

Acidic Hydrolysis of a Poly(vinyl acetate) Matrix by the Catalytic Effect of Ag Nanoparticles and the Micellization of Ag-Metal-Containing Polymer

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ABSTRACT: In this study, we conveniently obtained Ag(0)-polymer nanocomposites by reacting AgNO₃ with commercial poly(vinyl acetate) (PVAc) in the absence of a special reducing agent. The formation of Ag(0) metal was detected after formic acid (HCOOH) was added to a PVAc-AgNO₃ complex system, and some of the acetate groups of the PVAc backbone were hydrolyzed to form hydroxyl groups (OH) under the catalytic effect of the reduced Ag(O) metal. Here, the structure of the partially hydrolyzed PVAc backbone was represented as PVOH-PVAc. X-ray diffraction spectra showed that the Ag(0) metal generated in this method was in the form of Ag crystals. The structure of the

Ag(0)-polymer was analyzed by ¹H-NMR and ¹³C-NMR spectroscopy. The micellization of the Ag(0)-polymer was also investigated by the addition of an inducing solvent to the formic acid solution of Ag(0)-polymer. The image showed that the morphology of the Ag micelles in the H₂O-induced solvent was a Ag corona with a Ag shell, and that in the *p*-xylene induced solvent showed a Ag cluster core structure. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1457–1464, 2006

Key words: metal-polymer complexes; mycelles; nanocomposites; catalysis

INTRODUCTION

The most valuable feature of polymers containing metal nanoparticles is their potential for the preparation of films, coatings, fibers, and so on for use in electronic, magnetic, optical, and catalytic materials.^{1–8} Recently, many practical methods for the preparation of metal nanoparticles with amphiphilic copolymers have been developed and reported in literature.^{9–13} The underlying principle for these methods is the trapping of metal salts in amphiphilic copolymer micelles formed in a selective solvent. With organic solvent as the medium, the amphiphilic copolymer can have its hydrophilic part coordinated with the metal particles and its hydrophobic part tied in with the liquid medium. A large variety of metal nanoparticles, mainly, Au, Pt, and Pd, have been prepared in organic solvents with reverse micelles, such as those based on polystyrene-poly(2-vinyl pyridine) (PS-P2VP)¹¹ and poly(acrylic acid)-polystyrene (PAA-PS).¹²

Metal micelles can also be prepared in aqueous medium, but only a handful of studies have been

reported in the literature. One typical report included a poly(ethylene oxide) polyetherimide (PEO-PEI) diblock copolymer for the complexation of noble metal compounds and a double hydrophilic copolymer for the interaction of metal compounds.¹³ However, because they were restricted by the need for a prepared amphiphilic copolymer, the aforementioned methods are usually comprised of rather complicated steps when adopted in the synthesis of metal nanoparticles. Therefore, we investigated and report in this article the feasibility of using a commercial homopolymer to replace the prepared copolymer in these methods.

The main concept in this study was as follows: after metal ions were coordinated and reduced in the homopolymer matrix and the polymer backbone was transformed to an amphiphilic backbone by a system reaction, the resultant metal-containing polymer became more hydrophilic in an aqueous medium. The metal-containing polymer was subsequently dissolved in a good solvent; then, a selective solvent was added, and the solution was induced to undergo micellization, by which metal nanoparticles associated with polymer micelles were formed.

A Ag(0)-metal-containing polymer was thus synthesized in this study by the introduction of AgNO₃ aqueous solution into a commercial poly(vinyl acetate) (PVAc) matrix in the presence of formic acid. As

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ascertained in our previous study, the formic acid acted as a reducing agent that reduced Ag(I) ions to Ag(0) metal in the PVAc–AgNO₃ metal chelate polymer. Two primary concerns of this study are reported here. We first focus on the effect of the reduced Ag(0) metal on the hydrolysis of the PVAc matrix; for this purpose, the characteristics of the Ag(0)–polymer and the structure of the hydrolyzed polymer (PVOH/PVOH) chain were studied by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, and NMR spectroscopy. In these analyses, no hydrolyzed segment (PVOH) was detected for the Ag(I)–polymer, but the backbone of the Ag(0)–polymer changed to the PVOH/PVAc structure. These results show that the acidic hydrolysis of the PVAc matrix was accelerated by the generated Ag(0) metal.

Our second concern was on the ability of Ag(0)–polymer to conduct micellization; to this aim, Ag micelles were prepared by the addition of an inducing solvent, such as polar H₂O or nonpolar *p*-xylene, to the formic acid solution of Ag(0)–polymer. The various microstructures of these Ag-containing micelles were then examined by transmission electron microscopy (TEM).

