Preparation and Characterization of the Structure of PSt-*b*-PAA/Co Composite Material

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ABSTRACT: The polystyrene-*block*-polyacrylic acid (PSt-*b*-PAA) copolymer is obtained through the reversible addition-fragmentation chain transfer polymerization (RAFT). Then the cobalt (Co) nano-particles are synthesized by loading the Co^{2+} salt into the polymer and reducing them. Polymer–matrix composites with an average particle size of 10 nm have been formed by a simple technique. The technique exploits the dispersed phase of the polymer to form numerous identical nanoreactors. In this approach, nanoparticles are rigidly attached to the support surface to prevent their agglomeration. FT-IR and TEM analysis of these polymer–matrix composites revealed that nano-structures are formed and the shape can be controlled. Vibrating sample magnetometer is also used to study the magnetic property of the materials at room temperature. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 1290–1294, 2012

Key words: polymer–matrix composites; magnetic properties; assembly; nanostructures; block

INTRODUCTION

Since the 20th century, scientists and engineers have endeavored to combine the best properties of both components in hybrid materials. Because the application of many of these materials will ultimately require the integration of nanoscale components into larger meso-, micro-, and macroscale contexts, the development of methods for reliably locating metal atoms or clusters in three dimensions within polymer matrices is a research area of ongoing concern.[1–3] A great deal of interests have been developed in the related areas of microcontact printing,[4] nanocontact molding,[5] and dippen nanolithography.[6] A number of methods for controlling the positioning of metallic species within polymer matrices on the nanometer scale have been developed.[7]

Self-assembly of block copolymers in selective solvents and the resultant polymeric nano-objects have received much attention in both theory fields and application fields. Block copolymers can be self-assembled into nano-micelles with many morphologies such as sphere, rod, vesicles, bi-layers, and so on.[8–12] In recent years, much attention was drawn to the complexation of a block copolymer with inorganic nano-particles and metallic nano-particles.[13,14] The nano-micelles formed by the self-assembly of block copolymer can also be used as nano-reactor, where many kinds of inorganic nano-particles and metallic nano-particles can be synthesized. The resultant copolmer/nano-particle hybrid materials have the properties of both from block copolymers and from the nano-materials, and this kind of materials has great latent applications as catalysts, biosensors, membranes.[15–18] Nanofibrous materials with magnetic properties with potential applications in memory storage devices, bioanalysis, catalysis, loudspeaker coils, and in the medical field have been prepared.[19] For example, they are used for NMR contrast agents and for cell separations.[20]

In this article, the block copolymer PSt-*b*-PAA, was obtained through the RAFT polymerization, using PSt as macro-CTA (chain transfer agent).[21] The block copolymer was coordinated with Cobalt(II) chloride ($CoCl_2$) in *N,N*-dimethylformamide (DMF) and was reduced by potassium borohydride (KBH_4). Their self-assembly behavior was also studied. We use self-assembly of PSt-*b*-PAA to make nano-reactor, where Co magnetic nano-particles are synthesized. The structure and content of the material were studied with FT-IR and TEM. Vibrating sample magnetometer was also used to study the magnetic property of the materials at room temperature. Note that polymer with nanoparticles may have a significant effect on the physical and chemical properties of both the nanoparticles and polymer. This interaction may underlie new practical applications of the systems in question, e.g., in electronics and in medicine.[22,23]
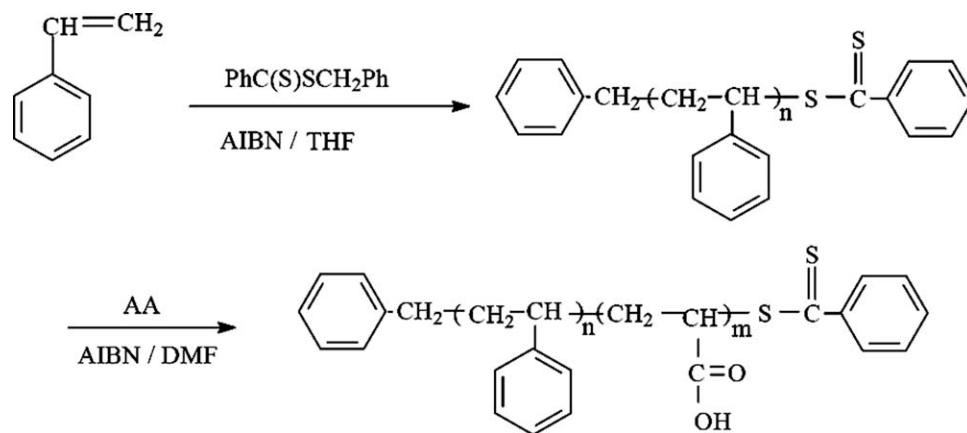
Figure 1 Formation of PSt-*b*-PAA.

