

Preparation of Polystyrene/Poly(vinyl acetate) Nanocomposites with a Core–Shell Structure via Emulsifier-Free Emulsion Polymerization

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ABSTRACT: Polystyrene/poly(vinyl acetate) latex nanoparticles with a core–shell morphology in an emulsifier-free emulsion polymerization system were prepared with purified styrene and vinyl acetate (VAc) as monomers and 2,2'-azo bis(2-amino propane) dihydrochloride (ABA,2HCl) as the initiator and emulsifier. The optimized conditions of polymerization of VAc, on top of the already-formed polystyrene as a core polymer, with a core–shell morphology were obtained using various parameters such as volume ratio of the first and second stages, type of process, and

reaction time. The morphologic structure of the nanoparticles was studied by scanning electron microscopy and transmission electron microscopy. The latex nanoparticles and polymers were characterized by differential scanning calorimetry. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2409–2414, 2006

Key words: nanocomposites; polystyrene/poly(vinyl acetate); core-shell; emulsifier-free; emulsion polymerization

INTRODUCTION

Copolymerization of styrene with vinyl acetate (VAc) is virtually impossible because of the reactivity ratios of the system^{1,2} and also because polystyrene is not compatible with poly(vinyl acetate). So preparation of polystyrene/poly(vinyl acetate) (PS/PVAc) with a core–shell structure might have special uses.

Since 1965, when Matsumoto and Ochio³ first reported that a monodisperse microsphere could be prepared by emulsifier-free emulsion polymerization based on a styrene/potassium persulfate/water system, the technique has become of significant interest. In particular, how an emulsifier-free emulsion polymerization system gains colloid stability via the involvement of components that act as emulsifiers has been the subject of several studies. For examples, ionizable initiators, such as potassium persulfate^{4–7} or azobis(isobutylamidine hydrochloride),⁸ can behave as emulsifiers in an emulsifier-free emulsion polymerization system.

Core–shell materials consist of a core structural domain covered by a shell domain. The core–shell domains are composed of a variety of materials, including polymers, inorganic solids, and metals.⁹

Core–shell particles generally have been prepared by interfacial polymerization,^{10,11} but they also have been prepared by emulsion or suspension formation followed by solvent extraction.^{12,13}

Some of the main problems encountered to date in core–shell particle manufacture have been the production of monodisperse, liquid cores, complete and even shell coverage and subsequent characterization of shell thickness and morphology.¹⁴ Morphology of core–shell polymers depends on the following factors: (1) properties of the monomers used, such as the hydrophilic; (2) the solubility characteristics of the monomers¹⁵; and (3) the way that the polymer is prepared, including the batch process, the successive addition process, and the continuous time-controlled addition of the monomers.¹⁶

EXPERIMENTAL

Materials

Styrene and vinyl acetate monomers were supplied by Merck Chemical company (Whitehouse Station, NJ). The styrene was purified by distillation under vacuum, and the vinyl acetate was purified by atmospheric distillation (0.5% CuI was used in order to prevent the polymerization of styrene and vinyl acetate during distillation). The chemical used as an initiator and also an emulsifier was 2,2'-azo bis(2-amino propane) dihydrochloride (ABA,2HCl; Wako Chemical Company, Richmond, VA). Distilled water and

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TABLE I
Recipe for Emulsifier-Free Emulsion Polymerization of Styrene

Styrene (mL)	Water (mL)	Initiator (g)	Temperature (°C)	pH	Speed (rpm)
5.5	100	0.23	70	7	320

hydrochloric acid were used to control the pH during polymerization.

Polymerization process

An emulsifier-free emulsion two-stage polymerization process was used to prepare the PS/PVAc nanocomposite particles. The recipe and polymerization conditions are shown in Tables I and II, respectively.

All reactions were carried out in a 150-mL round-bottomed flask with a three-necked flanged top within a constant-temperature water bath at 320 rpm and under a nitrogen gas blanket, conditions that were maintained in the reacting medium throughout the reaction.