EXPERIMENTAL

Preparation of Ag(I)–polymer, Ag(0)–polymer, and pure PVAc products

A 25 wt % solution of PVAc/tetrahydrofuran (THF), formed by the dissolution of 25 g of PVAc (Kanto Chemical Co., Kanagawa, Japan) into 75 g of THF (Merk-Schuchardt Co.), and an aqueous solution of silver nitrate (AgNO₃; Merk-Schuchardt, Germany), formed by the dissolution of 0.126 g of AgNO₃ (equivalent to 0.5 wt % of the polymer weight) into 5 mL of distilled water, were made. By blending the two solutions and stirring at 45°C in air for several hours, we formed a PVAc–AgNO₃/THF mixture. The PVAc–AgNO₃/THF mixture (10 g) was taken and coated onto a clean glass substrate. The glass plate was then dried in an electric oven with forced ventilation at 80°C for 25 min to form a Ag(I)–polymer film. After it was completely dried, this film was peeled off from the glass substrate and cut into slices for XRD and FTIR analyses. Another 40 g of the PVAc–AgNO₃/THF mixture was taken and poured into 1000 mL of distilled water to precipitate the Ag(I)–polymer product.

The other 50 g of the PVAc–AgNO₃/THF mixture was taken and added with 9.2 g (0.2 mol) of formic acid (HCOOH; analytical grade from Nacalai Tesque, Inc., Kyoto, Japan) and with continuous stirring at 60°C in air for 24 h. A PVAc–AgNO₃/THF/HCOOH

complex was formed. Then, 10 g of this PVAc–AgNO₃/THF/HCOOH complex was taken to prepare the Ag(0)–polymer film by the aforementioned procedure of film formation, and the rest of the mixture was poured into distilled water to obtain the Ag(0)–polymer product.

PVAc (12.5 g) was dissolved in 37.5 g of formic acid to form a 25 wt % solution of PVAc/HCOOH. After it was continuously stirred at 60°C in air for 24 h, the PVAc/HCOOH solution was poured into distilled water to precipitate out the pure PVAc product. The pure PVAc product was used as a blank sample for comparison with the Ag(I)–polymer and Ag(0)–polymer samples. All of the prepared samples were dried in vacuo at 40°C for XRD, FTIR, and NMR analyses.

Micellization of the formic acid solution of Ag(0)–polymer in H₂O and *p*-xylene solvents

Two samples of the 2 wt % Ag(0)–polymer/HCOOH solution, each prepared by the dissolution of 0.2 g of Ag(0)–polymer into 9.8 g of formic acid, were then added dropwise and slowly to 10 mL of water and 10 mL of *p*-xylene, respectively. The mixtures were vigorously stirred for several hours to trigger the micellization.

The resultant Ag(0)–polymer/HCOOH/H₂O micelle solution displayed one phase. A droplet of the solution was put on a carbon-coated copper grid and subsequently blotted with filter paper after 3 min. This copper grid specimen was placed in air for solvent evaporation before TEM examination.

The resultant Ag(0)–polymer/HCOOH/*p*-xylene micelle solution, because of the incompatibility between *p*-xylene and formic acid, displayed two separate uniform layers. After the micelle solution was centrifuged, the upper *p*-xylene phase layer was separated from the lower HCOOH phase layer. From the *p*-xylene phase solution and the HCOOH phase solution, one droplet was taken and placed on the carbon coated copper grid to prepare the specimens for TEM analysis with the aforementioned procedure.

Instruments

XRD analysis of the samples was carried out by a Mac Science MPX3 diffractometer (Japan) with Cu K α X-rays operated at 40 kV and 30 mA. The scanning speed of the spectrometer was 3°/min spanning from 20 to 80°. FTIR absorption spectra were recorded by a PerkinElmer Paragon 500 spectrometer at a resolution of 4 cm⁻¹. All NMR samples were dissolved (3–5 wt %) in dimethyl-*d*₆ sulfoxide (DMSO-*d*₆), which served as an internal locking agent. The spectra of these NMR solutions were analyzed with a Varian INOVA 600 spectrometer at room temperature, operating at 600 and 150 MHz, respectively, for the ¹H and ¹³C analy-

