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Formation of Hollow Polymeric Microspheres with Functionalized Surface on the Basis of Latex Particles with Multilayered Structure

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Summary: Latices with "core-shell" particle morphology containing polar "core" and a shell on the basis of copolymer of styrene and functional vinyl monomer (allyl alcohol, vinyl acetate, methacrylic acid) has been obtained as a result of graft-copolymerization initiated from the surface of (meth)acrylate latex particles previously modified with functional polyperoxides. The processes of functional shell grafting as well as the processes of latex particle swelling with obtaining hollow microspheres due to neutralization of core carboxylic groups have been studied.

Keywords: "core-shell" particles; graft-polymerization; hollow microspheres; latex; polyperoxide

Introduction

Nowadays the obtaining and application of the systems with lowered dimensions including quantum dots, nanowires, monomolecular well-ordered layers, or nanocrystals are the basic directions of nanotechnologies. Nanosized objects possess unique properties strongly different from the properties of corresponding macromaterials. Hollow polymeric nano- and microspheres with functionalized outer surface are extremely interesting objects for many diverse applications. The possibilities of nanoparticle organization into periodical structures allow to obtain useful applications not only from constituent materials as individual units, but also from their long-range mesoscopic ordering.[1] Hollow polymeric microspheres (HMS) are sharply interesting objects for the creation of well-ordered 2D and 3D structures due to the interactions of functional groups immobilized on their surface.

In order to produce HMS diverse approaches are utilized. So, the use of inorganic particles (silica particles) as the templates of HMS followed by core elimination with HF has been proposed.[2] Polystyrene microspheres have been synthesized via suspension polymerization of monomer droplets in the presence of hexadecane.[3] In this case the cavities are formed as a result of phase separation of polystyrene and hexadecane. The use of "core-shell" latex technology for the synthesis of precursores that after elimination of core polymer form hollow particles is the prospective method for their obtaining.[4] On the other hand the technique of the ordered cluster creation as a result of mixing of latices with particles carrying opposite charges – negative (sulfonate groups) and positive (amidine groups $C(NH_2)=NH_2^+$) ones - has been described.[5]

We have developed a new method for obtaining the latices with a "core-shell" morphology of the particles. As compared with known methods, the main distinction of the developed method consists in chemical modification of the surface of core particles by peroxide surface-active copolymers serving at the next stage as macroinitiators (PMI) for the process of shell formation.[6] As a result the reactions of initiation and chain growth during the shell

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polymerization are localized at the particle surface thus diminishing the probability of secondary particle formation.

In the present paper we report on the results of the investigations aimed at the latex obtaining with ''core-shell'' particle morphology with the particle shell containing diverse functional groups (alcohol, carboxylic, ester) as well as at the formation of hollow polymeric microspheres on their basis.

Experimental Part

Materials

Monomers: styrene (St, Merck), methyl methacrylate (MMA, Aldrich), acrylic (AAc, Aldrich), and methacrylic (MAc, Aldrich) acids were purified by double vacuum distillation. Vinyl acetate (VA, Aldrich) was purified by distillation at normal pressure. Allyl alcohol (AlAlc, Aldrich) was used as received. Divinylbenzene (80%) (DVB, Aldrich) was washed with a 5 wt % sodium carbonate solution three times for the removal of the inhibitor, and then it was washed with distilled water five times and was dried with a 4-Å molecular sieve.

Ammonium persulfate (APS, Merck) was used as initiator of emulsion polymerization. Dowfax 2EP (Dow Co.) was used as surfactant for latex stabilization.

As peroxide macroinitiator (PMI) we have used peroxide-containing surface-active cooligomer of 5-tert-butylperoxy-5-methyl-1-hexene-3-yne with maleic anhydride (51: 49% mol) synthesized via radical copolymerization of monomers in acetone in the presence of lauroyl peroxide as initiator as described elsewhere.[7]

Procedure

Core latices were synthesized via conventional emulsion copolymerization of vinyl monomers [8] in the presence of Dowfax 2EP as emulsifier and ammonium persulfate as initiator at 343K. Composition and some colloidal-chemical characteristics are presented in Table 1.

