ISSN 1070-3632, Russian Journal of General Chemistry, 2007, Vol. 77, No. 3, pp. 354–362. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © A.Yu. Men'shikova, B.M. Shabsel's, Yu.O. Skurkis, K.S. Inkin, N.A. Chekina, S.S. Ivanchev, 2007, published in Zhurnal Obshchei Khimii, 2007, Vol. 77, No. 3, pp. 386–394.

Magnetic Polymer Particles: Synthesis and Properties

A. Yu. Men'shikova[a], B. M. Shabsel's[a], Yu. O. Skurkis[a], K. S. Inkin[a], N. A. Chekina[b], and S. S. Ivanchev[b]

[a] *Institute of High Molecular Compounds, Russian Academy of Sciences,*
Bol'shoi pr. 31, St. Petersburg, 199004 Russia
e-mail: asya@hq.macro.ru
[b] *Boreskov Institute of Catalysis, St. Petersburg Branch,*
Russian Academy of Sciences, St. Petersburg, Russia

Received October 30, 2006

Abstract—A possibility of preparation of monodisperse magnetic polymer particles containing carboxylic groups by the methid of emulsion (co)polymerization in the presence of a magnetic liquidis considered. Angulation of the magnetite nanoparticles by polymeric spheres of styrene–acroleine copolymer followed by incapsulation to the polystyrene coat is studied. Monodisperse particles with inclusion of the magnetite nanoparticles 30 nm to 1 μm size containing up to 5.6 μmol g^{-1} surface carboxylic groups are obtained, their electrosurface and magnetic properties are studied.

DOI: 10.1134/S1070363207030061

Monodisperse polymeric microspheres produced commonly by the method of emulsifierfree emulsion (co)polymerization find wide application in many areas of science and technology. In biotechnology, they are used for separating and concentrating biopolymers aqueous solutions [1]. Microspheres with functional groups for covalent binding of bioligands are widely used in immunoanalysis as carriers for the immunoreagents at visualization of immunochemical reactions. A perspective direction is preparation of magnet controlled carriers for the immunoreagents or sorbents for capturing certain biomolecules, such as nucleic acids and proteins, and fragments of viruses and bacterial cells [2–6]. Specific binding of targeted molecules with recognizing them ligands on a magnetic particle surface followed by their separation from admixtures by the action of magnetic field allows simplify significantly many processes in biotechnology and immunoanalysis [2, 3]. In analytical microchips such particles can be used for selective transfer of the components of biological fluids under the action of magnetic field [7]. Biocompatible magnetic particles are used in vivo for predetermined transport of bound by them remedies to a target organ [8], as contrasting reagent in diagnosis by the methods of computer tomography [9], and for treatment of damaged tissue where the magnetic particles are concentrating by their local heating at the action of magnetic field [7, 8]. Each area requires development of the methods for preparation of magnetic polymer particles with predefined dispersion, surface functionality and magnetic characteristics. In this aspect, our work is aimed at the synthesis of monodisperse particles in the nanometer range possessing surface functional groups for binding bioligands, based on magnetite nanoparticles, synthetic polymers and natural polysaccharide dextran. Besides, it was reasonable to prepare particles of micrometer size which could be used as carriers for immunoreagents in the immunoanalysis.

RESULTS AND DISCUSSION

In the first series of experiments the magnetite containing particles were prepared by polymerization of styrene and copolymerization of styrene and methacrylic acid in the presence of a magnetic fluid stabilized by polyvinyl alcohol (Table 1, exp. no. 1m, Fig. 1b). Preparing the magnetite-containing polymer particles in the absence of an emulsifier and ionogenic monomer (exp. no. 1) due to deficiency in stabilizers resulted in formation of polydisperse composite particles. (Fig. 2a). Insertion of anionactive emulsifier Aerosol OT and methacrylic acid as a carboxyl-containing comonomer only allowed to obtain a stable dispersion of magnetic latex with particle size about 100 nm (exp. no. 2, Fig. 2b). It was a result of formation of mixed layers of the emulsifier and polyvinyl alcohol on the surface of growing polymer-monomeric particles and formation of electrostatic barrier at the ionization of carboxylic groups in the links of metha-

Table 1. Characteristics of magnetic fluids

Magnetic fluid no.	Fe_3O_4, mg ml^{-1}	Dry residue, mg ml^{-1}	Fe_3O_4 in dry residue, weight fraction	Polymer stabilizer in dry residue, weight fraction
1m[a]	49	128	0.38	0.62
2m	2.73	20.7	0.13	0.87
3m	6.84	79.8	0.08	0.92
4m	9.03	71.4	0.13	0.87
5m	30.5	276	0.11	0.89

[a] Magnetic fluid stabilized with polyvinyl alcohol, other are stabilized with dextran.

crylic acid and sulfonic groups in emulsifier, preventing aggregation of particles in the process of the synthesis.

