Magnetic Composite Based on Vinylic Template

N. Tudorachi, A. P. Chiriac

''Petru Poni'' Institute of Macromolecular Chemistry, Polymeric Materials Department Grigore Ghica Voda Alley No. 41 A, RO-700487 Iasi, Romania

ABSTRACT: This article presents the achievement of a magnetic composite having a vinylic polymeric structure as matrix based on a styrene/methyl methacrylate/2,3-epoxypropyl methacrylate. The synthesis of the copolymers performed through an emulsion polymerization process was realized in the presence of potassium persulfate as radical initiator and sodium lauryl sulfate as anionic tensioactive agent. To have a network capable for a better coupling of the ferrite, the vinylic polymeric structure was crosslinked with a diamino-compound. The magnetic composite obtainment was confirmed by the IR, DSC, and thermogravimetric analysis, as well as by optic and electronic microscopy, and also by the determination of the magnetic susceptibility of the products. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 3690–3695, 2008

Key words: core-shell magnetic composite; poly(styrene-*co*-methyl methacrylate-*co*-2,3-epoxypropyl methacrylate); *in situ* magnetite

INTRODUCTION

There is worldwide interest in the use of ferrite nanoparticles embedded in functionalized polymers as magnetic carriers for diagnostics, therapeutic, and related research applications. Thus, because of their relatively rapid and easy magnetic separation, magnetic polymeric particles are used in biomedical and bioengineering field such as cell separation,[1,2] immunoassay,[3] and nucleic acids concentration.[4] Also, magnetic polymeric particles offer a high potential in several areas of application such as detoxification of biological fluid and the magnetic guidance of particle systems for specific drug delivery process.[5] The pioneering work of Ugelstad et al.,[6,7] based on the preparation of hydrophobic monosized polystyrene magnetic particles, opened the research in this domain. Numerous attempts have been made to obtain core-shell magnetic composite with polymer structure as core and inorganic magnetic material as shell.[1,2]

The methodology used in preparation is basically based on direct precipitation of iron salt inside the pores of the porous polystyrene seed. The obtained particles exhibit large particles size (i.e., 2.8 and 4.5 mm) with a good magnetic separation.

The magnetic carriers are usually composed of two parts, core and shell. One is the magnetic core, which can be inorganic magnetic nanoparticles such as Fe_3O_4, nickel, as well as a polymeric matrix. The other is the shell around the core being this times the polymer layer or the magnetic particle. These architectures must provide favorable biocompatibility, high magnetic susceptibility, appropriate size distribution, and abundant functional groups on the surfaces of covalently coupled ligands for selective binding. There are two main ways to prepare the magnetic polymer microbeads. One is coating or encapsulating of magnetic particles with performed polymer.[8] The other is using monomer polymerization, which is used more widely. Several kinds of polymerization can be used such as emulsion polymerization,[9] dispersion polymerization,[10] suspension polymerization,[11] and microemulsion polymerization.[12]

The objective of this work is to report the preparation and characterization of a core-shell magnetic composite having as matrix a core with vinylic structure based on styrene, methyl methacrylate, 2,3-epoxypropyl methacrylate crosslinked with ethylenediamine, and a shell of magnetite *in situ* obtained and coupled through physical links to the polymer core.

EXPERIMENTAL

Materials

The reactants used in the experiments are as follows: styrene (S), methyl methacrylate (MMA), and 2,3-epoxypropyl methacrylate (GMA) (all purchased from Fluka Chemie, Seelze, Germany Merck, Darmstadt, Germany) were purified through distillation under reduced pressure and stored in refrigerator until use. Ethylenediamine (also from Fluka Chemie) was used without further purification.

Correspondence to: A. P. Chiriac (achiriac1@yahoo.com).

TABLE I
Recipe and Reaction Conditions for the Polymeric Matrix Synthesis

Monomers (% mol)	Potassium persulfate (% mol)	Tensioactive (% mol)
Styrene = 40.37		
Methyl methacrylate = 43.70	9.50×10^{-4}	0.0027
2,3-Epoxypropyl methacrylate = 15.97		
Ethylene diamine = 0.052		

Ratio for one recipe: 9.96 g styrene (0.096 mol), 10.37 g methyl methacrylate (0.104 mol), 5.38 g 2,3-epoxypropyl methacrylate (0.038 mol), 16 g ethylenediamine (0.052 mol). Reaction conditions: temperature during reaction 70–75°C, during treatment 80–85°C. Reaction time: prepolymerization, 20–25 min; polymerization, 300–330 min.

