Magnetic Composites Obtainment Based on Styrene Polymers

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ABSTRACT: Three styrene-based matrices for hybrid composites with ferrite have been obtained by emulsion polymerization in the presence of a tensioactive system: sodium *n*-dodecylbenzene sulfate ($C_{12}H_{25}C_6H_4SO_3Na$) as anionic agent and poly(oxyethylene) nonylphenyl ether [$C_9H_{19}C_6H_4(OCH_2CH_2)_{30}OH$] as nonionic tensioactive agent. The system assures the steadiness of the emulsion during the reaction and the stability of the latices. The surfactants act as a protective colloid component and thickening agents determining an optimum viscosity and conditions for the further catching of the inorganic oxide with magnetic properties. The obtained polystyrene and styrene copolymers with acrylamide and methacrylamide were analyzed by elemental analysis, IR spectroscopy, DSC, and their viscosity data have been characterized. The size as well as the magnetic properties of composites were also appreciated. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 4133–4141, 2006

Key words: emulsion polymerization; styrene polymers; magnetic composites

INTRODUCTION

Nanostructured materials with magnetic properties have multiple applications in medical diagnostic technologies, magnetic drug delivery and cell-sorting systems. The application of polymeric materials for medical purposes is also growing very fast. Polymers have found applications in such diverse biomedical fields as tissue engineering, implantation of medical devices and artificial organs, prostheses, ophthalmology, dentistry, bone repair, and separation of products with biologic activity by means of a continuous external magnetic field, and also local drug delivery. These kind of magnetic composites polymer-based delivery systems enable controlled slow release of drugs into the body. They also make possible targeting of drugs into sites of inflammations or tumors. Polymeric materials have extensively been used for biosensors, in testing devices, and for bioregulation. Analytical applications often require a separation step. Magnetic particles were found suitable as solid phases in immunoassay, since after the capture step the target molecules can easily be separated upon applying a magnetic field.[1–8]

In this context, magnetic composites are produced in a number of ways but usually involve the coating of magnetically susceptible particles with synthetic polymers having convenient sites for the affinity ligand attachment. Alternatively, conventional supports can be postmagnetized by treatment with magnetic ferrofluids without any loss of subsequent binding activity. One of the method to prepare magnetic particles is to separately synthesize the inorganic and polymer materials first. Then, polymer chains can be grafted or adsorbed into an inorganic core, generally composed of iron oxide. Otherwise, when mixed with magnetic material, polymer chains can eventually be crosslinked to form large and polydisperse polymer beads containing magnetic material.

The use of styrene and some of its copolymers in the obtainment of polymer latices as microspheres with medical and biochemical applications, including absorbents, latex diagnostics, affinity bio-separators, and drug and enzyme carriers, and also as organic matrix for monodisperse particles consisting of magnetite and styrene polymer, is well known. The polystyrene is practically considered as a classic matrix of bioactive structure.[9,10] Other crosslinked synthetic polymers and copolymers are used as polymeric matrix for synthesizing magnetic composites with interesting results. Thus there is a growing interest for the obtainment of macromolecular matrices with capability for clutching biological active substances.

In the production and application of emulsion polymers, surfactants play a significant role. They control the particle size and distribution, which in turn dictates the rheology and viscosity of the final latex. They prevent particle coagulation during polymerization and storage of the latex and they can confer electrolyte

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TABLE I
Recipe for the Obtainment of 100 g Vinyl Latex

Variant	Monomers, M	Potassium persulphate, M	Water, M	Sodium *n*-dodecyl-benzene sulfate	Poly(oxyethylene) nonylphenylether
				Tensioactive system, M	
A	Styrene = 245×10^3	1.387×10^{-3}	4.16	3.24×10^{-3}	1.72×10^{-3}
B	Styrene = 232.8×10^{-3}/Acrylamide = 10.6×10^{-3}	1.387×10^{-3}	4.16	3.24×10^{-3}	1.72×10^{-3}
C	Styrene = 192.03×10^{-3}/Methacrylamide = 58.82×10^{-3}	1.387×10^{-3}	4.16	3.24×10^{-3}	1.72×10^{-3}

and/or freeze/thaw stability to the latex as required by the formulator. Through careful surfactant selection, the skilled emulsion polymer formulator can control the film-forming properties of the final latex; parameters such as adhesion, film clarity, water resistance, and gloss are all influenced by surfactant type.

In an earlier study, the emulsion polymerization of styrene in the presence of an anionic surfactant was presented.[11] To perform the polymerization process at better reaction rate and better conversion and to obtain a stable macromolecular compound, it has been continued by improving the single surfactant with an anionic/nonionic tensioactive system. At the same time, the addition even of small percentage of functional groups at the homopolymer matrix improves the kinetics of polymerization and enhances the characteristics of the macromolecular structure to be used as matrix for inorganic or bioactive substances.