In the next series of experiments, the composite particles were formed by copolymerization of styrene with methacrylic acid in the presence of magnetic fluids stabilized with dextran (Table 1, exp. nos. 2m–5m). Table 2 shows conditions of the syntheses and average size of the obtained composite particles. In all the cases with two-step loading of initiator, except exp. no. 6, stable dispersions were obtained. By means of electron spectroscopy we showed that they were distributed by size in narrow enough region 30–115 nm. The largest particles were obtained in exp. no. 3, where monomers were loaded to the reaction mixture in portions. But from the electron microscopy data follows that not all amount of magnetite was introduced to the polymer particles (Fig. 3). In exp. no. 3 the magnetite particle localized on the microsphere surface, in exp. no. 7 and some others the free magnetite nanoparticles remained in the dispersion medium. Due to magnetic interaction, the nanoparticles of the parent fluid are difficultly separating from the composite particles forming in the course of polymerization.

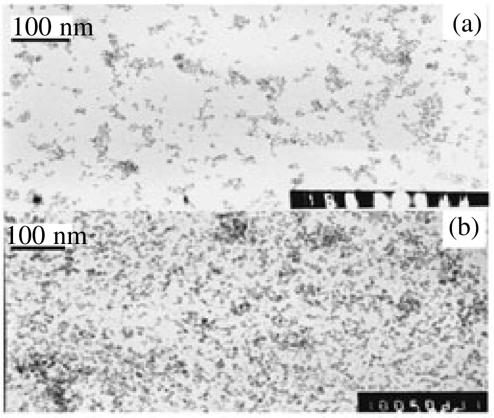

Fig. 1. Magnetic fluid stabilized with (a) dextran and (b) polyvinyl alcohol.

For improving synthetic procedure we increased concentration of the magnetic fluid stabilized with dextran (Table 1, exp. no. 5m). This allowed us to perform this synthesis in more favorable concentration range. Besides, for providing stability of growing particles we added to reaction mixture Disponil AES 60 IS, an anionactive emulsifier which is used for production of highly disperse emulsion polymers. We

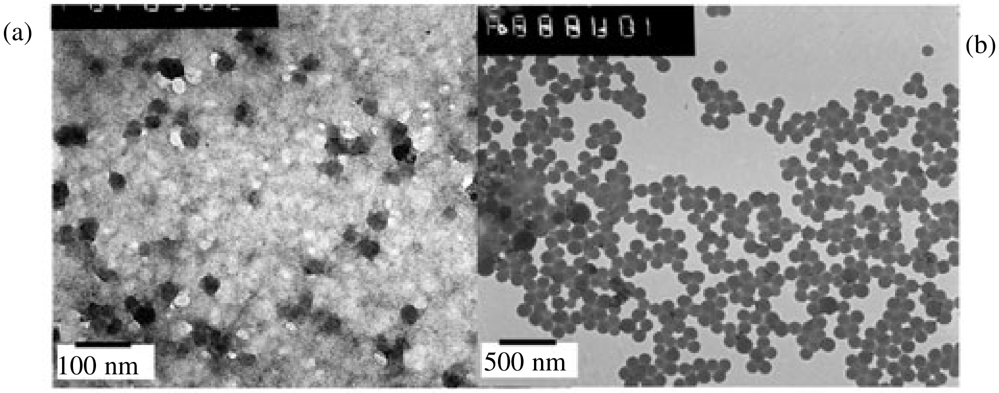

Fig. 2. Particles obtained by polymerization in the presence of magnetic fluid stabilized with polyvinyl alcohol, (a) exp. no. 1 and (b) exp. no. 2.

Table 2. Synthesis of magnetic particles based on styrene copolymer with methacrylic acid (10:1)

Exp. no.	Reaction mixture composition, wt% to water			Average diameter of particles, nm
	Fe_3O_4	monomers	$K_2S_2O_8$	
3	0.26	2.6	0.04 (loading in portions)	115
4	0.50	5.3	0.07	31
5	0.50	5.3	0.15	85
6	0.50	2.6	0.07 + 0.08 (after 100 min)	65
7	0.60	6.0	0.19	59
8	0.60	6.0	0.27	80
9	0.30	3.0	0.1	75

varied the monomer nature (styrene was mixed either with methacrylic acid, or with methyl methacrylate), the magnetic fluid stabilizer type (dextran or polyvinyl alcohol), and initiator type [potassium persulfate or 4,4'-azobis(4-cyanovaleric acid)] (Table 3). This approach allowed us to obtain stable dispersions of composite particles with the size in the range 30–54 nm. The experiments in the absence of buffer sodium hydrophosphate in the reaction mixture were unsuccessfull. Thus, in exp. no. 10 free magnetite coexisted with composite particles of styrene and methacrylic acid copolymer (Fig. 4a). In exp. no. 13 the magnetic fluid stabilized by polyvinyl alcohol (Table 1, exp. no. 1m) mostly coagulated in the first step of the synthesis. Instability of the polymerization system at the initiation with potassium persulfate can be a result of acidification of reaction mixture due to transfer of radicals to water [13].