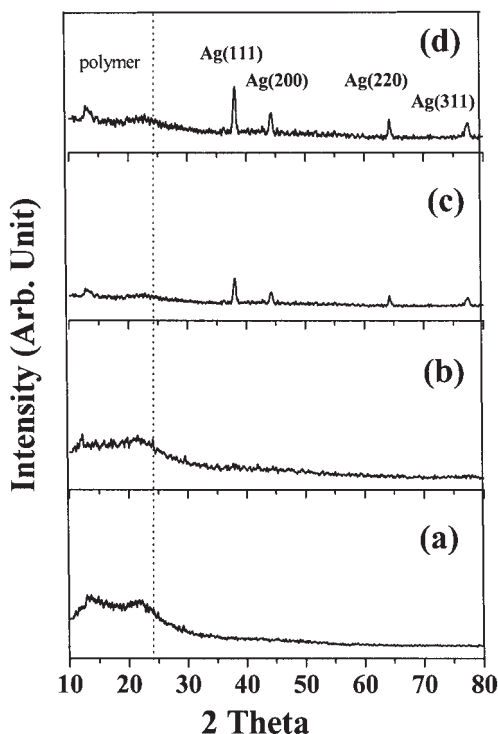


Figure 1 XRD spectra of films prepared from the (a) pure PVAc/HCOOH, (b) PVAc-AgNO₃/THF, (c) PVAc-AgNO₃/THF/HCOOH, and (d) PVAc-AgNO₃/HCOOH systems.

ses. The Ag(0)-polymer specimens prepared as discussed previously were examined by a Zeiss 902A transmission electron microscope (Germany) operating at 80 kV.

RESULTS AND DISCUSSION

Effects of the reduced Ag(0) metal on the hydrolysis of the PVAc matrix

The XRD spectrum of the pure PVAc/HCOOH film is shown in Figure 1(a). No diffraction peak of the Ag(0) metal was observed in the spectrum of the PVAc-AgNO₃/THF film, and its spectrum was similar to that of the pure PVAc/HCOOH film, as shown in Figure 1(b). It was evident that the Ag(I) ions in the PVAc-AgNO₃/THF film were not reduced to Ag(0) metal crystals. Figure 1(c) shows the spectrum of the PVAc-AgNO₃/THF/HCOOH film, which confirmed that Ag(0) metal crystals were formed in the polymer matrix after HCOOH was introduced into the nanocomposite system. For those PVAc-AgNO₃/HCOOH films prepared by the addition of formic acid instead of THF solvent, the existence of Ag(0) metal crystals was also evidenced by the XRD spectra, as shown in Figure 1(d). From these results, we concluded that in the PVAc-AgNO₃/THF/HCOOH and PVAc-AgNO₃/HCOOH systems, Ag(0) metal was generated in the polymer matrix via the reduction of Ag(I) ions by the oxidation of the added HCOOH, and Ag(0)-polymer nanocomposites were formed.

The FTIR spectrum of pure PVAc is shown in Figure 2(a). The bands and their corresponding stretching frequencies were C—H, C=O, C—O—C, and C—O at 2800–3000, 1738, 1241, and 1022 cm⁻¹, respectively. The weak absorption band near 3500 cm⁻¹ was a result of residual O—H groups from the commercial process. As shown in Figure 2(b), the FTIR spectrum of the Ag(0)-polymer prepared from PVAc-AgNO₃/

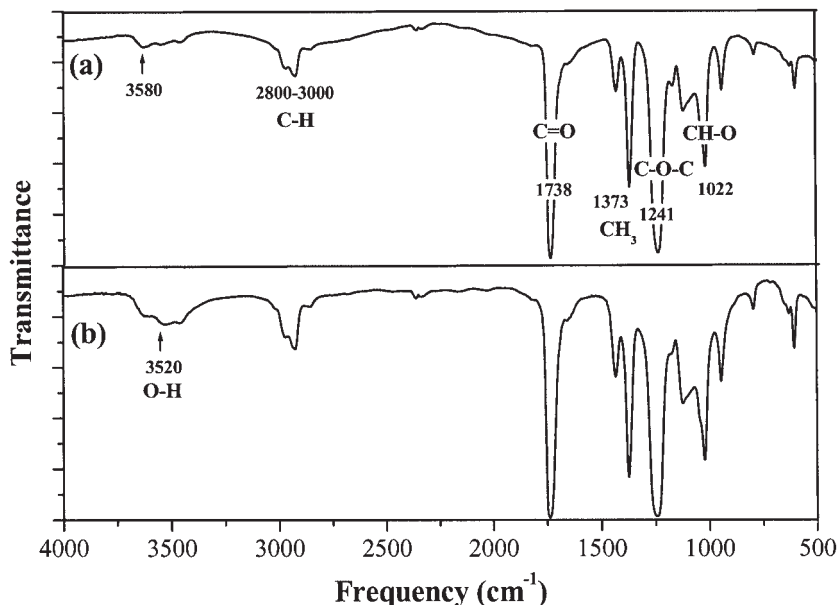


Figure 2 FTIR spectra of the (a) PVAc and (b) Ag(0)-polymer.