This paper presents the preparation and characterization of the latex matrices for magnetic composites that can catch bioactive substances. The synthesized macromolecular structures are based on polystyrene, and two styrene copolymers with acrylamide and methacrylamide, respectively.

EXPERIMENTAL

Materials

Styrene (St, Fluka, Germany) was freshly distilled before use. Acrylamide (AAm, Merck, Germany) and methacrylamide (MAAm, Merck) were used after recrystallization from methylene chloride.

The tensioactive system made of sodium *n*-dodecyl-benzene sulfate ($C_{12}H_{25}C_6H_4SO_3Na$) (cmc = 1.15×10^{-3}, $M_w = 348.47$)[12] as anionic agent and poly(oxyethylene) nonylphenyl ether [$C_9H_{19}C_6H_4(OCH_2CH_2)_{30}OH$] (cmc = 7.8×10^{-5}, $M_w = 1541.9$)[13] as nonionic tensioactive agent, both from Merck, have been used without further purification. The gravimetric ratio between anionic and nonionic tensioactive agents is 1:1.

Potassium persulphate was recrystallized from bi-distilled water. In all experiments, the used water was double distilled and contained no foreign ions.

Ferrite with average particle size of 3–6 μm was purchased from "Sinteza" Oradea (Romania). Before use, milling at <3 μm reduced the dimensions.

Polymer synthesis process

The recipes as well as the reaction conditions during the syntheses of macromolecular compounds are presented in Table I and Table II.

To obtain particles with uniform size, a multistage seeded emulsion radical polymerization procedure has been used.

The polymerization was started with 10 wt % of the emulsion constituted from monomers, half part of tensioactive system, 90% of initiator content, as well as 30% from water substance, which has been added into the reaction vessel comprising the rest of surfactants and 60% from the reaction medium. After about 1 h, the second step of reaction was started, when the remaining emulsion of monomers was continuously added into the vessel for about 2 h. After 8 h reaction time, a posttreatment at 75–80°C for 1 h was performed, by adding 10% of water and 10% initiator for the finishing of the polymerization process.

The same reaction conditions were kept for the copolymerization reaction of styrene with acrylamide and methacrylamide, respectively.

The macromolecular matrices have been purified to remove the tensioactive agents and residual monomer, eventually. Thus, the obtained latices were dried at 40°C for 24 h, washed with bi-distilled water and dialyzed until the UV spectrum of the washing water corresponds to the pure water.

TABLE II
Reaction Conditions for the Vinyl Latex Synthesis

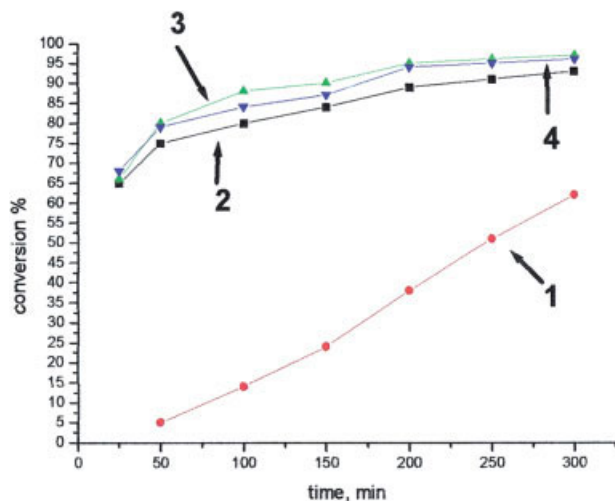| Synthesis variant	T(°C)	Time of reaction and thermal treatment (min)	Rotation (min^{-1})
A	70–75	540 + 60	300
B	70–75	540 + 60	300
C	70–75	540 + 60	300

Figure 1 Kinetic data for the synthesis of styrene polymers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.].

min, in airflow of 30 mL/min, and with reference material α-Al$_2$O$_3$.

e. The synthesized polymers have been characterized through DSC measurements, which were carried out by means of a Mettler 12E type DSC, at a heating rate of 15°C/min under inert atmosphere of N$_2$, and 25–400°C temperature range.

f. The electrical conductivity of 1% concentrated latex in water (dipole moment $\mu = 1.84$) and 1% polymer film in tetrahydrofuran (THF, dipole moment $\mu = 1.75$) was established with a PP-type conductometer of liquids, investigation temperature being 25–35°C.

g. Intrinsic viscosities were measured in THF, using an Ubbelohde suspended-level viscosimeter. The investigation temperature was 25 ± 0.2°C.

h. The swelling degree (α) has been determined in CCl$_4$ vapors atmosphere , at 20°C, until constant weight.