Peroxidic modification of core latices was performed as follows. Water-alkaline solution of 10% PMI was prepared separately and then added to core-polymer latex (5% PMI with respect to core latex polymer). The mixture was stirred firstly at ambient temperature for 30 min and then at 353 K for 80 min. As a result the latices containing particles with grafted PMI layer were obtained.

Formation of polymer shell was carried out via graft copolymerization of styrene and functional monomers with DVB as curing agent initiated from peroxidized surface of core latex particles. The initiation was realized owing to redox decomposition of previously immobilized PMI in the presence of Ferrous-Trilon complex and rongalite as reducing agent at 318 K. Monomer mixture was added dropwise during 2 hours to create the conditions of ''monomer starvation''.

Hollow microspheres has been obtained from ''core-shell'' latex particles as a result of latex heating at the temperature close to glass transition temperature of shell polymer during 1.5 hours in the presence of neutralizing agent. 10% solution of NH_4OH or NaOH has been used as neutralizing agent at mole ratio of core carboxylic groups to base as 1:2.

Analysis

The control of monomer conversion was performed by estimation of non-volatile

Table 1.
Composition and Some Colloidal-Chemical Characteristics of Initial Core and Peroxidized Core Latices.

Latex polymer	NVR, %	Conversion, %	pH	D_{part}, nm	Surface tension, mN/m	TFC, mmol/l
poly(MMA-co-AAc) (85:15)	10.1	97	2.6	120	52.2	280
poly(MMA)	10.2	98	2.8	100	55.8	90
poly(MMA-co-AAc) with grafted PMI	10.0	–	6.5	120	48.6	250
poly(MMA) with grafted PMI	10.1	–	6.6	110	49.5	80

residue (NVR) as well as with the aid of gas-liquid chromatography.

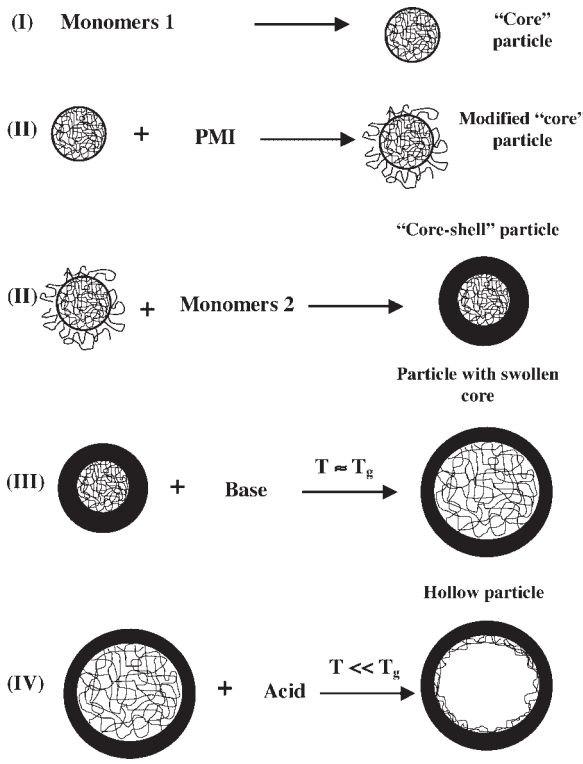
Particle sizes were determined applying Malvern System 3000. Latex stability to electrolyte effect was studied determining threshold of fast coagulation (TFC) by ''minute turbidity''.[9] Surface tension on the latex-air phase boundary was determined by the method of maximum pressure in bubble using PPNL device (Ukraine). IR spectra of latex polymer were obtained with Specord M80 spectrophotometer. Amount of peroxide groups on the surface of latex particles after PMI grafting was measured using gas-liquid chromatography as well as complex thermal analysis of the samples latex polymer precipitated into methanol (that is the solvent for PMI) with ''Derivatograf Q-1500D''. Optical density of polymer films was measured using photocolorymeter LMF 72M (Ukraine).

Results and Discussion

The main idea of proposed approach for creation of hollow microspheres is presented in Scheme 1.

The latices on the basis of copolymers of methyl methacrylate and acrylic acid as well as methyl methacrylate latex for comparison were used as core particles (Table 1). These latices are adsorptive unsaturated but possess quite high stability to electrolyte.