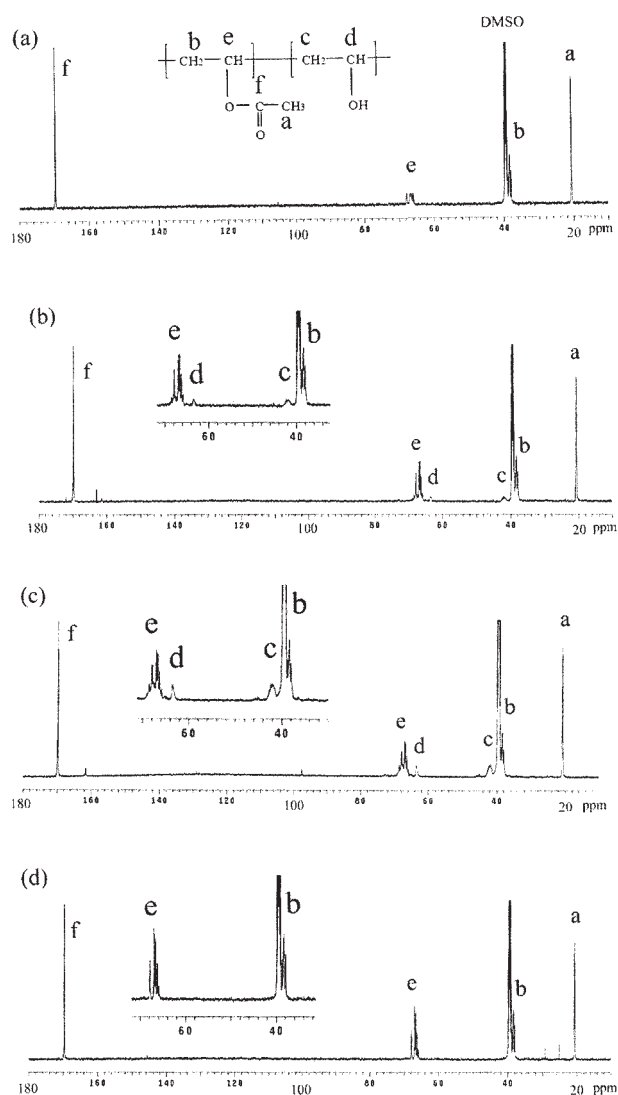


Figure 3 ^{13}C -NMR spectra of the (a) pure PVAc (PVAc/HCOOH system), (b) Ag(0)-polymer (PVAc-AgNO₃/THF/HCOOH system), (c) Ag(0)-polymer (PVAc-AgNO₃/HCOOH system), and (d) Ag(I)-polymer (PVAc-AgNO₃/THF system) in DMSO.

THF/HCOOH was similar to that of the pure PVAc but with a broader and stronger O—H absorption band in the Ag(0)-polymer, which meant that the Ag(0)-polymer chain contained more OH groups than the pure PVAc.

The ^{13}C spectra of the pure PVAc, Ag(0)-polymer prepared from PVAc-AgNO₃/THF/HCOOH and PVAc-AgNO₃/HCOOH system, and Ag(I)-polymer prepared from PVAc-AgNO₃/THF system are shown in Figure 3, which shows the characteristic chemical shifts of carbon in the polymers. In the spectrum of pure PVAc [Fig. 3(a)], the methyl carbon of the acetate groups had a peak at 20.7 ppm, and the methylene carbon of the polymer backbone had peaks located at 38.7, 38.5, 38.3, and 38.0 ppm. The isotactic C(mm)

carbon of the backbone methine had a peak at 67.9 ppm; the heterotactic C(mr) carbon had peaks at 67.0, 66.6, and 66.3 ppm; and the syndiotactic C(rr) carbon had a peak at 65.9 ppm. The carbonyl carbon of the acetate groups had a peak located at 169.7 ppm.^{14–17}

In addition to these peaks, the Ag(0)-polymer [Fig. 3(b,c)] had extra peaks at 63.5 and 42.6–42.0 ppm contributed by the methine carbon (CHOH) and the methylene carbon (CH₂CHOH) of the polymer backbone, which was evidence that the polymer chain in the Ag(0)-polymer system was changed to the PVOH/PVAc structure. In addition, the ^{13}C spectrum of Ag(I)-polymer prepared from the PVAc-AgNO₃/THF system was similar to the spectrum of pure PVAc, in which both peaks of the methine carbon (CHOH) and methylene carbon (CH₂CHOH) were still absent, as shown in Figure 3(d). The ^{13}C -NMR data of all of the samples are listed in Table I.