The magnetic composites obtainment procedure

The ferrite composite is carried out using the macromolecular matrix as core. By mixing the latex of polymer ($\rho = 2.4$ g/cm^3-suitable for obtaining magnetic composites) of 25 wt % concentration with powdered iron oxide, a ratio of styrene polymer/iron oxide about 1/1 was achieved. The adsorption of the ferrite on the particles surface took place for 24 h under slow mixing and a temperature of 30°C.

Methods of investigation

The synthesized polymers are evaluated from the viewpoint of their kinetic synthesis and of some physicochemical properties, as follows.

a. The kinetic evolution of the polymerization process of styrene and copolymerization of styrene with acrylamide or methacrylamide, according to the recipes above described are presented in Figure 1. The conversion of homo- and copolymers was determined gravimetrically. Reproducible sets of data were recorded on multiple syntheses.

b. IR absorption spectra have been recorded on a Perkin–Elmer 577 spectrophotometer for equal quantities of polymer films synthesized in emulsion.

c. The copolymers were analyzed through the Kjeldahl method, to determine the nitrogen content.

d. TG and derivative thermogravimetry (DTG) curves were recorded on a MOM Budapest derivatograph under the following operational conditions: sample weight 50 mg, heating rate 12°C/

The magnetic composite characterization

a. The size of polymer and magnetic composites were determined by the micrographs obtained by means an SEM BS 340 TESLA type. The films were covered with pure metallic Ag. The laying down of Ag was carried out using evaporation of the metal under a high vacuum, to give a thickness of around 15–20 Å. Magnification was 510× for the polymers matrix and 4200× for polystyrene/ferrite composite respectively, and of 1230× for poly(styrene co acrylic acid) composite.

b. The magnetic properties were determined on a homemade device. The experiments were conducted directly on latex samples prepared as mentioned and the sample being placed in a cylindrical sample holder.

The magnetic character of the composites was evidenced by the magnetic susceptibility measurements:

The force (F) that operates in the cylindrical sample length, with known length and section situated with the inferior extremity in an electromagnet pole was indirectly measured by the increase of the apparent mass of the sample in the magnetic fields:

$$F = \mu_0 S \frac{\chi}{2} \int_{H_i}^{H_e} \frac{dH^2}{dz} \, dz \tag{1}$$

where χ - magnetic susceptibility (fine particles suspension), ℓ- cylindrical length, S-section, H_i–intensity of the magnetic field inside the magnetic pole, and H_e-intensity of the magnetic field outside the magnetic pole.

TABLE III
Reactivity Constants Data of Styrene and Used Comonomers[14,15]

Monomer 1	Monomer 2	r_1	r_2
Styrene	Acrylamide	1.13	0.59
	Methacrylamide	1.44	0.54

If $H_e \ll H_i$ then:

$$F = \frac{1}{2}\mu_0 \chi S H_i^2 \qquad (2)$$

Taking into consideration that $F = g\Delta mF$, where g is gravitational acceleration ($= 9.81$ m/s^2) the next relation was derived:

$$\chi = \frac{2g\Delta m}{\mu_0 S H_i^2} \qquad (3)$$

This relation is valid if the sample length is so large that the superior extremity is without magnetic field of the electromagnet. The sample length ℓ that satisfies this condition was determined experimentally.

If $H_e \ll H_i$ is possible to approximate $H_e \approx 0$, and Δm is independent of the sample length (ℓ).

RESULTS AND DISCUSSION

The study pursues the polymer latices synthesis with improved kinetics and yield, in the condition of a certain tensioactive system use. At the same time, the obtained properties are correlated with the later applications, such as macromolecular matrices for magnetic composites. Although the matrices do not require crosslinked structures, reduced amounts of comonomer with functional groups are used in the synthesis for the increasing of coupling with magnetic inorganic oxide or bioactive substance.

Thus, the ratio between styrene and functional comonomers allows further solubility being preferred for the achievement of a large network instead of a deep reticulation.

According to the recipe and synthesis procedures, stable polymeric latices were obtained with high homogeneity, the particle dimensions being in the range of 0.01–0.03 μm.

The selected comonomers have the appropriate reactivity constants (Table III), so the obtained copolymers are considered as random ones.