EXPERIMENTAL

Materials

Styrene (St) and acrylic acid (AA) were distilled under vacuum and were stored at $-15°C$. AIBN was recrystallized by water before used. DMF was freshly distilled at room temperature under vacuum. THF, $CoCl_2 \cdot 6H_2O$, and KBH_4 were purchased from the First Shanghai Chemical Reagent Company, which were analytical grade and no further purification was performed. Deionized water was used in all experiments. PSt macro-CTA (chain transfer agent) was prepared according to our previous work.[24]

General procedure for polymerization from macro-CTA (chain transfer agent)

Into a dried glass tube with a magnetic bar, initiator (AIBN) was added, and then monomer (AA), macro-CTA, and DMF were added. The mixture was degassed by three freeze-pump-thaw cycles. The tube was sealed under vacuum, and then immersed in a water bath thermostated at $80°C$. After the reaction was carried out for a prescribed time, the tube was broken. Polymer samples were dissolved in DMF. By adding polymer solution into an excess of ether, the polymer was precipitated, filtered and dried at $40°C$ in a vacuum oven for 24 h. The synthesis route is displayed in Figure 1.[25]

Preparation of PSt-*b*-PAA/Co polymer–matrix composites

PSt-*b*-PAA block copolymers under study were dissolved in DMF, which is a good solvent for both PSt blocks and PAA blocks. Then $CoCl_2$ was dissolved in DMF using ultrasonic technique. $CoCl_2$/DMF solution was added very slowly to the polymer solution under vigorous mixing, leading to the formation of PSt-*b*-PAA/$CoCl_2$ block copolymers, the concen-

tration of PSt-*b*-PAA in the final solutions was 1 mg mL^{-1}. After the formation of PSt-*b*-PAA/$CoCl_2$ block copolymers, we use dialysis bag to dialyze the polymer–matrix composites in DMF. If the Co^{2+} can not be dialyzed, we think the ratio of Co to acrylic acid is fixed. The ratio of Co^{2+} groups per acrylic acid was 1/10. The mixture was stirred for 72 h. Then a solution-phase metal salt deposition method was applied to PSt-*b*-PAA polymer to prepare PSt-*b*-PAA/Co polymer–matrix composites.[26] KBH_4 dissolved in DMF, which was used as reducing agent, was added to the polymer solution. Then adding polymer solution into an excess of ether, the polymer–matrix composites was precipitated, filtered and dried at $40°C$ in a vacuum oven for 24 h.

Characterization

The IR spectra was recorded in solid state using KBr pellet. A MAGNA-IR 750 (Nicolet Instrument, USA) was used to record the spectra in the range of 400–4000 cm^{-1}. Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) equipped with a Waters 1515 pump and Waters 2414 differential refractive index detector (set at $30°C$). It used a series of three linear Styragel columns HT2, HT4, and HT5 at an oven temperature of $35°C$. The eluent was DMF at a flow rate of 1.0 mL min^{-1}. A series of low polydispersity polystyrene (PSt) standards were employed for the GPC calibration.

Transmission electron microscopy

The morphologies of the polymer–matrix composites were studied by transmission electron microscopy (TEM) performed on a JEOL JEM100SX-EM microscope. To prepare TEM samples for the study of the size and the morphology of the aggregates, a drop of dilute solution (about 0.5 mg mL^{-1}) was deposited onto a copper EM grid, which had been

precoated with a thin film of Formvar and then coated with carbon. When taking photos, the polymer films were not stained with any chemicals, and the contrast of the image in the TEM photos can only originate from the cobalt complexes incorporated into the copolymers.