The tensioactive sodium *n*-dodecylbenzene sulfate ($C_{12}H_{25}C_6H_4SO_3Na$) (cmc = 1.15×10^{-3}, M_w = 348.47 from Merck)[13] as anionic agent, ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), and ammonium hydroxide (30% concentration) with analytical purity have been used without further purification.

Potassium persulfate was recrystallized from bidistilled water. In all experiments, the water used was double distilled and contained no foreign ions.

Vinylic matrix preparation

The recipes as well as the reaction conditions during the synthesis of macromolecular compounds are presented in Table I. To obtain lattices with uniform size, a seeded emulsion radical polymerization procedure has been used with 10% of the monomers mixture. This first step last for 10 min and is followed by the addition of the remaining monomers for the next 20–25 min, and then started the proper reaction which is maintained at 70–75°C for 5 h. The thermal treatment is performed at 80–85°C for 1 h. The synthesized latex is treated with ethylene diamine (mol 0.052) and the crosslinking reaction is performed for 2 h at 80–85°C. Then, it is centrifuged (5000 rot/min) and the copolymer particles are washed 3–4 times with distilled water to remove diamine and the nonreacted monomers.

Magnetic composite obtainment

Copolymer particles (55 g) were introduced in water (80 mL) to take part to the preparation of ferrite from the reaction between $FeCl_2 \times 4H_2O$ (1.44 g) and $FeCl_3 \times 6H_2O$ (0.76 g), which were previously solved in 50 mL distilled water the mixture being shake it for 1 h at reduced pressure and 80°C. After that, 25 mL NH_4OH 30% was introduced, and a black color of the entire mixture was obtained. This attests the preparation of the magnetite. The obtained product was cooled at the room temperature, separated through filtration, washed several times with distilled water, and finally dried under reduced pressure at 50–55°C for 72 h.

Characterization

IR absorption spectra have been recorded on M 80 Specord (Germany) spectrophotometer for equal quantities of polymer particles synthesized in emulsion as well as for magnetic composites (Fig. 1).

NMR spectra were obtained at 34°C with Varian EM-390 NMR spectrometer using 2.5% (wt/v) polymer solutions in the deuterated-DMSO (DMSO-d_6) (Fig. 2), which confirm the preparation and structure of the copolymer based on styrene/methyl methacrylate/2,3-epoxypropyl methacrylate (5.9 ppm: C_6H_5 and 5.64: CH_2 from styrene, 6.098 and 6.38 ppm: CH_2, 5.26: CH_3 from MMA).

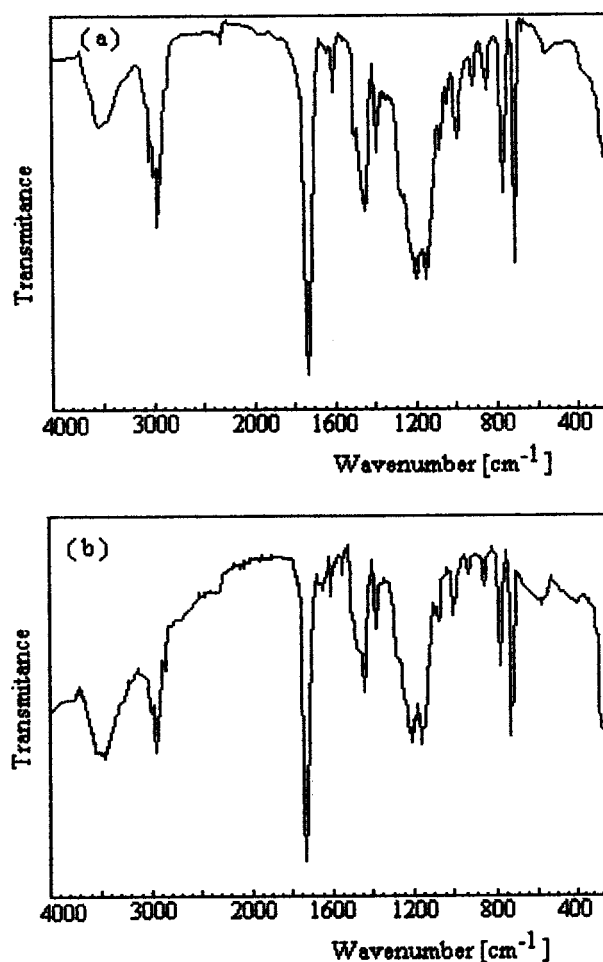TG and derivative thermogravimetric (DTG) curves were recorded on a MOM Budapest derivato-