The development of styrene polymerization process in emulsion as well as the syntheses of styrene copolymers with acrylamide and methacrylamide are plotted in Figure 1. The reactions are initiated with potassium persulphate, and the surfactant is sodium n-dodecyl benzene sulfate and the system: n-dodecyl-
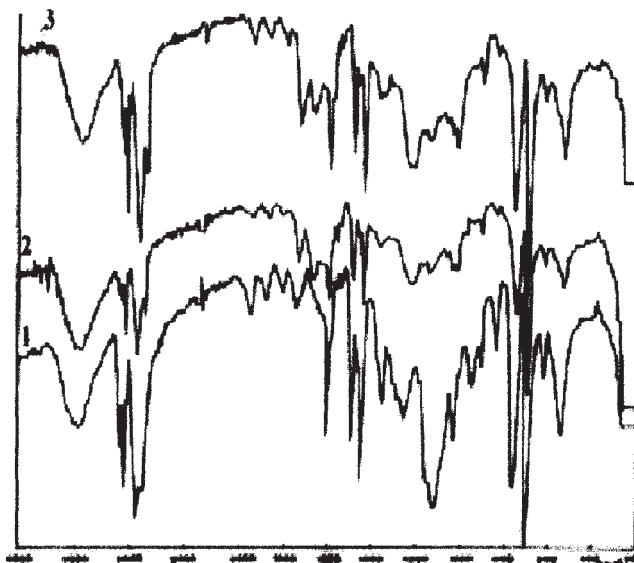

Figure 2 IR spectra of the poly(styrene) (1) and of the copolymers of styrene with acrylamide (2) and methacrylamide (3).

benzene sulfate as anionic agent and poly(oxyethylene) nonylphenyl ether as nonionic tensioactive.

Kinetic data presented in Figure 1 (curves 2, 3, 4) underline the advantage offered by the anionic/nonionic tensioactive system in comparison with variant of polystyrene synthesis in the presence of anionic tensioactive agent n-dodecylbenzene sulfate having the concentration of $3.24 \times 10^{-3}ML^{-1}$ (curve 1, Fig. 1). Thus, besides the diminution of induction period of the process, the increase of the reaction rate and conversion are obvious.

The addition of the comonomers with functional groups is materialized in small increase of the conversion and reduction of reaction time. The facts are justified by small quantity of the added comonomer and by very close reactivity constants of monomers

TABLE IV
Characteristic Bands of the Studied Monomers[16]

Monomers	Characteristic bands
Styrene	3299, 3082, 3060, 3027, 3009, 2980, 1966, 1946, 1876, 1821, 1689, 1630, 1601, 1576, 1496, 1449, 1412, 1383, 1334, 1317, 1290, 1202, 1182, 1155, 1083, 1021, 992, 909, 841, 777, 738, 698, 650, 555, 442
Acrylamide	3362, 3172, 3105, 3034, 2813, 2791, 1921, 1676, 1613, 1413, 1363, 1281, 1138, 1062, 990, 962, 840, 819, 709, 664, 610
Methacryl-amide	3386, 3196, 3098, 2969, 2927, 2855, 2781, 2221, 2209, 1888, 1663, 1603, 1450, 1434, 1408, 1387, 1371, 1236, 1110, 1011, 966, 933, 828, 815, 778, 638, 631, 626, 583, 521

TABLE V
The Comparative Nitrogen Content

Polymeric matrix	Theoretic content of N_2 (%)	Determined content of N_2 (%)
P(S-*co*-AAm)	0.59	0.54
P(S-*co*-MAAm)	0.725	0.755

involved in study. Thus, at the same reaction time, 96 wt % conversion is obtained in case of polystyrene, 98.53 wt % for copolymer with acrylamide, and 98.97 wt % for the copolymer with methacrylamide, respectively.

The determined physicochemical characteristics differentiate polystyrene from its copolymers. Thus:

The IR spectra confirm the presence of the comonomers in the structure of the macromolecular chains, as can be examined from Figure 2:

Comparing the specific bands of the studied monomers (Table IV) with the obtained spectra of the synthesized macromolecular compounds (Fig. 2), there are evidently both the characteristic bands of styrene in the homopolymer spectrum as well as the specific vibrations of the comonomers that attest their presence in copolymers. Thus, the bands from 1460 cm^{-1} and 1500 cm^{-1}, support the presence of the aromatic ring, while the amide group in acrylamide is confirmed by the bands from 1660 cm^{-1} (=C—N—stretch) and 3550 cm^{-1} (—N—H stretch). The characteristic bands of methacrylamide from the copolymer P(S-*co*-MAAm) are evidenced by the bands at 1300–1060 cm^{-1} (=C—N stretch), 1660 cm^{-1} (=C—N—stretch), 1750 cm^{-1} (—C=O stretch), and 3550 cm^{-1} (—N—H stretch).

Nitrogen elementary analysis confirms the functional group presence in the copolymers. The values of nitrogen content with respect to the copolymers are in concordance with the theoretic values (Table V).