^1H -NMR analysis was also carried out on the pure PVAc, Ag(0)-polymer, and Ag(I)-polymer. Figure 4(a) shows the ^1H -NMR spectrum of pure PVAc. The peak of the methylene (CH₂—CHOCOCH₃) was at 1.75 ppm, the peak of the methine (CH—OCOCH₃) was at 4.78 ppm, and those of the methyl (CH₃) were at 1.97, 1.94, and 1.91 ppm; the peaks of DMSO and H₂O were at 2.5 and 3.31 ppm, respectively.^{18–21}

Figure 4(b) shows the ^1H -NMR spectrum of Ag(0)-polymer product prepared from PVAc-AgNO₃/THF/HCOOH system, and all of the peaks that were recorded in the pure PVAc also appeared in the spectrum of Ag(0)-polymer. In addition, three additional new peaks of the hydroxyl proton (OH), methine proton (CH—OH), and methylene proton (CH₂—CHOH) were recorded at 4.55–4.25, 3.61/3.43, and 1.5–1.3 ppm, respectively. These additional peaks were evidence of the formation of a new PVOH backbone. The degree of hydrolysis of the Ag(0)-polymer were determined from the integrated ^1H -NMR spectra. The degree of hydrolysis of the sample was calculated from the integral ratio of the signals assigned to the methylene proton (CH₂—CHOH) of PVOH to the signals of the methylene groups (CH₂—CHOH and CH₂—CHOCOCH₃) in the PVOH/PVAc structure. The calculated results of the Ag(0)-polymer products for the PVAc-AgNO₃/THF/HCOOH and PVAc-AgNO₃/HCOOH systems were 24.95 and 25.06%, respectively. The consistency of these calculated results indicated that the polymer chains of Ag(0)-polymer containing 0.5 wt % AgNO₃ underwent partial hydrolysis in the system, and the PVOH composition of Ag(0)-polymer sample was about 25%.

The spectrum of the Ag(I)-polymer prepared from PVAc-AgNO₃/THF system was similar to that of the pure PVAc [Fig. 4(a)], in which the hydroxyl proton contributed from the PVOH backbone was absent. The ^1H -NMR data of all of the samples are summarized in Table II.

TABLE I
 ^{13}C -NMR Spectra for the Pure PVAc and PVA Ag(0)-Polymer

δ (ppm)			
PVAc	Ag(0)-polymer	PVA	Assignment
169.7	169.7	—	Carbonyl, C=O
67.9	67.9	—	Methane, C(mm)H—OCOCH ₃
67.0	67.0	—	Methane, C(mr)H—OCOCH ₃
66.6	66.6		
66.3	66.3		
65.9	65.9	—	Methane, C(rr)H—OCOCH ₃
38.7	38.7	—	Methylene, CH ₂ —CHOCOCH ₃
38.5	38.5		
38.3	38.3		
38.0	38.0		
20.7	20.7	—	Methyl, CH ₃
—	63.5	67.74/65.82/63.81	Methine, CH—OH
—	42.6	46.17	Methylene, CH ₂ —CH—OH
	42.3	45.77	
	42.1	45.28	
	42.0	44.65	

From the results of the XRD, FTIR, and NMR analyses, it was evident that no hydrolysis of the polymer backbone occurred in either the PVAc–AgNO₃/THF system without formic acid or the PVAc/HCOOH

system without Ag(0) metal, and therefore, no PVOH structure from hydrolysis was detected in these systems. However, in contrast, the Ag(I) ions of the PVAc–AgNO₃/THF/HCOOH and PVAc–AgNO₃/HCOOH systems were reduced to Ag(0) metal, and the polymer backbone was partially hydrolyzed to form the PVOH/PVAc structure. These results indicate that HCOOH reduced the Ag(I) ions to Ag(0) metals, which then promoted the acidic hydrolysis of the PVAc matrix to attain the PVOH/PVAc structure.

In addition, to understand the interaction between the OH groups of the polymer chains and the metal or metal ions, the ^{13}C -NMR and ^1H -NMR spectra of poly(vinyl alcohol) (PVA) hydrolyzed from commercial PVAc were also measured. The synthesis of PVA was performed by the saponification of PVAc. The experimental process of the saponification was as fol-