Equipment

The samples were characterized by scanning electron microscopy (SEM; ZEISS DSM 960A, Oberkochen, Germany), transmission electron microscopy (TEM; CEM 902A ZEISS, Thornwood, NJ), and differential scanning calorimetry (DSC; PL DSC, England), and the samples were microtomed using an ultramicrotome (V 2088 LKB, Pharmacia, Piscataway, NJ).

Sample preparation

Samples were prepared for SEM and gel permeation chromatography (GPC) according to the methods reported previously.¹⁷

Each emulsion sample for the TEM analysis was diluted 1:10,000 (v/v) in water. This diluted emulsion was stained with a 2% aqueous solution of osmium tetroxide. After 1 h the sample was washed with distilled water and the water was removed according to the schedule given in Table III. The procedure given in Table IV was followed in order to eliminate the

TABLE III
Sample Washing Conditions

Ethanol/water (v/v)	50:50	25:75	10:90	0:100
Time (min)	15	15	15	60

TABLE IV
Ethanol Elimination Conditions

Ethanol/epoxy resin (v/v)	1:1	1:2	1:3	0:1
Mixing time (h)	1	2	6	6

ethanol before treating the samples with epoxy. The samples were centrifuged for 6 h in epoxy resin and molded for 24 h at 60°C. The molded samples were ultramicrotomed with a 50- to 70-nm-thick glass knife.

RESULTS AND DISCUSSION

The optimized conditions of polymerization of styrene via emulsifier-free emulsion polymerization were obtained by examination of various parameters such as pH, monomer concentration, and initiator concentration. The details of the experimental procedure were reported previously.¹⁷

Some studies¹⁸ reported a 2:1 monomer ratio to form core-shell structure polymer and that this was the best monomer ratio for preparing a core-shell morphology.

As mentioned above, the second stage of polymerization was started with a 2:1 monomer ratio.

Using a previously reported experimental procedure,¹⁷ polystyrene was formed, and then immediately, the whole of vinyl acetate was added in one portion to the reactor. Table V lists the different polymerization times of vinyl acetate. The effect of the type of process on the morphology of nanoparticles also was examined.

In experiment 1 polymerization was stopped after 8 h. Figures 1 and 2 present scanning electron micrographs of the polystyrene and polystyrene/poly(vinyl acetate) (core-shell) nanoparticles, respectively.

The nanoparticles of polystyrene shown in Figure 1 are uniform in shape and size, but those shown in

TABLE II
Recipe for Emulsifier-Free Emulsion Polymerization of Core-Shell

Styrene (mL)	Water (mL)	Initiator (g)	Vinyl acetate (mL)	t_1 (h)	t_2 (h)	Temperature (°C)	pH	Speed (rpm)
5.5	100	0.23	3	24	24	70	7	320

t_1 = Reaction time of polymerization of styrene (core).

t_2 = Reaction time of polymerization of vinyl acetate (shell)

TABLE V
Effect of Different Polymerization Times on Vinyl Acetate

Experiment (#)	Styrene (mL)	Water (mL)	Initiator (g)	Vinyl acetate (mL)	t_1 (h)	t_2 (h)	Temperature (°C)	pH	Speed (rpm)
1	5.5	100	0.23	3	24	8	70	7	320
2	5.5	100	0.23	3	24	12	70	7	320
3	5.5	100	0.23	3	24	24	70	7	320

t_1 = Reaction time of polymerization of styrene (core).
 t_2 = Reaction time of polymerization of vinyl acetate (shell).