After latex modification with peroxide-containing copolymer latex particle size does not changes that witnesses in favour the absence of particle flocculation during PMI immobilization via the radical grafting reactions at the expense of partial decomposition of peroxide groups of PMI. The results of complex thermal analysis prove chemical bonding of PMI to the latex



Scheme 1.
Hollow polymeric microsphere formation with the use of peroxide macroinitiators.

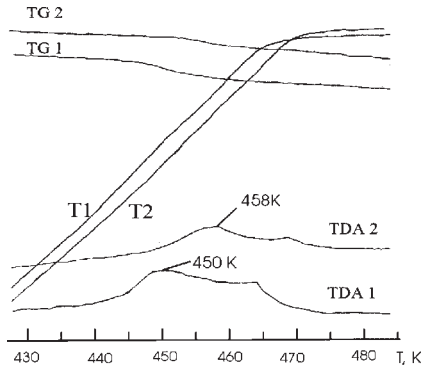


Figure 1.
Derivatograms of PMI (1) and poly(MMA-co-AAc) latex modified by it (2).

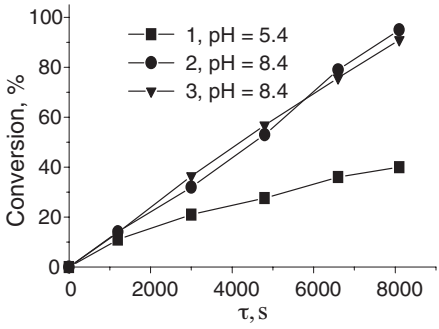


Figure 2.
Kinetics of pSt shell polymerization at diverse initial latex pH. Core - poly(MMA-co-AAc) (1, 2), poly(MMA) (3); "core":"shell" = 1:2.

particle surface. Importantly, more than 80% of initial peroxide groups are conserved in immobilised PMI.

One can see that the peak, corresponding to exothermic effect of PMI peroxide group decomposition is present on both derivatograms (Figure 1). Its negligible shift towards higher temperature for the sample of peroxidized latex can be explained evidently by low thermal conductivity of latex polymer that results in some delay of real temperature in the sample as compared with the device indications.

Obtained peroxidized latices have been used as the seeds for the formation of the latices with "core-shell" particle morphology. The studies of shell polymerization kinetics at different initial latex pH reveal that in alkaline medium 90-95% conversion is reached whereas in the case of acidic pH polymerization stops at 40-50% conversion (Figure 2). This phenomenon can be caused by the anionic nature of PMI. In alkaline medium its chains are unfolded that facilitates the access of redox system components and monomers to its peroxidic groups.

One can see that quite stable latex with a low content of residual monomer has been obtained (Table 2). As a result of shell formation latex particle size increases and within the limits of the methods the size conforms with calculated values (Figures 3,4). This witnesses the formation of latex with "core-shell" particle morphology as well as the absence of homonucleation of new polymer particles in the latex. The presence of polar functional groups in the outer layer influences essentially the stability of obtained latices, which decreases in the case of introduction of methacrylic acid or vinyl acetate links into the shell structure.

Reflection IR-spectra of latex polymer films prove the formation of functionalized

Table 2.
Characteristics of "core-shell" Latices ("core":"shell" = 1:6).

Shell polymer	NVR, %	Conversion, %	pH	D_{part}, nm	Surface tension, mN/m	TFC, mmol/l
core polymer - poly(MMA-co-AAc) (85:15)						
poly(St-co-DVB) (100:0.5)	10	95	7.3	300	56.8	60
poly(St-co-AlAlc-co-DVB) (95:5:0.5)	9.4	89	7.1	310	58.2	80
poly(St-co-MAc-co-DVB) (95:5:0.5)	9.6	89	6.6	430	51.5	30
poly(St-co-VA-co-DVB) (95:5:0.5)	9.5	88	6.8	400	51.8	35
core polymer - poly(MMA)						
poly(St-co-DVB) (100:0.5)	10	96	7.1	240	52.6	75

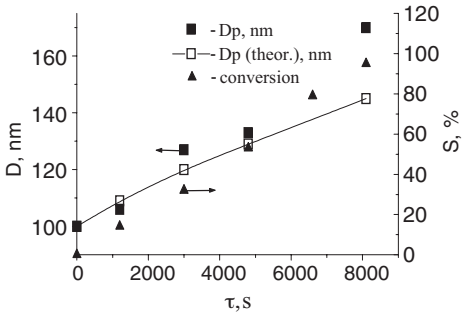


Figure 3.
Dependence of shell monomer conversion and latex particle diameter on polymerization time. (''core'': ''shell'' = 1:2; core - poly(MMA-co-AAc), shell - poly(St-co-DVB)).