Comparative thermogravimetric data referring to characteristic temperatures, overall activation energy (E_a) and reaction order (n) for the PSt and its tested copolymers are listed in Table VI. The onset temperature for the decomposition process of the copolymers is lower than that for polystyrene. A decrease of the activation energy for the copolymers in comparison with polystyrene is observed. Both variations indicate
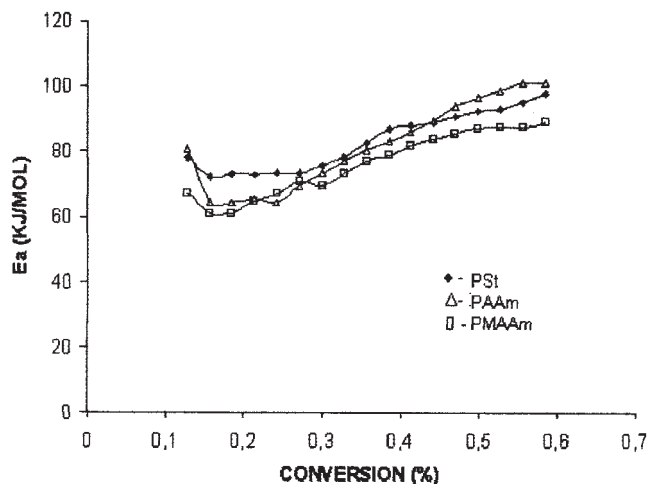

Figure 3 Dependence of E_a on conversion degree of polystyrene and styrene copolymers with acrylamide and methacrylamide.

the presence of the functional groups, more accessible to the destruction process reflected in a lower thermal stability of the copolymers.

Nevertheless, the weight losses in this decomposition step are lower for the copolymers. This fact is attributed to the small supplementary reticulation links generated by the comonomers.

Figure 3 shows the variation of E_a with conversion for polystyrene and its copolymers. No important differences in the shape of curves are observed in the domain of low conversion. However, for $\alpha > 0.3$, the E_a values for copolymers are lower than for polystyrene according to variation of the overall activation energy determined by Coats–Redfern method.[17–19]

Differential scanning calorimetric analyses (DSC) show small modifications of glass transitions temperature values between polystyrene and its copolymers (Fig. 4). Thus, by incorporating small amount of functional comonomer, an increase of the glass transition temperature of polystyrene from 95°C (close enough to value of 100°C given in literature[20]) to 98°C for P(S-*co*-AAm) copolymer and to 96°C for P(St-*co*-MAAm) is noticed.

This is due to different supplementary inter- and intramolecular linkages, like dispersion forces, which are due to instantaneous dipoles, and/or hydrogen

TABLE VI
Thermogravimetric Data

Sample	T_{10} (°C)	T_{50} (°C)	T_m (°C)	T_i (°C)	F_a kj/mol	n	Δw (%)
PSt	322	395	400	210	64.624	0	83
P(S-*co*-AAm)	315	400	402	240	61.9772	0	88.2
P(S-*co*-MAAm)	302	390	407	240	56.7038	0	87.25

Δw, weight loss; T_{10}, T_{50}, temperature corresponding to 10 and 50 wt % weight loss; T_m, temperature of maximum rate of weight loss; T_i, temperature corresponding to the beginning of decomposition process.
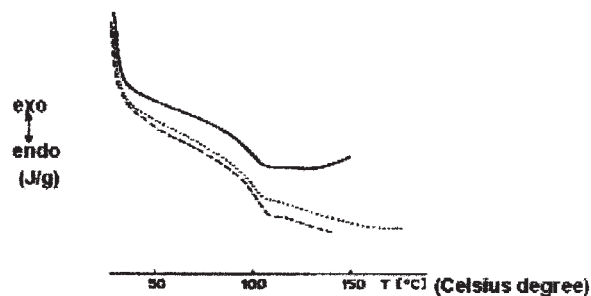
Figure 4 DSC curves of PSt (___) and styrene copolymers P(St-*co*-AAm) (- - -) and P(St-*co*-MAAm) (. . .).

Figure 6 Electrical conductivity of synthesized lattices 1%. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

bonding. It is also observed that the presence of methyl groups in P(St-*co*-MAAm) determined a decrease of the transition temperature comparatively with the copolymer with acrylamide in composition, even though the percentage of functional comonomer is higher.

The synthesized latices are physically coupled with a magnetic inorganic oxide. For the purpose of reaching the best conditions for the realization of a magnetic composite, the viscosity, the swelling degree, and the stability expressed by the electrical conductivity, are evaluated.

Intrinsic viscosities [η] of the synthesized polymers measured in THF and correlated with the solution concentrations are presented in Figure 5.