To avoid this effect we added to the reaction mixture a salt (sodium hydrophosphate) which maintained weak alkaline medium in the course of the synthesis. Under these conditions the links of methacrylic acid and terminal carboxylic groups from the residue of azo-initiator provided enough negative charge to the growing particles surface [15]. This allowed us to obtain the magnetite-containing particles of plymethylmethacrylate and styrene with methacrylic acid copolymer with less size than in the preceding series of experiments. The carboxylic group concentration on the surface of polymethylmethacrylate microsphere prepared with the carboxylcontaining azo-initiator was naturally higher than with potassium persulfate. Comparison of carboxylic groups concentration on the surface of polymethylmethacrylate particles in exp. no. 11 and no. 14 at initiation polymerization with 4,4'-azobis(4-cyanovaleric acid) shows that particle surface carboxylation is markedly higher with dextran as polymer-stabilizer.

Occurrence of polyvinyl alcohol in the reaction mixture equalizes effects of the modes of introduction the carboxylic group containing particles into surface level, by methacrylic acid links or by carboxyl-containing azoinitiator. Average concentration of carboxylic groups at the surface was achieved the values in the range 1.73–1.95 μmol g^{-1}. The composite nanoparticles also were close by average size, about 50 nm. Study of the samples obtained by the method of electron microscopy showed that occurrence of buffer salt in the mixture results in formation of stable dispersions of the composite particles with enough narrow for the nanometer scale distribution by size (Fig. 4).

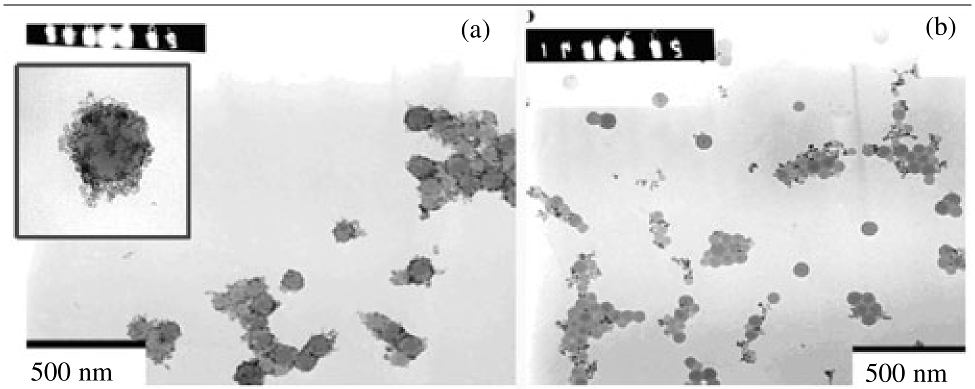

Fig. 3. Particles prepared by coplymerization of styrene with methacrylic acid in the presence of magnetic fluid stabilized with dextran in (a) exps 3 and (b) exp. 7 (Table 3).