Figure 2 are not, with some nanoparticles bigger than others, which are bigger than the polystyrene (core) nanoparticles (Fig. 1). So it was found that a core-shell structure was formed, but that it did not have the best morphology of a core-shell. This structure was confirmed by Figure 3, which is a transmission electron micrograph of a microtomed section of the polystyrene/poly(vinyl acetate) nanocomposite particles, with the darker areas poly(vinyl acetate) regions and

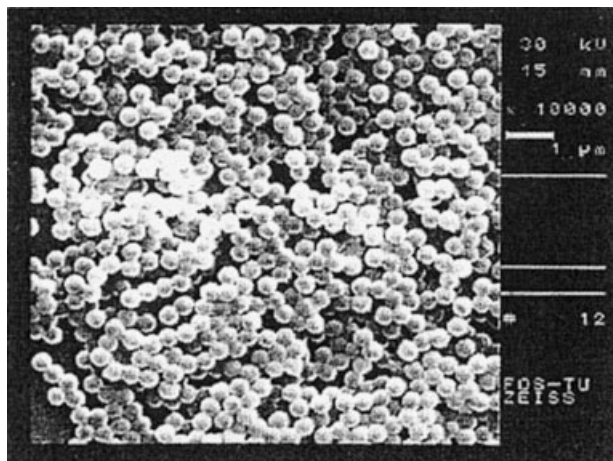


Figure 1 SEM micrograph of PS (core polymer).

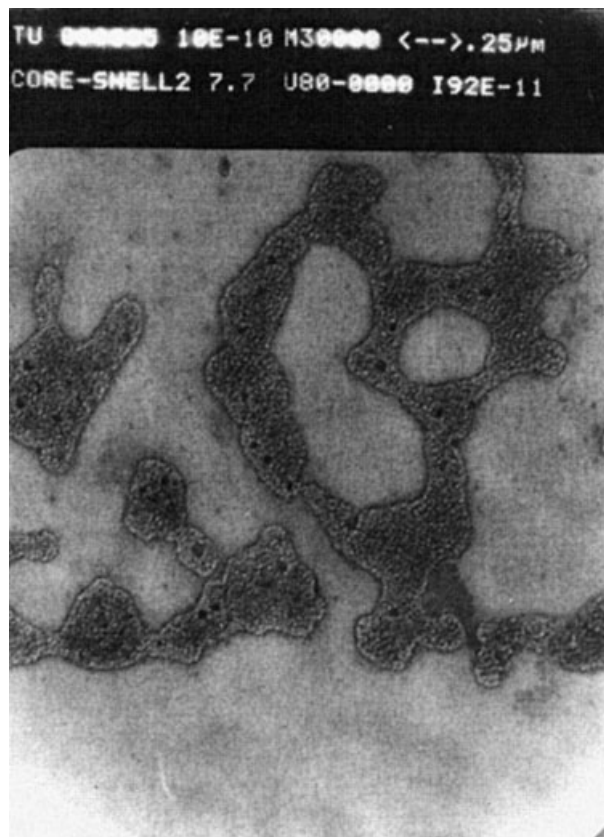


Figure 3 TEM micrograph of polystyrene/poly(vinyl acetate).

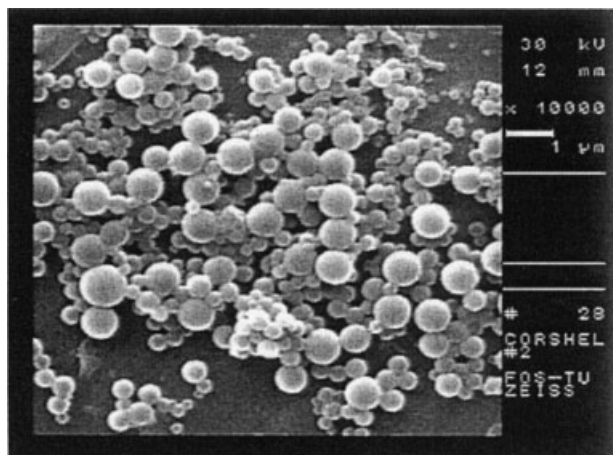


Figure 2 SEM micrograph of polystyrene/poly(vinyl acetate).