The increase of intrinsic viscosities registered in case of copolymers with AAm and MAAm, respectively, is also justified by the orientational interaction, inter- and intramolecular linkages done by the instantaneous dipoles, and/or hydrogen bonding. In case of the copolymer with acrylamide, an increase of the intrinsic viscosity was observed. The absence of the steric hindrances of the methyl group as in case of the copolymer with MAAm (which determines higher vis-
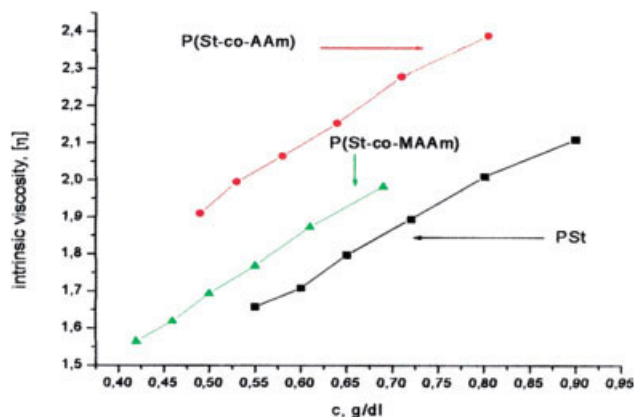
cosity) is balanced by acrylamide, a more polar monomer that induces additional inter- and intramolecular interactions.

Small values of electrical conductivity of polymer in emulsion and in solution of THF reflect the stability of the synthesized latices (Figs. 6, 7). At the same time, the smaller values in solution are justified by lower dipole moment for THF ($\mu = 1.75$) and by removing of the tensioactive agent from the system.

The kinetic study of swelling in the CCl$_4$ vapors for the polymer films (Fig. 8) confirms the presence of comonomers with functional groups. Initially, a reduced swelling was observed for the two copolymers justified by the supplementary inter- and intra/molecular linkage. Thus, the presence amido groups determines an increase of swelling degree (α) and a faster

Figure 5 Intrinsic viscosities of the synthesized polymers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
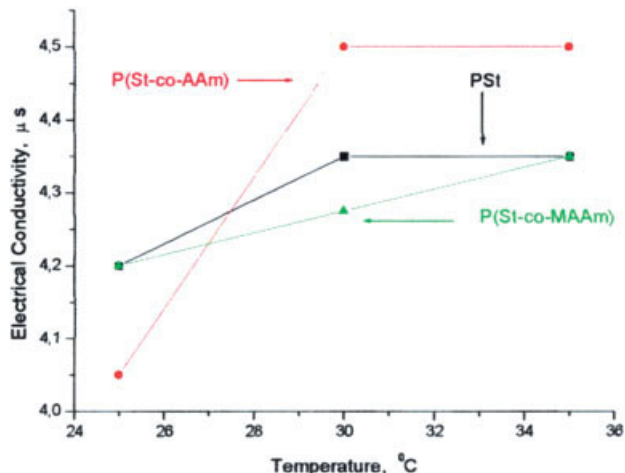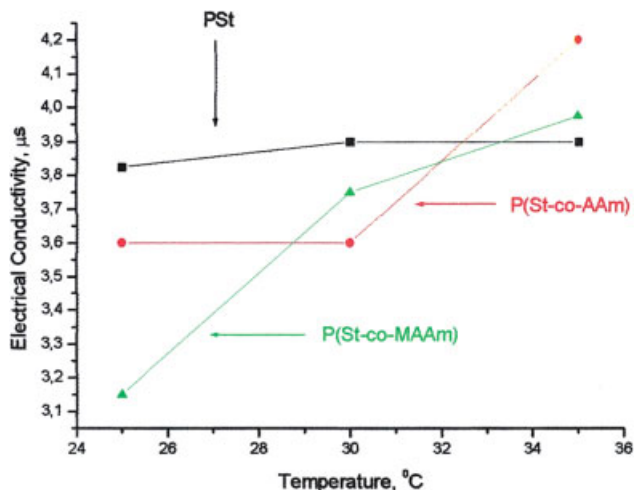

Figure 7 Electrical conductivity of 1% THF solution of polymers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
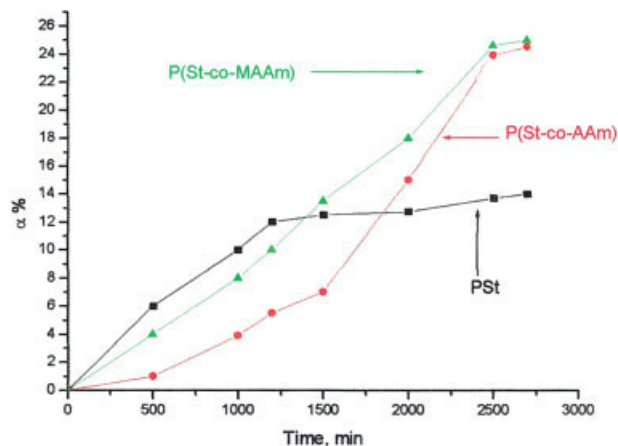
Figure 8 Kinetic study of swelling for the synthesized polymers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 9 SEM micrographs of poly(styrene) (a) and poly-(styrene-*co*-acrylamide) (b).

capacity of swelling owing to the comonomer existence.