Figure 1 IR spectra of poly(styrene-*co*-methyl methacrylate-*co*-2,3-epoxypropyl methacrylate) (a), and of the composite with magnetite *in situ* synthesized (b).
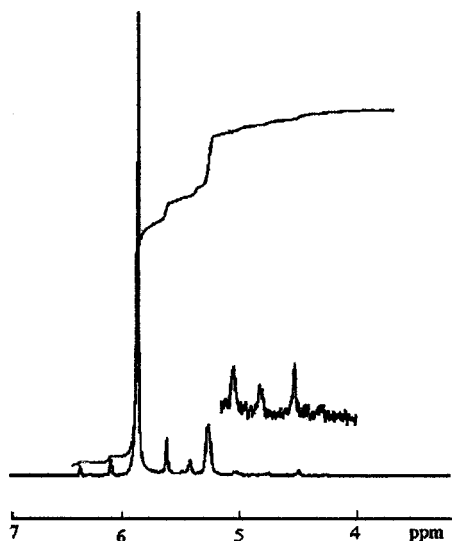
Figure 2 NMR spectra of the polymeric template.

graph under the following operational conditions: sample weight 50 mg, heating rate 12°C/min, in air flow of 30 mL/min, and with reference material α-Al_2O_3 up to 600°C.

The thermal properties of all polymers and blend films were measured using a Mettler 12E type DSC (Switzerland). The instrument was calibrated using an indium standard. Sample size was kept at 10–12 mg and heating rate was maintained at 10°C/min. An inert atmosphere was maintained throughout the DSC run. The first heating was realized from the room temperature to 170°C. The second heating of the same sample was performed after its cooling and also on the same temperature range.

The polymer and magnetic composites morphology was determined by means of a scanning electron microscope (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 7700× for the polymers

matrix and 4200× for polymer/ferrite composite section, respectively, and 370× for composite surface.

The magnetic properties were determined on a homemade device.[14] The experiments were conducted directly on magnetic composite samples prepared as mentioned earlier, the sample being placed in a cylindrical sample holder. The magnetic character of the composites was evidenced by the magnetic susceptibility measurements.

RESULTS AND DISCUSSION

The study pursues the polymer lattices synthesis based on styrene/methyl methacrylate/2,3-epoxypropyl methacrylate with improved kinetics and yield in the presence of usual tensioactive. The structure of the copolymer illustrated in the following image as well as its properties are toughened and correlated with the subsequent applications of polymer, especially as macromolecular matrices for magnetic composites.
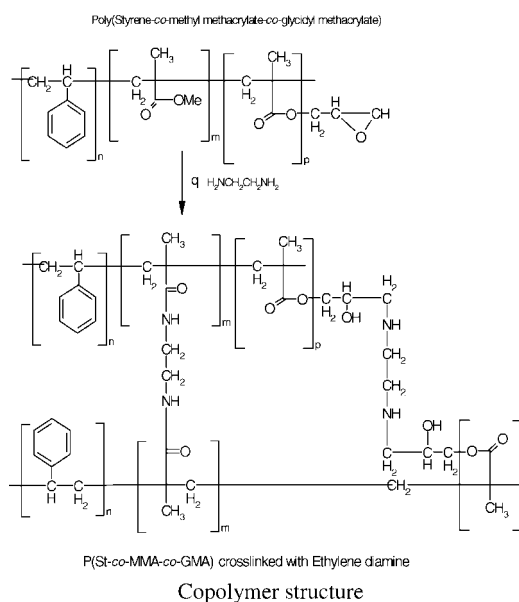