shell on the surface of latex particles (Figure 5). One can see that in the spectrum of core poly(MMA-co-AAc) latex (Figure 5-1) adsorption bands are presented assigned to carbonyls of MMA and AAc links (~1730 cm^{-1} and ~1700 cm^{-1}, respectively). In the spectrum of ''core-shell latex'' with poly(St-co-AlAlc-co-DVB) shell (Figure 5-2) the bands appear corresponding to δ_{C-H} of aromatic ring (1948 cm^{-1}, 1868 cm^{-1} and 1800 cm^{-1}).

From the other hand the band corresponding to acidic carbonyl (~1690 cm^{-1}) practically disappears. At the same time in the spectrum of latex with with poly

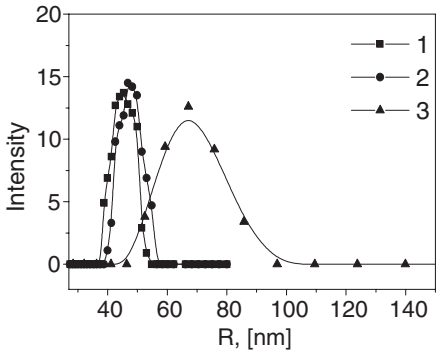


Figure 4.
Curves of size distribution of latex particles obtained by dynamic light-scattering. Poly(MMA-co-AAc) latex (1), poly(MMA-co-AAc) latex modified with PMI (2), ''core-shell'' latex (pSt shell, ''core'':''shell'' = 1:6) (3).

(St-co-MAc-co-DVB) shell (Figure 5-3) the adsorption bands assigned to δ_{C-H} of aromatic ring are present as well and the intensities of the bands of ester and acid carbonyls are almost the same because the quantity of MAc introduced into the particle shell is close to MMA amount in the core.

Hollow microspheres have been obtained by heating of obtained ''core-shell'' latices at the temperature close to glass transition temperature of shell polymer in the presence of neutralizing agent. The processes of particle swelling with hollow formation have been studied depending on the nature of core and shell polymer as well as on the nature of neutralizing agent. Characteristics of neutralized latices are presented in Table 3.

One can see that KOH is more effective neutralizing agent as compared with water ammonia. Besides, it is significant that the highest swelling degree is observed for the latex particles with poly(MMA-co-AAc) core and poly(St-co-DVB) or poly(St-co-AlAlc-co-DVB) shell. In the case of latex particles on the basis of homo poly(MMA) particle swelling is not observed. Obviously, in the case of the carboxylic group absence in the particle core the hydrogel that causes the increase of osmotic pressure at elevated temperatures and as a result particle swelling is not formed. Latices containing MAc and VA links in particle shell show similar behaviour. For these latices the higher ratio of neutralizing agent to acrylic acid links is necessary, because some amount of base is consumed for neutralization of shell carboxylic groups in the case of poly(St-co-MAc-co-DVB) and on the other hand in the case of poly(St-co-VA-co-DVB) shell the hydrolysis of vinyl acetate links proceeds with the formation of carboxylic groups. At the same time the introduction of allyl alcohol links does not practically influence swelling degree of latex particles.

In order to prove the structure of obtained latex particles we have studied optical properties of the films obtained from core latices, ''core-shell'' latices