In the kinetic curve of swelling, even a reduced amount of functional comonomer, like 3%, determines a decrease of time for reaching the maximum capacity of swelling, justified by the supplementary inter- and intramolecular linkage. It is also observed, the presence of methyl groups in P(St-*co*-MAAm) determined an increase of the capacity of swelling compared with P(St-*co*-AAm) and PSt. This can be explained by higher percent of methacrylamide (5%) comparing with 3% of acrylamide, and by the existence of supplementary steric hindrances, which do not allow the chains wrapping and thus, making possible the solvent diffusion between the macromolecular chains.

At 2580 min swelling time, the degree of swelling ($\alpha = \dfrac{m - m_0}{m_0} \times 100$, with m_0 = initial weight of polymer, and m = polymer weight after a certain swelling time) is in case of:

P(St-*co*-MAAm) = 22.45%,
P(St-*co*-AAm) = 21.53%, and
PSt $\cong$ 13

Thus, the loose set of connections obtained in the copolymers with functional comonomers allow a better and a deepest swelling with solvents of the network. These aspects are into the benefit of applying copolymers as matrices for bioactive substances, for their catching.

The magnetic composites obtainment

The magnetic composites were obtained according to above described procedure. The deposition of iron oxide on polymers particles is more homogeneous on copolymers surface even in the presence of ferrite as
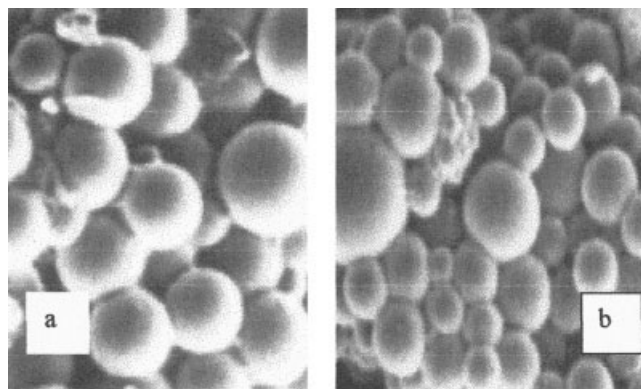
can be observed from the SEM micrographs (Figs. 9, 10).

The overall size of the composite particles is between 3 and 6 μm. The microspheres rapidly responded to a magnetic field. After the removal of the magnet, the particles did not stick together.

The variation of the magnetic susceptibility with intensity of the magnetic field and the magnetization curves for the magnetic composites are presented in Figure 11(a)–(c).

The magnetic susceptibility of the ferrite-covered poly(styrene) has reduced values comparing with those of the ferrite covered by the two copolymers. So, the magnetic composite containing copolymers as matrices have improved magnetic parameters. The increasing magnetic susceptibility (from 4 for polystyrene to 5.6[8] for the copolymers) and maximum magnetization (from 3000 GS to 5000 or 5600 for S/AAm and respectively, S/MAAm copolymers) higher relative absorption capacity is expected.
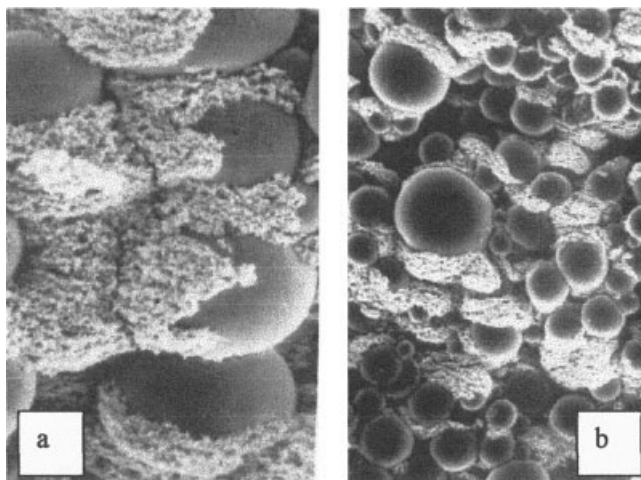