Copolymer structure

TABLE II
Characteristic Infrared Absorption Frequencies

| Frequency range (cm^{-1})	Compound type and bond
1,735 stretch	νC=O from methyl and 2,3-epoxypropyl methacrylate
700–900 vibrations	νCH aromatic rings of styrene
1,380 and 2,962 stretch	νCH_3 methyl and 2,3-epoxypropyl methacrylate
2,853 scissoring and bending vibrations	νCH_2
1,430–1440 vibrations	δCH_3 asymmetric group $COOCH_3$
910 stretch vibrations	Epoxy group and its crosslinking with ethylenediamine
1,140–1,200 stretch vibrations	νC=O
1,600 vibrations	δNH
350–430, 600–630	Fe_3O_4
1,550 and 1,630 stretch	O=C—N amide and carbonyl from epoxy group transformation
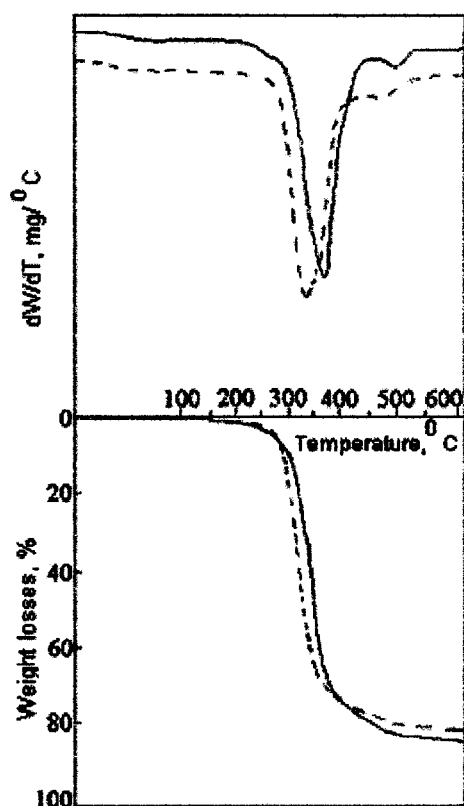
Figure 3 DTG and TG diagrams of the styrene/methyl methacrylate/2,3-epoxypropyl methacrylate copolymer (——) and of the magnetic composite (– – –).

NMR and IR spectra (Figs. 1 and 2) and Table II confirm first by the synthesis as well as the structure of the obtained copolymer based on styrene/methyl methacrylate/2,3-epoxypropyl methacrylate, and secondly, the preparation of the magnetic composite.

All the essential peaks and bands correspond to the main groups in monomers and prove the structure of the polymer. The band from 1600 cm^{-1} also evidences the crosslinking of the copolymer with ethylenediamine, the fact being confirmed by the elemental analysis which proved the presence of 0.67% nitrogen into the composition of the polymeric matrices.

The presence of the magnetite is also noticed by IR spectra through supplementary bands from 350–430 cm^{-1} and 600–630 cm^{-1}, as well by the additional peaks from 1550 and 1630 cm^{-1} typical for
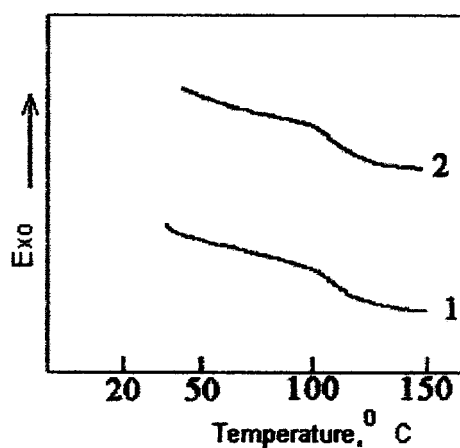

Figure 4 DSC spectra of the styrene/methyl methacrylate/2,3-epoxypropyl methacrylate copolymer (1), and of the magnetic composite (2).

amidic groups and to their bonding interactions with iron.

Figures 3 and 4 illustrate DTG and DSC diagrams of the copolymer as well of the prepared magnetic composite. The corresponding thermal characteristics are presented in Table III.