Magnetic properties

The cobalt nanoparticle dispersions stabilized with polymer was sealed into 4-mm-diameter glass tubes under an argon atmosphere. Magnetic properties of the cobalt dispersions were measured, using a vibrating sample magnetometry (VSM): MODEL VSM VT-800 (Riken Densh). The magnetic moment of the sample was measured in fields from 0 to 25 kOe.[27,28]

RESULTS AND DISCUSSION

FT-IR analysis

The IR spectra of (a) PSt macro-CTA, (b) PSt-b-PAA, and (c) PSt-b-PAA+CoCl$_2$ are shown in Figure 2. From the IR spectra, the peak at 1600 cm^{-1} is indicative of benzene absorption of PSt macro-CTA [Fig. 2(a)]. Although carboxylic acids and their salts all had carbonyl group, the IR spectra of bands were different. The band at 1750–1770 cm^{-1} is due to the carbonyl group of carboxylic acids of the block AA chain, the presence of the above bands in the block copolymer gives strong evidence of block [Fig. 2(b)]. The band at 1550–1650 cm^{-1} is due to the carbonyl group of their salts [Fig. 2(c)]. PSt-b-PAA in Figure 2(b) revealed the C=O and O—H stretching bands at 1400–1428 cm^{-1} and 1250 cm^{-1}, which was not presented at the spectra of PSt-b-PAA+CoCl$_2$. These peaks originate from the carbonyl in the acid radical group. It is disappeared due to the acid radical cooperated with cobalt ions, which further confirms the presence of the reactions. The number average molecular weights (M_n) and the molecular weight distribution were determined by GPC. The molecular weight and distribution of PSt macro-CTA were 8.0 × 10^3 and 1.10, while those of PSt-b-PAA were 17 × 10^3 and 1.16.

Transmission electron micrographs of cobalt dispersion in polymer

According to our previous investigations, a number of cobalt–polymer hybrid systems have also been described in the literature.[29] Figure 3 shown that cobalt nanoclusters with polymer ligands have typically been prepared by the reduction of Co^{2+} salts by KBH$_4$ in the presence of a range of stabilizing molecules, which prevent aggregation into larger agglomerates. TEM of cobalt dispersions using PSt
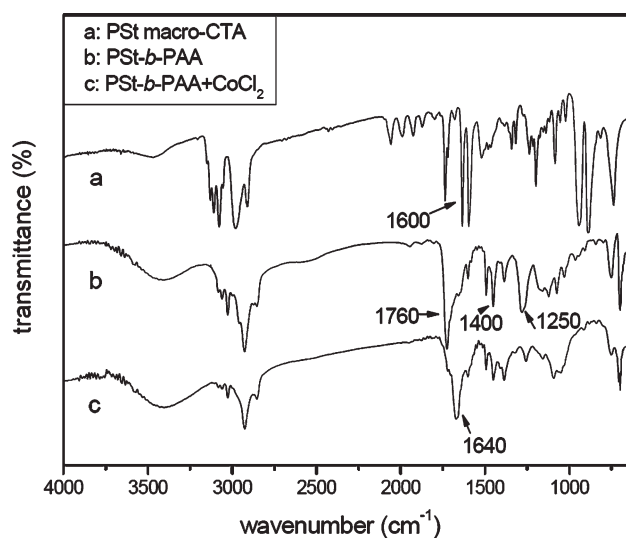

Figure 2 FT-IR spectra of (a) PSt macro-CTA, (b) PSt-b-PAA, and (c) PSt-b-PAA +CoCl$_2$.