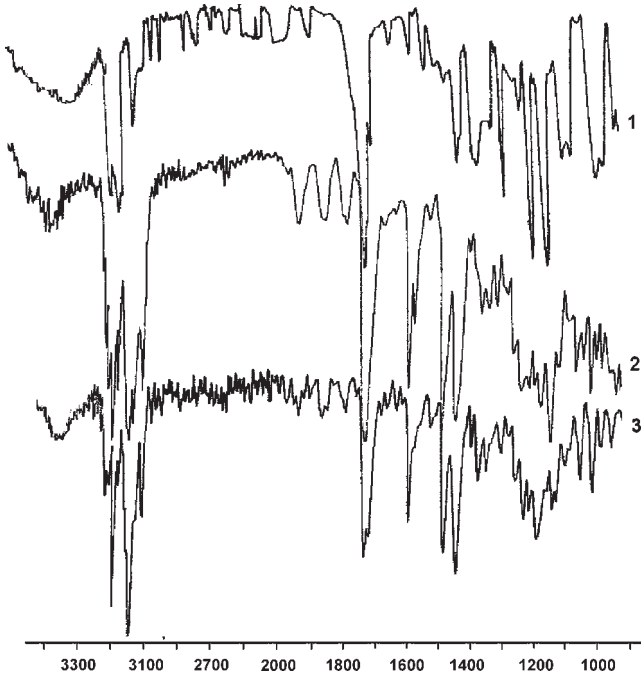


Figure 5.
Reflection IR-spectra of latex polymers. Core poly(MMA-co-AAc) latex (1), latices ''core-shell'' with poly(-St-co-AlAlc-co-DVB) shell (2), poly(St-co-MAc-co-DVB) shell (3).

and ''core-shell'' latices after neutralization of carboxylic groups (Table 4). One can see that the optical densities of peroxidized core latex and core shell latex are almost the same. At the same time the optical densities of the films on the basis of neutralized ''core-shell'' latices increase sharply. Obtained data witness the void formation in latex particles. As it is known microspheres that contain voids scatter light much better than solid particles because of great difference of refractive indices

Table 3.
Characteristics of Neutralized ''core-shell'' Latices.

Shell polymer	pH		D_p, nm	
	Before heating	After heating	Before heating	After heating
Neutralizing agent – KOH				
poly(St-co-DVB) (100:0.5)	11.5	10.9	330	410
poly(St-co-AlAlc-co-DVB) (95:5:0.5)	11.8	10.7	300	360
poly(St-co-MAc-co-DVB) (95:5:0.5)	11.8	10.6	410	420
poly(St-co-VA-co-DVB) (95:5:0.5)	11.4	9.7	390	410
poly(St-co-DVB) (100:0.5)*	11.2	10.6	230	240
Neutralizing agent – NH_4OH				
poly(St-co-DVB) (100:0.5)	10.1	9.7	330	390
poly(St-co-AlAlc-co-DVB) (95:5:0.5)	10.5	10.2	300	320
poly(St-co-MAc-co-DVB) (95:5:0.5)	10.5	10.1	415	420
poly(St-co-VA-co-DVB) (95:5:0.5)	10.6	9.8	390	400
poly(St-co-DVB) (100:0.5)*	10.2	9.9	230	235

[Core polymer - poly(MMA-co-AAc) (85:15), ''core'':''shell'' = 1:6, T = 368 K].
* - core polymer – poly(MMA).

Table 4.
Optical Properties of Latex Films

Latex nature	Film thickness, μm	Optical density, μm^{-1}
poly(MMA-co-AAc)	80	0.10
poly(MMA-co-AAc) with immobilized PMI	85	0.48
"Core-shell" latex with poly(St-co-AlAlc-co-DVB) shell ("core":"shell" = 1:6)	91	0.45
"Core-shell" latex neutralized with KOH	89	0.78
"Core-shell" latex neutralized with NH_4OH	90	0.56

on the polymer-polymer and polymer-air interphace

Conclusions

A method has been developed that allows to obtain latices with "core-shell" particle morphology, with a core that consists of copolymers containing carboxylic groups and is able to swell under certain condition in water-alkaline medium, and a shell on the basis of partially cross-linked copolymers of styrene, divinylbenzene, and functional monomer. Stable "core-shell" latices with the shell bearing various functionalities (e.g. carboxyl, hydroxyl, ester) have been obtained. Study of the shell formation process showed the latex particle size increasing as conversion is enhancing. That witnesses the formation of the particles with a core-shell structure. Moreover the presence of only one peak in the curve of the particle size distribution points out no nucleation of new particles in the water phase taking place in this system. IR-spectra of latex films prove the formation of functionalized shell on the surface of peroxide-modified core latex particles. Hollow microspheres with functionalized shell have been obtained on the basis of synthesized latices with multilayered particles that can be used for the creation of well ordered 2D and 3D structures due to the interactions of functional groups immobilized on their surface.

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