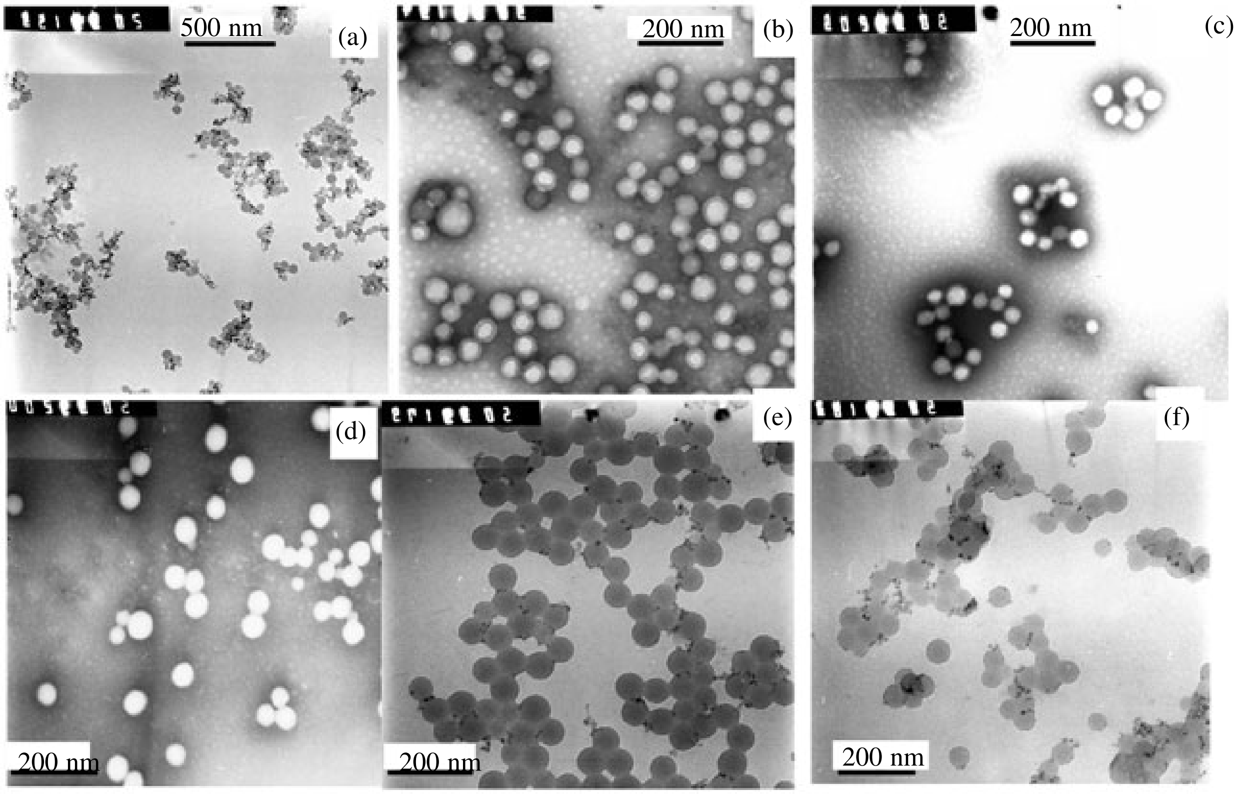

Fig. 4. The partyicles of styrene–methacrylic acid coplymer (10, 15, 16) and polymethylmethacrylate (11, 12, 14) prepared in the presence of magnetic fluid stabilized with dextran in the syntheses: (a) 10, (b) 11, (c) 12, (d) 14, (e) 15, and (f) 16 (Table 4).

Figure 5 shows plots of ζ-potential of the surface of magnetic fluid particles stabilized with dextran (Table 1, exp. no. 2m) and of a series of magnetic latexes on pH and ion strength of the disperse medium. The magnetite particles possess weak positive charge in the region pH < 10, that is, under conditions of the polymerization process. On the contrary, all the obtained composite nanoparticles were charged negatively due to occurrence of carboxylic and sulfonic groups at the surface. The same character of the par-

Table 3. Synthesis of latexes in the presence of magnetic fluid and Disponil AES 60 IS emulsifier

Run no.	Components of reaction mixture[a]					Characteristics of latexes			
	Fe_3O_4, wt %	monomers	stabilizer	initiator	NaH_2PO_4	dry residue, %	Fe_3O_4 in dry residue, weight fraction	average particle size, nm	$[COOH] \times 10^5$, μmol g^{-1}
10	1.65	St/MA	Dextran	$K_2S_2O_8$	–	1.18	–	47	–
11	1.67	MMA[b]	Dextran	CVA[c]	10^{-2} M	4.35	0.11	45	5.62
12	0.86	MMA	Dextran	$K_2S_2O_8$	10^{-2} M	9.92	0.03	30	0.93
13	1.65	St/MA	PVA	$K_2S_2O_8$	–	3.27	–	74	–
14	1.67	MMA	PVA	CVA	10^{-2} M	7.35	0.10	45	1.73
15	1.67	St/MA	PVA	CVA	10^{-2} M	8.94	0.08	54	1.95
16	1.67	St/MA	PVA	$K_2S_2O_8$	10^{-2} M	8.87	0.11	45	1.88

[a] The components of reaction mixture in wt% to water: monomers 15 including styrene/methacrylic acid (St/MA) 10 : 1; dextran 13.3; polyvinyl alcohol (PVA) 2.7; initiator 0.3; Disponil AES 60 IS (sodium alkylarylpolyglycol ether sulfate) 1.5. [b] MMA is methylmethacrylate. [c] CVA is 4,4'-azo-bis-4-cyanovaleric acid.