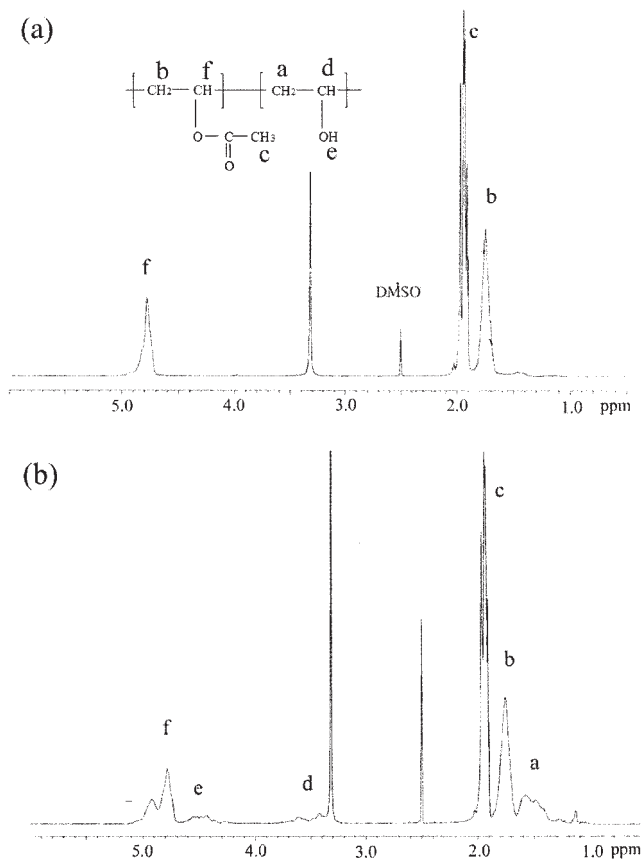


Figure 4 ^1H -NMR spectra of the (a) pure PVAc (PVAc/HCOOH system) and (b) Ag(0)-polymer (PVAc–AgNO₃/HCOOH system) in DMSO.

TABLE II
 ^1H -NMR Spectra for the Pure PVAc and PVA Ag(0)-polymer

δ (ppm)			
PVAc	Ag(0)-polymer	PVA	Assignment
	4.92		Methine, CH—OCOCH ₃
4.78	4.78	—	
—	4.55–4.25	4.67/4.48/4.23	Hydroxyl, OH
—	3.61	3.89	Methine, CH—OH
	3.43	3.84	
1.97	1.97	—	Methyl, CH ₃
1.94	1.94		
1.91	1.91		
1.75	1.75	—	Methylene, CH ₂ —CHOCOCH ₃
—	1.5–1.3	1.5–1.3	Methylene, CH ₂ —CHOH

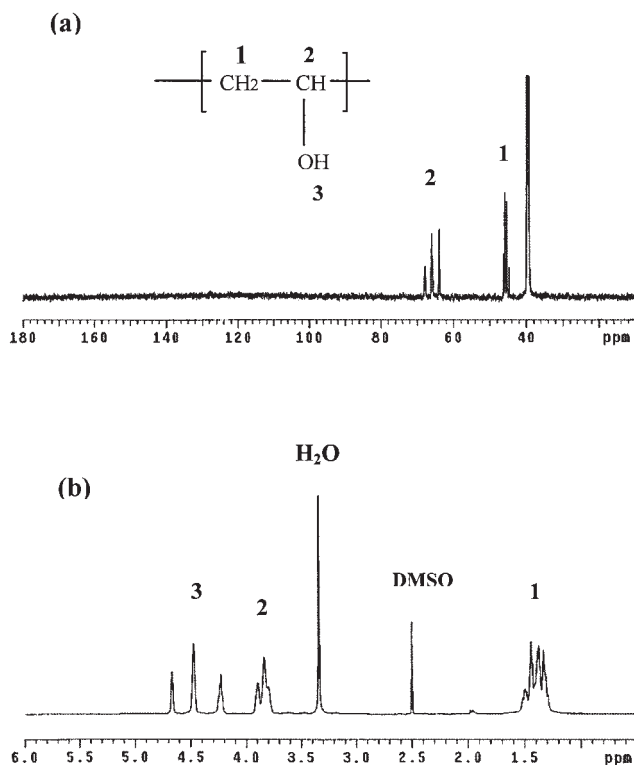


Figure 5 (a) ¹³C-NMR and (b) ¹H-NMR spectra of the PVA product.

lows: we dissolved 5 g of PVAc in 100 mL of methanol (analytic grade) and prepared 100 mL of a methanolic solution of NaOH (1.0 wt % NaOH). Then, we poured the 1.0 wt % NaOH/methanol solution into a 250-mL, three-necked, round-bottom flask and heated it to 45°C. Under vigorous stirring, we slowly added the PVAc/methanol solution over 30 min. The beginning of the hydrolysis was indicated by the occurrence of turbidity. After the complete addition of 100 mL of the PVAc/methanol solution, we continued stirring for 1 h. We isolated and precipitated the PVA by means of a suction pump. We then washed the PVA product at 35°C in vacuo.