polymer in DMF as stabilizing molecules show that agglomerates of particles with aggregate sizes about 50 nm in diameter and the aggregation number (number of nanoparticles per aggregate) was lying between several tens and hundred [Fig. 3(A)]. In TEM images, the nanoparticles appeared as dark spheres. These agglomerates were thought to be formed because PSt polymer cannot coordinate with Co^{2+} ions efficiently. TEM of cobalt dispersions using PSt-b-PAA polymer in DMF shown nano particle sizes (10 nm) with none aggregation were observed [Fig. 3(B)]. The size of the cobalt nanoparticles, determined as the average over 113 nanoparticles stabilized on the PSt-b-PAA polymer, was 10 nm. Thus, the carbonyl on the copolymer was able to coordinate with Co^{2+} to ensure that each particle forms within the polymer and that aggregation is avoided. The negatively ionized PAA block interacts strongly with the positively-charged nanoparticles, thus playing the role of an anchoring block. The particle structure and particle size can be observed clearly from Figure 3(C) which is the enlarged view of Figure 3(B). Figure 3(D) was thought to be micelle aggregates essentially stained with cobalt dispersions using Co and PSt-b-PAA copolymer in DMF/H$_2$O solvent. As for PSt-b-PAA copolymer, H$_2$O is a good solvent for PAA block, but it is not a good solvent for PSt block, leading to the formation of aggregates with compact cores of insoluble blocks surrounded by a soluble shell composed of soluble blocks. The self-assembly of PSt-b-PAA into micelles in selective solvent were observable in the TEM photomicrographs from analogous copolymer solutions. The common solvent (DMF) mainly modifies the degree of the stretching of the core-forming block in the core. After reduction, the Co nano-particles were
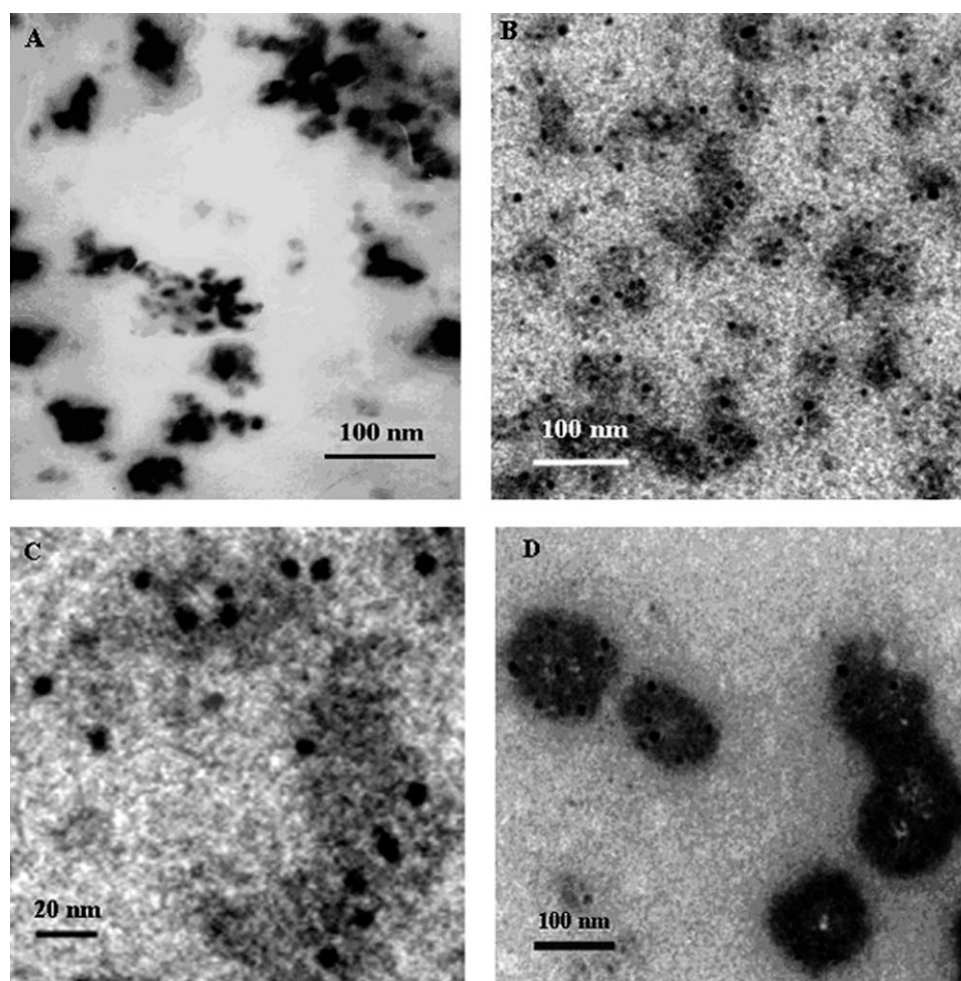
Figure 3 TEM images of the polymer–matrix composite particles. (A) TEM image of PSt polymer/Co in DMF, (B) A low magnification TEM image of PSt-*b*-PAA/Co in DMF, (C) an enlarged TEM image of PSt-*b*-PAA/Co in DMF, (D) TEM image of PSt-*b*-PAA/Co in DMF/H_2O.