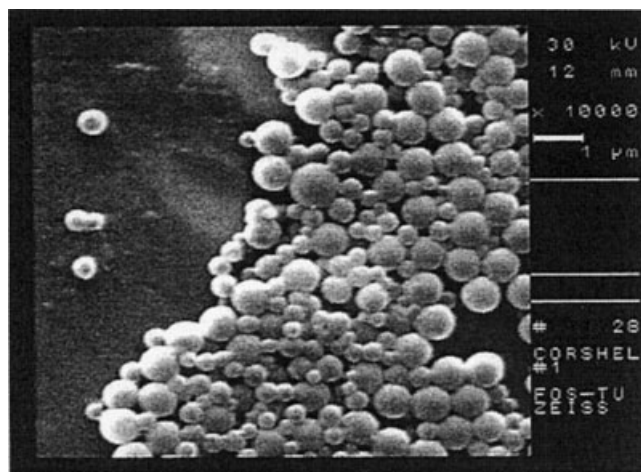


Figure 4 SEM micrograph of polystyrene/poly(vinyl acetate).

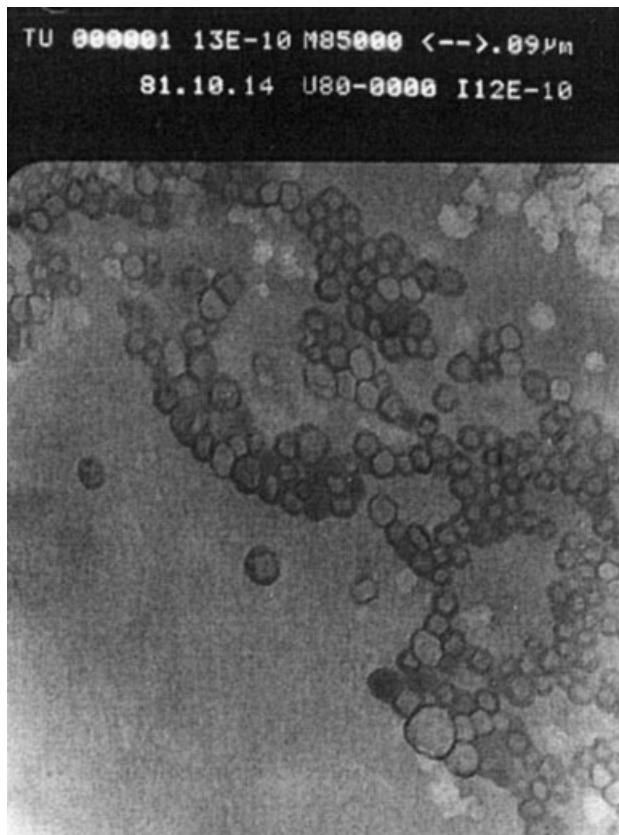


Figure 9 TEM micrograph of polystyrene/poly(vinyl acetate).

(addition in one portion). Hence, experiment 2 was repeated, and the vinyl acetate was added gradually at a rate of 1 mL/min. Figures 6 and 7 show the results of this change. The nanoparticles shown in Figure 6 are much more uniform than those shown in Figure 4,

and the surfaces of the nanoparticles (Fig. 6) appear to be covered by small particles. These were identified as poly(vinyl acetate) domains.

Because it was hypothesized that the small nanoparticles on the surface of the polystyrene (Fig. 6) might be converted to a thin layer of poly(vinyl acetate) nanoparticles by increasing reaction time, experiment 3 was designed.

The results of experiment 3, shown in Figures 8 and 9, indicate that the polystyrene/poly(vinyl acetate) nanoparticles were uniform, with a core-shell morphology and particle-size distribution that was monodisperse.

The differential scanning calorimetry (DSC) analysis of the polystyrene/poly(vinyl acetate), performed during experiment 3 (Fig. 10), showed two peaks, at 48°C and 110°C. These were the glass-transition temperatures of poly(vinyl acetate) and polystyrene, respectively.