The ¹³C-NMR and ¹H-NMR spectra of the PVA product are shown in Figure 5. The ¹H-NMR spectra of the free OH groups of the PVA were sharper than those in the spectra of the OH units of Ag(0)-polymer shown in Figure 4(b). The results reveal that the broader OH signals of Ag(0)-polymer in the ¹H-NMR spectra were contributed by the effect of metal or metal ions associated with the OH groups.¹⁹ According to X-ray photoelectron spectroscopy analysis on Ag(0)-polymer done in our previous studies, these reduced Ag(0) metals also had interactions with the OH groups of the PVOH/PVAc structure.²⁰ The interaction provided an anchoring effect so that the Ag(0) metal could be held tightly by the polymer chain; therefore, the reduced Ag(0) metal could attach firmly

on the polymer matrix to form Ag(0)-polymer nanocomposites.

Preparation of Ag micelles by micellization of a formic acid solution of Ag(0)-polymer with a selective solvent

Because the Ag(0)-metal-containing polymer carried a partially hydrolyzed PVOH/PVAc structure, we expected the polymer backbone to be amphiphilic in nature; that is, we expected the PVAc to be mainly hydrophobic and the PVOH to become hydrophilic. By adding solvents with different polarity to the system, we induced the Ag-PVOH-PVAc macromolecules to exhibit various self-assembly behaviors on the basis of their amphiphilic properties.

Figure 6(a) shows the TEM image of a sample prepared by the placement of a droplet of Ag(0)-polymer/HCOOH solution on the carbon-coated copper grid. HCOOH was a good solvent for the Ag-PVOH-PVAc polymer; therefore, the polymer chains were completely soluble in HCOOH, and the anchored Ag(0) nanoparticles followed the polymer chains to spread randomly.

Figure 6(b) shows the TEM image of the Ag(0)-polymer/HCOOH solution added to 10 mL of water. Although the added water was fully soluble in HCOOH solution, it was a nonsolvent for the PVAc parts of the Ag-PVOH-PVAc polymer. Therefore, the PVAc backbone aggregated inward to get rid of the water molecules, turning the PVOH backbone to obtain affinity with the H₂O and to form the PVOH outer corona. Because of the strong metal chelating ability of the PVOH, the morphology of these micelles was spherical with a PVAc core, and Ag-PVOH shell. Figure 6(c) shows an enlarged image of Figure 6(b), and the selected area electron diffraction (SAED) pattern of the polycrystalline Ag(0) of the Ag micelles is shown in Figure 6(d).

It was also of interest to study the micellization behavior of the Ag-PVOH-PVAc polymer in a non-polar medium and to clarify the difference in an H₂O-induced medium. Figure 7 shows the TEM image of the Ag(0)-polymer/HCOOH solution with the *p*-xylene inducing solvent. Although *p*-xylene was a good solvent for the polymer chain, it was insoluble in the formic acid. When *p*-xylene was added into the Ag(0)-polymer/HCOOH solution and the solution was stirred for a long time, some of the Ag-PVOH-PVAc polymer originally in the HCOOH phase were abstracted and dissolved into the *p*-xylene phase to form the Ag micelles. In the *p*-xylene phase, the Ag micelles attained a morphology of nanocluster-containing spheres, in which the PVOH inner core was associated with Ag nanoparticles and the hydrophobic PVAc outer corona had an affinity with the *p*-xylene medium, as shown in Figure 7(a). Figure 7(b) shows an

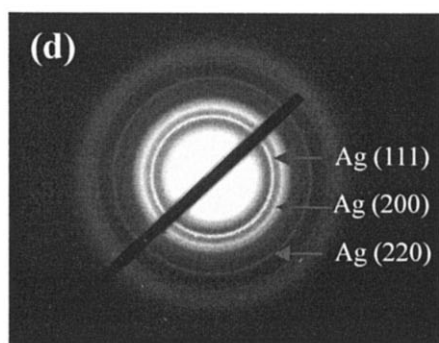
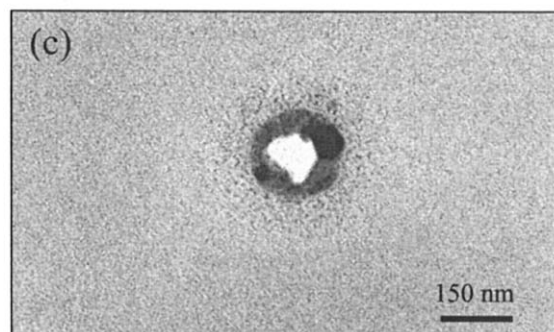
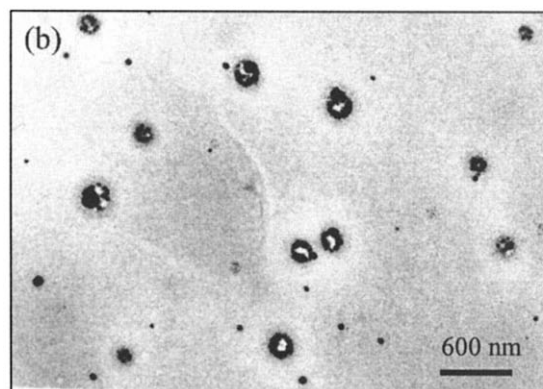
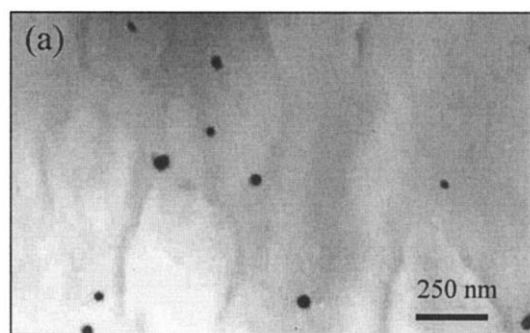