dispersed in the micelles, which can be observed clearly from Figure 3(D).

In general, the preparation of hybrid metal-block copolymer materials can be grouped into several general classes: (1) Direct polymerization of metal-functional monomers; (2) Direct assembly of block copolymers with nanoscale metallic species; (3) Preparation of ligand-functional block copolymers.[21] The block polymer, which is the amphiphilic block copolymers and has functional group coordinated with metal ions, could be used as nano-reactor.

Magnetic properties of the cobalt dispersions

Magnetization measurements of the cobalt fluids with specied cobalt concentrations were made on vibrating sample magnetometer (MODEL VSM VT-800) (Fig. 4). The saturation magnetization of the fluid in emu was read at an applied field strength of 20 kOe. The *y*-axis intercept of a plot of applied field strength versus magnetization provided the value for the saturation magnetization of the fluids in

emu. The (*g*) means a mass of magnetic polymer. For these samples, these values were very close to the maximum values read. Owing to the
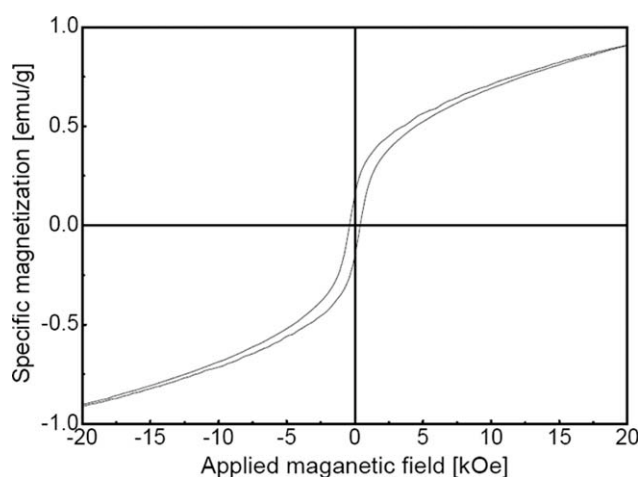

Figure 4 Hysteresis loops for PSt-*b*-PAA/Co nanoparticle, taken at room temperature.

ferromagnetic property of these polymer–matrix composites, they are fit to use as magnetic core of transformer. The magnetic core can reduce the surplus magnetic induction strength. Under the condition of the same output power and output voltage, the volume of the magnetic core and the pulse transformer product can be reduced. The weight and the cost of the product also can be reduced.

CONCLUSIONS

The polystyrene-*block*-polyacrylic acid copolymer was obtained through the RAFT polymerization. Cobalt nanocrystals can be prepared *in situ* in the presence of PSt-*b*-PAA block copolymer stabilizers. FT-IR and TEM analyses of these polymer–matrix composites revealed that nano-structures are formed. The procedure through which we obtain cobalt nanoparticles dispersed in a polystyrene-*block*-polyacrylic acid matrix is interesting for its apparent simplicity and straightforwardness. Vibrating sample magnetometer is also used to study the magnetic property of the materials at room temperature. The results show that it is fit to use as magnetic core of transformer. The control of particle size and relationships between coating efficiency and thickness will be subjects of further study.

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