Figure 10 Composite SEM micrographs of poly(styrene)/ferrite (a) and poly(styrene-*co*-acrylamide)/ferrite (b).
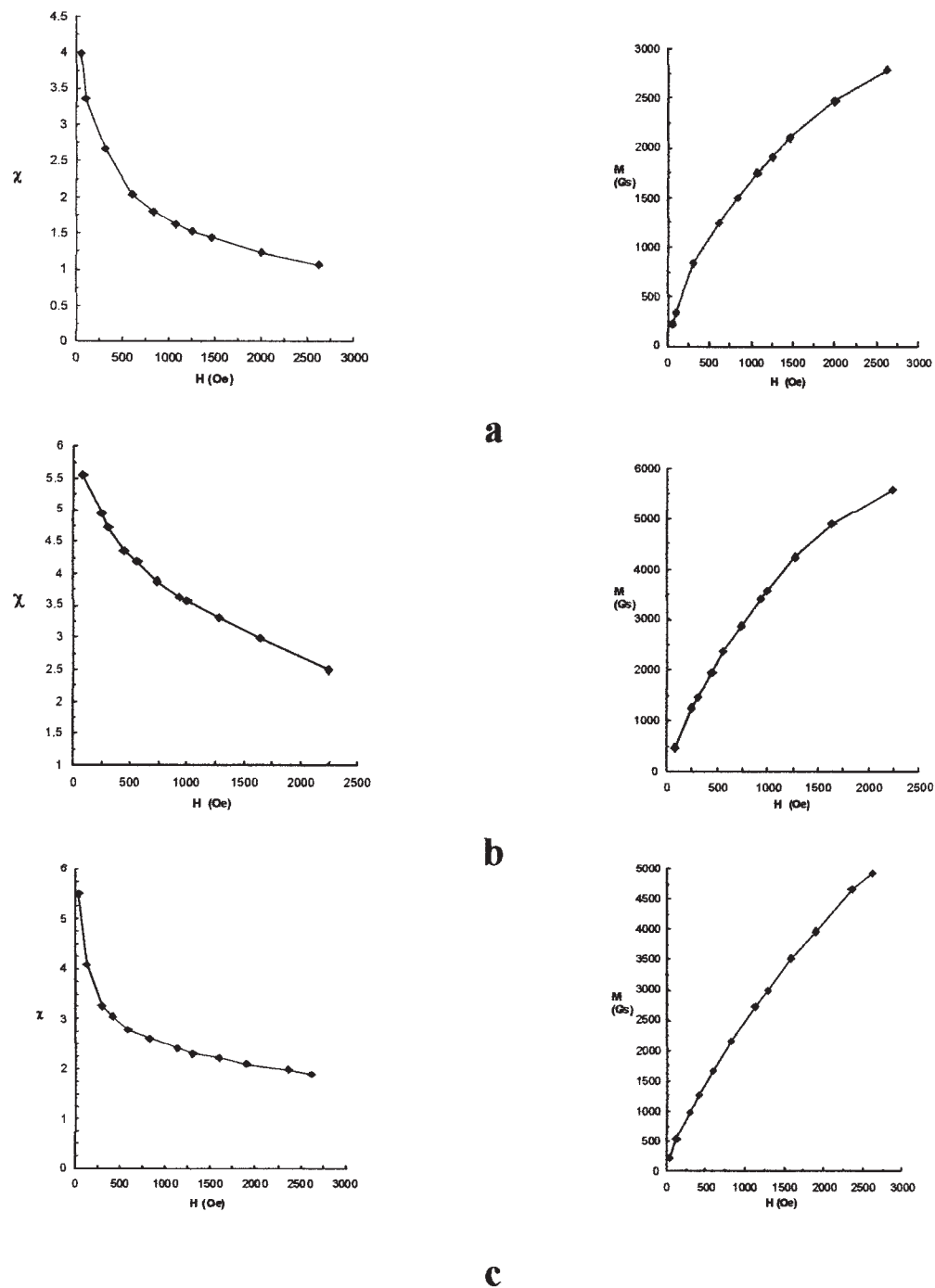
Figure 11 The evolution of the magnetic susceptibility for the magnetic composite with poly(styrene) (a), poly(styrene-*co*-acrylamide) (b), and poly(styrene-*co*-methacrylamide) (c) as matrix for iron oxide.

CONCLUSIONS

Polystyrene is commonly used for the preparation of magnetic particles. But polystyrene is not capable to offer the functional groups for the subsequent coupling with biological substances. From this point of view, we prepared the copolymers with acrylamide and methacrylamide. Styrene copolymers with polar groups and controlled dimension size (<3 μm) have been obtained.

The recipe of two comonomers, styrene and acrylamide or methacrylamide, and the synthesis procedures lead to the obtainment of stable polymeric latices with high homogeneity and the dimensions of the particles in the range of 0.01–0.03 μm. A large network instead of a deep crosslinking has been acquiring according to the ratio between styrene and functional comonomers. This quotient allows further solubility of the dried copolymers.

The tensioactive system allows the obtainment of the latices with higher rate and conversion. It assures the steadiness of the emulsion during the reaction as well the general stability of the dispersion. The tensioactive system assures also a good viscosity, which is of interest for many uses, as well as good behavior when stored.

The magnetic composites containing these copolymers have superior magnetic properties, so they are expected to have a good compatibility with biological substances, as demonstrated for the matrices studied.

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