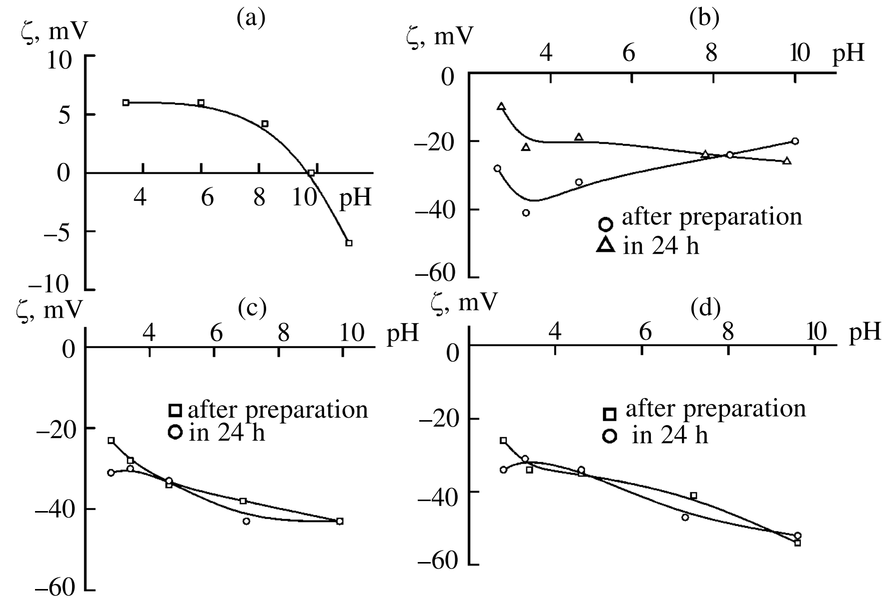

Fig. 5. Effect of pH on the ζ-potential of the particles of magnetic fluid stabilized with (a) dextran and of composite particles prepared in experiments nos.: (b) 10, (c) 11, and (d) 14.

ticles ζ-potential dependence on pH retained after keeping the obtained particles in acid or alkaline medium. This fact points to the absence of reactions at the surface and shows that whole magnetite is located in the bulk of the composite nanoparticles. Only in the case of the latex prepared in the absence of buffer salt in the reaction mixture (exp. no. 10) the ζ-potential value of the particles and the mode of its dependence on pH varies significantly pointing to the interaction of the nanoparticles not shielded by the polymer layer with the dispersion medium (Fig. 5b).

The data obtained allow to ascertain the mechanism of the process of filling the forming particles with magnetite in the process of polymerization. In the first step, thermal decomposition of the initiator affords anion-radicals which upon the progress of the process are converting into anionic groups at the ends of polymer chains and then at surfaces of the polymer-monomeric particles. The positively charged particles of magnetite are attracted by them electrostatically and are involved in the composition of a polymer particle. Besides, growing polymer chain can be grafted to the magnetic fluid polymeric stabilizer. Note that anionactive emulsifier used in this series experiments also maintains negative charge of the growing particles thus providing formation of stable magnetic latex.

In the next step we measured specific magnetic susceptibility of the magnetic fluids and related composite particles. The magnetic fluids stabilized by dextran fall by their magnetic susceptibility to the range $(5–7)\times10^{-5}$ cm^3 g^{-1}, which corresponds to ferromagnetic substances. The magnetic fluid stabilized by polyvinyl alcohol (Table 1, exp. no. 1m) shows even value of 9×10^{-5} cm^3 g^{-1} which is determined by a high content of magnetite. Magnetic susceptibility of composite particles was measured directly from dispersions using the latex samples and after drying the samples to powder consistency. The most these samples showed twofold larger magnetic susceptibility (Table 4). The highest magnetic property was demonstrated by the latex from exp. no. 11, which contained 11% of magnetite on dry residue and had the highest concentration of carboxylic groups at the surface, 5.62 μmol g^{-1}. Due to biocompatible polymetylmethacrylate polymer and natural polysaccharide dextran as stabilizer, it can be used in a living orgamism (in vivo) for the targeted delivery of a medicinal remedy which could be covalent bound up with carboxylic groups.

For the formation of monodisperse magnetic composite particles larger in size and with controlled morphology, the magnetite particles with carbon covering were precipitated on the 0.98 μm in diameter polymer microspheres of methylmethacrylate–acrolein (50:50 mol%) copolymer (Fig. 6a) with carboxylic (1.73 μmol g^{-1}) and aldehyde (2.96 μmol g^{-1}) groups on surface [16]. Then in the presence of such dispersion was performed polymerization for covering the magnetite layer by the formed polymer. Preliminary dependence of ζ-potential on the surface of methylmethacrylate–acrolein copolymer

