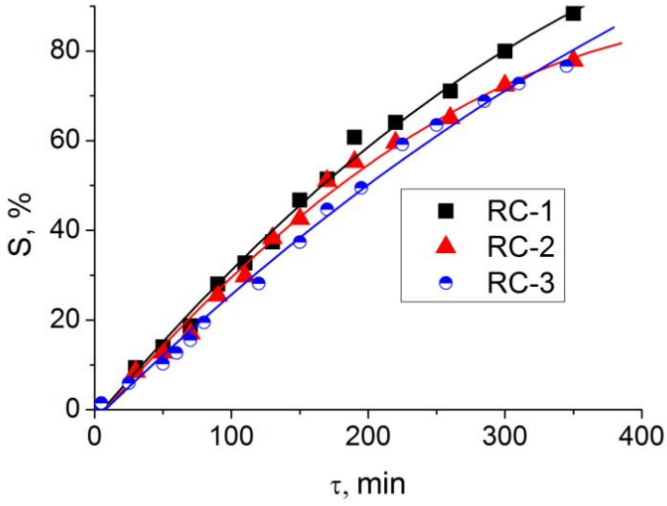

Fig.1. Dependence of copolymerization kinetics on the monomer composition

The content of monomer links in synthesized copolymer was determined and the influence of component concentration in reaction mixture on copolymer composition was studied (Table 1). One can see that the content of monomer links changes symbatically with the content of monomers in reaction mixture and copolymer composition is close to the monomer composition in reaction mixture. This is caused first of all by high monomer conversion. The increase in PM concentration leads to the molecular weight decrease of obtained peroxide-containing copolymers due to intencive chain transfer to PM molecules during copolymerization.

The dependence of kinetics of $SiO_2$ nanoparticle synthesis on the concentration and composition of reactive copolymers as well as on synthesis conditions was studied (Fig. 2, Table 2). One can see that the rate of particle growth is very fast. After 5 min the curves of dependence of particle size on time reaches the plateau. The increase in ammonia hydroxide concentration causes the increase in the rate of nanoparticle formation and as a result in increase of their size. At the same time with the rise of RC concentration in initial mixture from 5% to 50% with respect to the estimated weight of synthesized $SiO_2$ the nanoparticle size increases by 20-50% depending on the composition of RC.

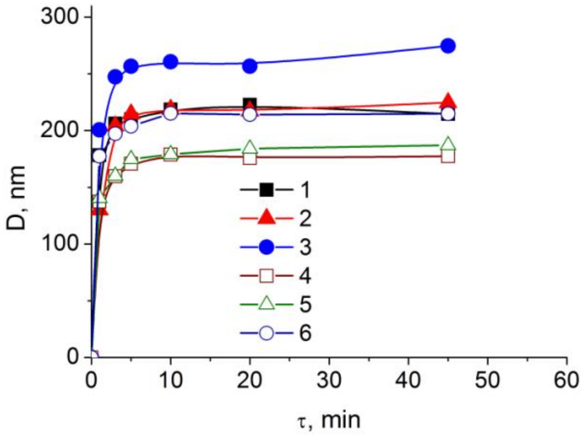

Fig. 2. Kinetic curves of $SiO_2$ nanoparticle size at different synthesis conditions. $C_{RC}$=5% (1, 4), 10% (2, 5), 50% (3, 6); $C_{NH4OH}$=5 mol/l (1-3), 2.5 mole/l (4-6)

It should be noted that the nature of RC has a significant influence on the size of $SiO_2$ nanoparticles. So, for nanoparticles synthesized in the presence of three-component RC-1 and RC-2 the particle size differs negligibly (2-7% at equal concentrations) but when we use four-component RC containing AcAm links the size of $SiO_2$ nanoparticles decreased by 40% (Table 2). Evidently such RC composition provides its higher surface activity compared to RC-1 and RC-2 that causes the decrease of the size of particles synthesized in its presence.

*Table 2*

Synthesis conditions and characteristics of $SiO_2$ nanoparticles with polymer shell

| № | RC composition | $C_{PK}$, % per $SiO_2$ | $C_{NH4OH}$, mole/l | Conversion, % | Dp, nm | $C_{O-O}$, % | $A_{RC}$, mg/g |
|---|---|---|---|---|---|---|---|
| S-14 | RC-1 | 5 | 2.5 | 96 | 200 | | |
| S-15 | "-" | 10 | "-" | 80 | 197 | | |
| S-16 | "-" | 50 | "-" | 81 | 277 | | |
| S-17 | RC-2 | 5 | "-" | 93 | 203 | | |
| S-18 | "-" | 10 | "-" | 82 | 205 | | |
| S-19 | "-" | 50 | "-" | 81 | 297 | | |
| S-8 | RC-3 | 5 | "-" | 98 | 177 | | |
| S-11 | "-" | 10 | "-" | 89 | 187 | | |
| S-7 | "-" | 50 | "-" | 86 | 215 | 0.48 | 214 |
| S-4 | "-" | 50 | 5.0 | 88 | 275 | 0.34 | 183 |

The content of irreversibly adsorbed peroxide-containing shell on $SiO_2$ NP surface determined by gas-liquid chromatography is rather high and increase with the decrease of ammonia concentration in reaction mixture (Table 3). This can be explained by the decrease in RC solubility in reaction solution with pH decrease that causes the enhancement of adsorption value of reactive copolymers.

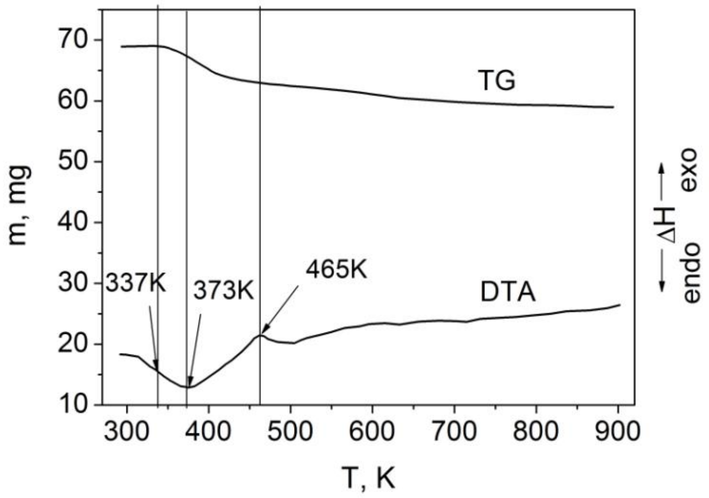

Fig.3. Derivatogram of $SiO_2$ nanoparticles with peroxide-containing shell (Sample S-4)

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 exothermic peak is observed on the DTA curve at 465K with simultaneous decrease of sample weight (Fig. 3) that corresponds to the decomposition of adsorbed peroxidic fragments.

## Conclusions

Thus, $SiO_2$ nanoparticles with irreversively adsorbed polymer shell based on reactive peroxide-containing copolymers were sunthesized using Stober sol-gel method. It was shown that that the rate of particle growth is very fast and after 5 min the curves of dependence of particle size on time reaches the plateau. Particle size depends on polymer composition and concentration in reaction mixture. It is larger for three-component RC as compared with four-component ones containing AcAm links and enhances with the increase in RC concentration. The content of irreversibly adsorbed peroxide-containing shell on $SiO_2$ nanoparticle surface is rather high that is proved by gas-liquid chromatography and derivatography

## References

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