As it is observed, the copolymer is more stable than the magnetic composite as follows: the maximum for 50 wt % weight loss corresponds to 358°C in case of the copolymer and to 330°C for the composite. This fact is attributed to the new links between polymer particle and magnetite to the detriment of the intramolecular forces as well also to the iron oxide presence that acts as catalyst during decomposition process. Activation energy (E_a) was determined according to the Coats-Redfern method.[15,16] Small increases of E_a are registered on the heating interval with the higher rate of decomposition. Also, the glass transition temperature does not change, being the same for the copolymer as well for the magnetic composite of about T_g = 110°C.

A successful polymer coupling of iron oxide particles requires a reduced difference of the polarity between polymeric network and magnetite as well as the presence of functional groups for better linkage between structures. In this order, the copolymer based on styrene/methyl methacrylate/2,3-epoxy-

TABLE III
DTG and DSC Data for the Copolymer and the Magnetic Composite

Sample	T_{10} (°C)	T_{50} (°C)	T_i (°C)	T_m (°C)	T_f (°C)	W_{Ti-Tf} (%)	E_a (kJ/mol)	n	T_g (°C)
Copolymer	305	358	195	360	440	75	101	1.3	110
Magnetic composite	290	330	205	322	410	72	137	1.8	110

T_{10}, T_{50}, temperature corresponding to 10 and 50 wt % weight loss, respectively; T_i, temperature corresponding to the beginning of decomposition process; T_m, temperature of maximum rate of weight loss; T_f, final temperature of the main decomposition process; W_{Ti-Tf}, weight loss during the main decomposition process; T_g, glass transition temperature.
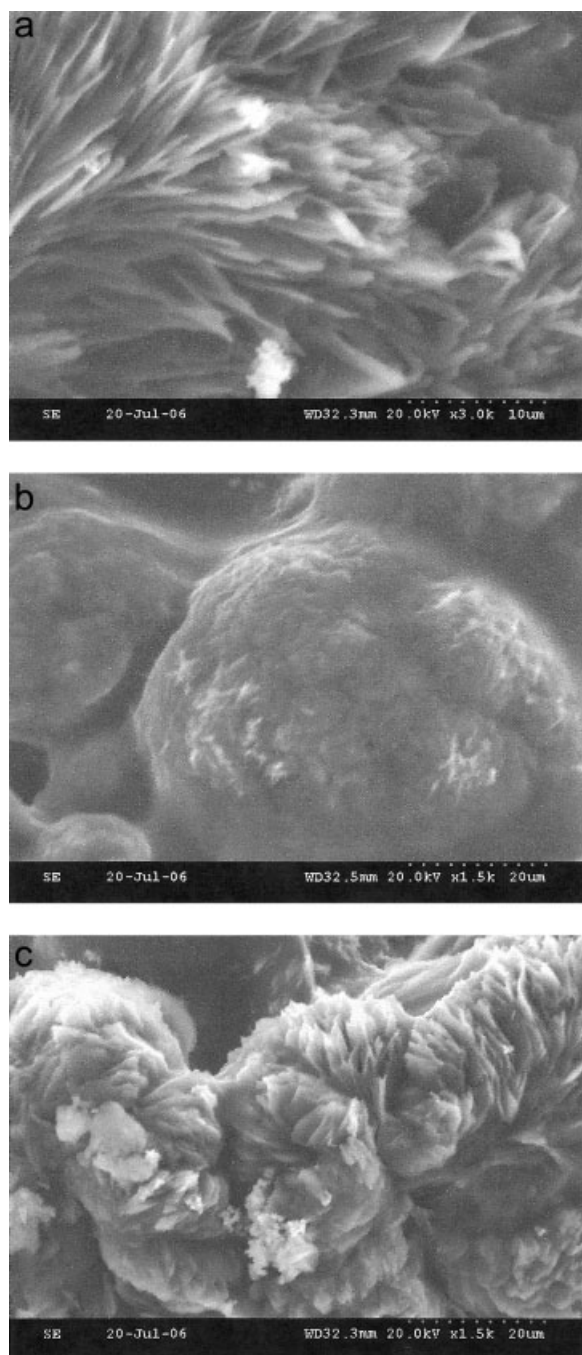
Figure 5 SEM micrographs of the latex particle: (a) styrene/methyl methacrylate/2,3-epoxypropyl methacrylate copolymer (×7700); (b) magnetic composite: particle surface (×4200); and (c) magnetic composite: section (×370).

propyl methacrylate was prepared, which was cross-linked with ethylene diamine—very useful for building blocks—to create the polymeric network structure more able for capturing the magnetite particle in its meshes.