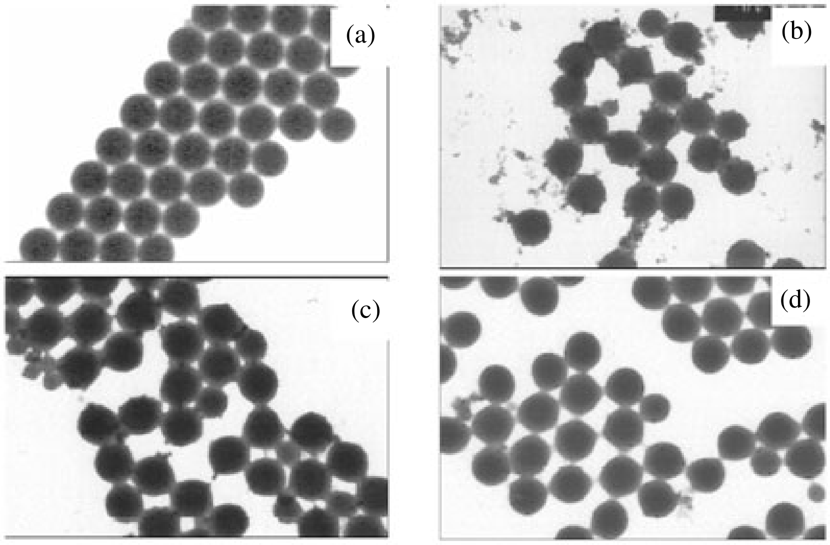

Fig. 6. Microphotographies of the particles of mathylmethacrylate–acrolein copolymer (a) before and (b) after adgulation of the magnetite nanoparticles and of composite particles from exps. (c) 17 and (d) 18.

and magnetite on the pH and ion strength of the dispersion medium was studied. We found that the magnetite particles retained their negative charge on the surface in a wide pH range (Fig. 7). On the contrary, the methylmethacrylate–acrolein copolymer particles gain positive charge on surface at $\mathrm{pH} < 2$, owing to protonation of surface aldehyde groups. It allows to apply the method of coagulation in acid medium for precipitation Fe_3O_4 particles on the surface of methylmethacrylate–acrolein copolymer particles bearing opposite charge, with the purpose of formation two-layers composite particles. Preliminary we calculated the magnetite quantity necessary for six-layers covering of latex particles from their specific surface value and cross section of magnetite particles considered as spheres. The dispersion of two-layers composite particles obtained by us (Fig. 6b) being stabilized by their own surface charge remains stable on keeping in distilled water for over one year. However, for introduction of functional groups appropriate for binding bioligands and for shielding them from direct contact with the magnetite we needed to form polymer shell on the obtained particles. In exp. no. 17 at formation of this shell based on polystyrene the composite particles formed were not exactly spherical (Fig. 6c). In the process of styrene polymerization new small polystyrene particles were formed and total quantity of the monomer was insufficient for covering composite particles by continuous polystyrene layer. In exp. no. 18 styrene and initiator concentrations were duplicated and content of methylnethacrylate–acrolein copolymer covered by magnetite layer in microspheres was triplicated, and this shifted the main zone of polymerization onto the composite microsperes surfaces, and new polystyrene particles were not detected. Thus we obtained three-shell monodisperse composite particles with regular spherical shape (Fig. 6d). They contained a

Table 4. Magnetic propwerties of prepared particles

Sample no.	Latex					Powder		
	volume, μl	dry residue, mg ml^{-1}	m, mg	E, μV	$\chi \times 10^5$, $\mathrm{cm}^3\,\mathrm{g}^{-1}$	m, mg	E, μV	$\chi \times 10^5$, $\mathrm{cm}^3\,\mathrm{g}^{-1}$
11	700	23.6	16.5	1.5	9.0	18.4	2.5	13.0
13	700	37.5	26.3	1.0	3.7	30.5	1.9	6.0
14	700	40.5	28.4	1.5	4.0	28.7	1.1	5.0
15	700	42.6	29.8	1.4	4.5	35.3	2.0	5.0
16	700	58.1	40.7	1.4	3.0	81.3	3.8	5.0

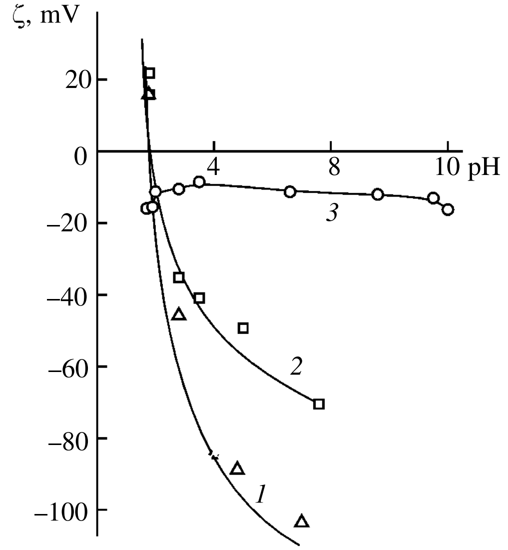

Fig. 7. Effect of pH ζ-potential of the particles of (*1, 2*) methylmethacrylate–acrolein copolymer, and (*3*) of magnetite particles with carbon covering at the NaCl concentration (*1, 3*) 10^{-3} M and (*2*) 10^{-2} M.

nucleus of methylmethacrylate–acrolein copolymer, magnetite layer and polystyrene shell with carboxylic groups for binding immunoreagents. Thermogravimetry showed that they contain 17 wt% of magnetite, in good agreement with calculation based on the quantity of loaded reagents. For preliminary studying magnetic properties of the obtained composite particles they were loaded as a dispersion into glass capillary tube and we followed their motion in a magnetic field. The motion rate was estimated from the shift of dispersion–air frontier. It achieved 2 cm $\min^{-1}$, attesting a possibility of application the obtained particles for the selective transfer of biological substances at the action of magnetic field in analytical microchips.