CONCLUSIONS

Use of the procedure presented in this article resulted in the preparation of a nanocomposite polymer with a core-shell morphology of styrene and vinyl acetate via emulsifier-free emulsion polymerization, with 2,2'-azo bis(2-amino propane) dihydrochloride playing the role of initiator and also of emulsifier.

The formation of the core-shell morphology is a strong function of the following factors: (1) miscibility and hydrophilicity of the different monomer-polymer combinations present, (2) type of surfactant, (3) volume ratio of the first and second stages, (4) type of process (batch, continuous, etc.), and (5) process temperature and individual glass-transition temperatures

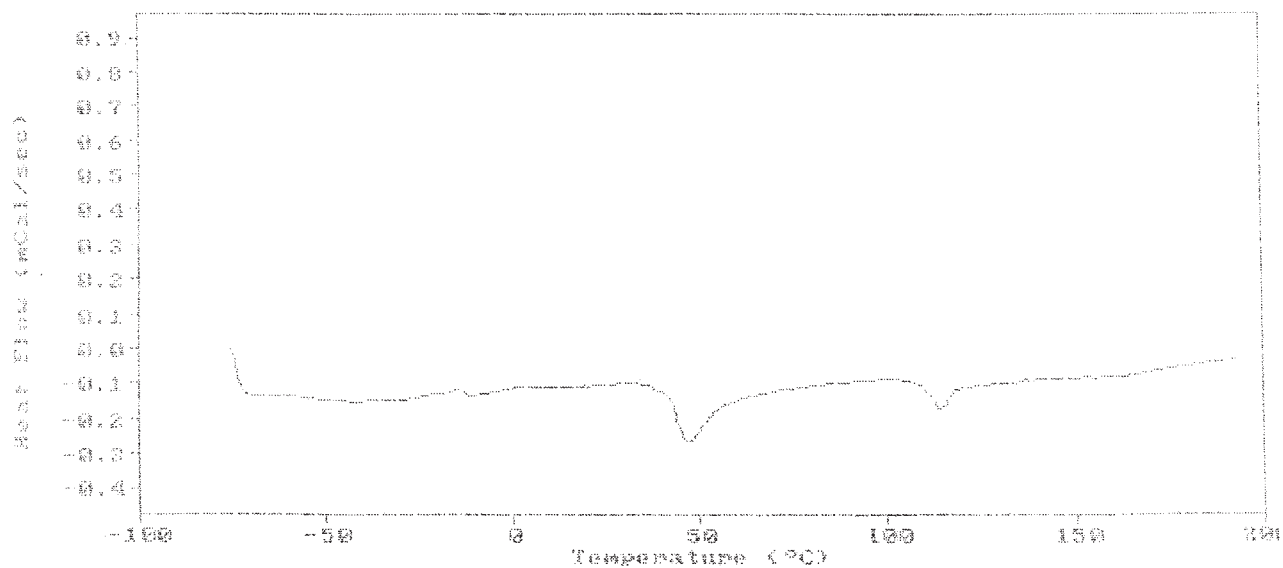


Figure 10 DSC trace of polystyrene/poly(vinyl acetate).

of the polymers involved. In the present study, all these parameters were considered. Polymerizing a hydrophilic monomer, that is, one that is immiscible with the core polymer, on top of an already-formed hydrophobic core polymer causes formation of an ideal core-shell morphology. So, in the present study, polystyrene was selected as the core polymer, and vinyl acetate was selected as the monomer that forms the shell polymer.

The way that polymer is prepared also is of great importance. In the present study, the continuous time-controlled addition of the second monomer caused uniform nanoparticles with core-shell structure to be prepared. The details about the experimental procedure and the best conditions for emulsifier-free emulsion polymerization were reported previously by Sharifi-Sanjani et al.¹⁷

Microscopic characterization to determine the structure of core-shell nanoparticles was examined by SEM and TEM. The DSC data helped us to perfect our conclusion.

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