Also, the copolymer, through their comonomers, has a reduced hydrophobicity and thus the system presents improved possibilities for better coupling of

the magnetite which are hydrophilic nanoparticles. In this way, we ensure that all the magnetite particles are transferred uniformly onto the resulting particles.

This kind of structure assures uniform distribution of magnetite, which can be large enough for quick magnetic separation, on the surface of the polymer particles.

SEM micrographs of the copolymer and magnetic composite are illustrated in Figure 5. It evidenced the homogeneous, uniform, and spongy aspect of the copolymer particles [Fig. 5(a)]. Also, it is evident by the integration of the magnetite into the sponges
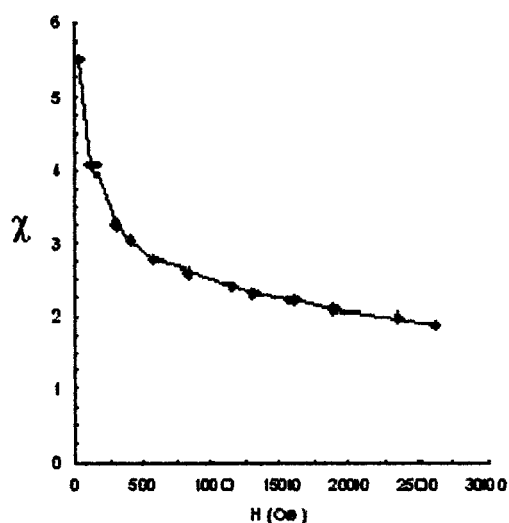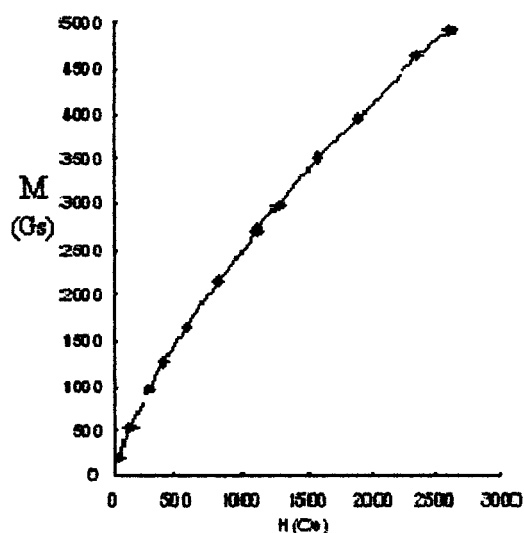
Figure 6 The evolution of the magnetic susceptibility as well of the magnetization for the magnetic composite based on the poly(styrene-co-methyl methacrylate-co-2,3-epoxypropyl methacrylate) as matrix for magnetite in situ synthesized.

of the copolymer as well as on its surface [Fig. 5(b,c)].

The distribution of magnetite particles onto the polymer surface also seems to be homogeneous, more than that it also seems to be rounded by the polymer, which confirms the involvement of the magnetic particles into the meshes of crosslinked polymeric chains.

The variation of the magnetic susceptibility with intensity of the magnetic field and the magnetization curves for the obtained magnetic composite are presented in Figure 6. The values of the magnetic susceptibility as well of the magnetization confirm the preparation of the magnetic composite, the obtained values being in agreement with the purpose of the study and with other researches in the field.[16]

CONCLUSIONS

The study confirms the preparation of a magnetic composite having a vinylic product as core based on styrene/methyl methacrylate/2,3-epoxypropyl methacrylate copolymer crosslinked with ethylenediamine and as shell the magnetite *in situ* prepared. The advantages are the obtainment of a polymeric network capable for a better coupling of the inorganic product, and also further intermediaries steps are avoided to prepare the magnetite. More than that the dimensions of the synthesized magnetite are uniform and the particles are small and well dispersed.

The magnetic susceptibility of the product evidences its capacity to respond at an external magnetic field.

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