Thus it was shown that introduction of carboxylic groups and anionic surfactants into surface layer of composite particles in the process of emulsion polymerization provides narrowing of their distribution by size and complete inclusion of magnetite nanoparticles into them. The nature of monomer, polymer-stabilizer and initiator influences considerably concentration of carboxylic groups on the surface of the formed particles and their magnetic properties. By the method of angulation of magnetite with polymer particles followed by incapsulation into polymer shell we obtained three-layer composite particles with carboxylic surface groups.

EXPERIMENTAL

The monomers: styrene, methacrylic acid and methylmethacrylate were purified by distillation according to common procedures. Dextran used had molecular weight 20 000 (Ferak, Germany) and 60 000 (produced by St. Petersburg Chemical Pharmaceutical Academy). Polyvinyl alcohol type 5/9 containing 11 mol% of residual acetate groups was produced according to GOST 10779-81 by Scientific and Research Division "Plastpolymer" (St. Petertsburg). Its average molecular weight calculated from the value of characteristic viscosity in water at 25°C according to Mark–Kuhn–Houwink equation with the parameters $K = 2.0 \times 10^{-4}$ and $\alpha = 0.76$ [10] is found equal to 17 000. As initiators were used 4,4'-azobis(4-cyanovaleric acid) from Waco Pure Chemical Industries Ltd. (Japan) and potassium persulfate, benzoyl peroxide and azodiizobutyric dinitrile of domestic production, which were purified by recrystallization from ethanol. The emulsifiers: Disponil AES 60 IS from Cognis (Austria) and Aerosol OT [sodium bis(2-ethylhexyl)-succinatosulfonate] from Acros Organics (Belgium) as well as iron(III) chloride, iron(II) sulfate, sodium hydrophosphate and aqueous ammonia (25%) of domestic manufacturing were used without additional purification.

The magnetic fluids which are dispersions of magnetite were prepared by coprecipitation of iron salts with aqueous ammonia in the presence of biopolymer dextran (concentration 11 wt% relatively to water phase) as a stabilizer, alongside the procedure in [11].

For comparison were studied particles of magnetic fluid prepared in the Research Institute of Specific Purity Biopreparations (St. Petersburg) with polyvinyl alcohol (5 wt% to water phase) as a stabilizer. Transparent electron microscopy showed that at stabilization with dextran the magnetite average size is about 10 nm. At the stabilization with polyvinyl alcohol the size achieved 20 nm, due to lower concentration of the polymer stabilizer (Fig. 1). The magnetite content determined by bichromatometric procedure [10] was 8–13 wt% to dextran and 38 wt% to polyvinyl alcohol (Table 1). The Fe_3O_4 concentration in the magnetic fluids prepared in the presence of dextran, exp. nos. 1m–3m, varied due to dilution at the purification by dialysis. In exp. no. 4m the magnetic fluid with magnetite content 31 g ml^{-1} was prepared using evaporaion.

The emulsion polymerization in the presence of a magnetic fluid was conducted at the action of radical initiators alongside the procedure in [4]. In exp. nos. 1

and 2 was used magnetic fluid stabilized with polyvinyl alcohol, concentration 0.3 and 0.38 wt%, respectively. In exp. no. 1 the styrene (5.4 wt%) polymerization was initiated with azo-bis-izobutyric dinitrile (0.012 wt%). In exp. no. 2 the copolymerization of styrene (6.8 wt%) with methacrylic acid (0.25 wt%) at the action of benzoyl peroxide (0.038 wt%) was performed in the presence of Aerosol OT (0.025 wt%). The reagents concentrations are given relatively to the aqueous phase. Conditions for exp. nos. 3–16 are listed in Tables 2 and 3.

Formation of the magnetite-containing particles with the size in micrometer scale was conducted in two steps: formation of two-layer particles and covering them by the polymer shell. In the first step, monodisperse particles of methylmethacrylate–acrolein copolymer and obtained by gas-phase procedure magnetite particles 20 nm in diameter with carbon covering protecting the magnetite to the influence of environment. The magnetite (0.02 g) was dispersed in bidistilled water (5 ml) by the action of ultra-sound for 10 min, simultaneously 1 ml of 10 wt% latex was diluted with 5 ml of bidistilled water and treated with ultra-sound for 3 min. To both the dispersions, 0.1 M nitric acid was added dropwise to achieve pH 1.8 and they were quickly mixed. The dispersion obtained was homogenous and did not separating into layers, and this fact attested that precipitation of the magnetite nanoparticles on the methylmethacrylate–acrolein copolymer microspheres was achieved.

In the second step, polymerization of 45 mg of styrene in the presence of 55 mg of the bilayer particles was performed under the action of 1 mg of a carboxyl-containing initiator at 70°C. For stabilization of the forming particles and for hydrophilization of their surface, 3 g of hydrophilic polymer, carboxymethyldextran with molecular weight 60000 was added, and it localized in the surface shell of a microsphere. For maintaining negative charge at the composite particles and preventing their coagulation in the process of polymerization, the disperse medium (40 ml) was bring to pH 8.5 by adding sodium hydroxide 0.1 M solution.

The particles diameter of the obtained latexes was measured by means of electron microscopy on a JEM 100 S JEOL, Japan instrument. Concentration of carboxylic groups on the composite particles surfaces was measured by the method of conductometric titration. Electrophoretic mobility of magnetic fluid particles and of a series of magnetic latexes after removing from them water–soluble admixtures by dialysis was studied by commonly used microelectrophoresis procedure in 10^{-2} M and 10^{-3} M NaCl solutions in the pH range 2.1–11.4. In the experiments as a dispersion medium was used bidistilled water with specific electroconductivity 1.2×10^{-4} Ω^{-1} m^{-1} and fixed concentration solutions of HCl, NaOH, and NaCl. On the basis of the data on electrophoretic mobility obtained were calculated ζ-potentials of the particles using Smolukhovskii equation.

Magnetic susceptibility æ of the obtained magnetic fluids and latexes was measured using an installation based on the Hall effect [12] from experimental measurements of electromotive force and weight of the prepared samples. For calibration, weighted quantity of tungsten powder was used.

ACKNOWLEDGMENTS

This work was supported by Russian Foundation for Basic Research (project no. 04-03-33080).

REFERENCES

1. Prokopov, N.I., Gritskova, I.A., Cherkasov, V.R., and Chalykh A.E., *Usp. Khim.,* 1996, vol. 65, no. 2, p. 178.
2. Elaissari, A., Veyret, R., Mandrand, B., and Chatterjee, J., *Biomedical Application for Magnetic Latexes, Colloidal Biomolecules, Biomaterials, and Biomedical Applications,* Elaissari, A., Ed., New York: Dekker, 2004, p. 17.
3. Hertzog, B., Mottl, T., Yim, D., and Mathiowitz, E., *Scientific and Clinical Applications of Magnetic Carriers,* Hafeli, U., Schutt, W., Teller, J., and Zborowski, M., Eds., New York: Plenum, 1997, p. 77.
4. Zheng, W., Gao, F., and Gu, H., *J. Magnetism and Magnetic Materials,* 2005, vol. 293, no. 1, p. 199.
5. Asheim, H.C., Deggerdal, A., Smeland, E.B., and Hornes, E.A., *Bio Techniques,* 1994, vol. 16, no. 4, p. 716.
6. Uhlen, M., *Nature,* 1989, vol. 340, no. 6236, p. 733.
7. Neuberger, T., Schopf, B., Hofmann, H., Hofmann, M., and Rechenberg, B., *J. Magnetism and Magnetic Materials,* 2005, vol. 293, no. 1, p. 483.
8. Yu, H., Raymonda, J.W., McMahon, T.M., and Campagnari, A.A., *Biosens. Bioelectron.,* 2000, vol. 14, nos. 10–11, p. 829.
9. Muir, P., Nicholson, F., Jhetam, M., Neogi, S., and Banatvala, J.E., *J. Clin. Microbiol.,* 1993, vol. 31, no. 1, p. 31.
10. *Polymer Handbook,* Brandrup, J., Immergut, E.H., and Grulke, E.A., Eds., New York: Wiley, 1999.

11. Gubin, S.P., Koksharov, Yu.A., Khomutov, G.B., and Yurkov, G.Yu., *Usp. Khim.,* 2005, vol. 74, no. 6, p. 539.
12. Kalashnikov, N.P. and Smondyrev M.A., *Osnovy fiziki* (Phisics Bsicity), Moscow: Drofa, 2003.
13. Eliseeva, V.I., *Polimernye dispersii* (Polymer Dispersions), Moscow: Khimiya, 1980.
14. Men'shikova, A.Yu., Evseeva, T.G., Shabsel's, B.M., Il'ina, I.E., and Vlasov G.P., *Kolloid. Zh.,* 1997, vol. 59, no. 5, p. 671.
15. Lee, J. and Senna, M., *Colloid Polym. Sci.,* 1995, vol. 273, no. 1, p. 76.