Figure 6 TEM images of dried specimens of the (a) Ag(0)-polymer/HCOOH solution and (b) Ag(0)-polymer/HCOOH solution added to 10 mL of water and cast on a formvar/carbon-coated copper grid and (c) a magnified image of the sample in part (b) and (d) the SAED pattern of the polycrystalline Ag (0) shown in part (c).

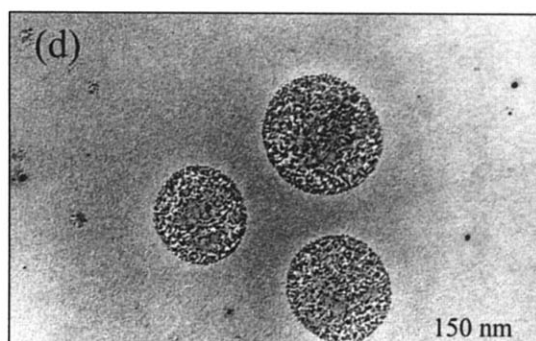
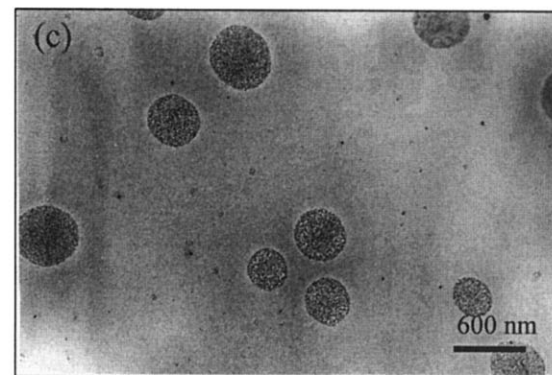
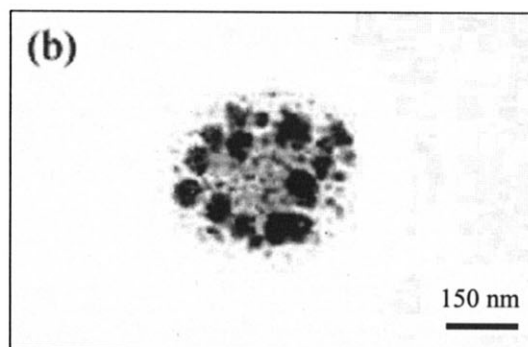
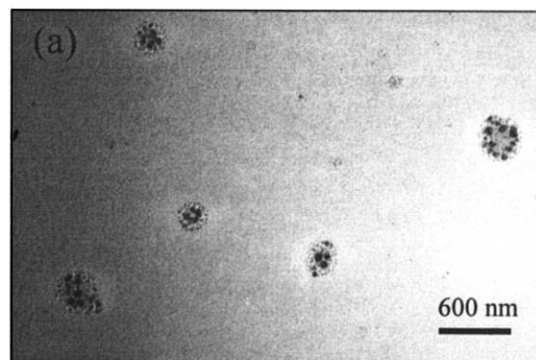


Figure 7 TEM images of dried specimens of the Ag (0)-polymer/HCOOH solution added to 10 mL of *p*-xylene and cast on a formvar/carbon-coated copper grid: (a) specimen in the *p*-xylene phase, (b) magnified image of the specimen in part (a), (c) specimen in the HCOOH phase, and (d) a magnified image of the specimen in part (c).

enlarged image of Figure 7(a). Figure 7(c) shows the morphology of the micelles in the formic acid phase. The microstructure of these micelles was quite different from the Ag shell sphere formed in the water-inducing solvent.

In addition, these results also demonstrate that there was a strong interaction between the reduced Ag(0) metal and the polymer chains. Therefore, when the polymer chains self-assembled to carry out micellization in the selected solution, the reduced Ag(0) metal could still attach firmly on the chains to form Ag micelles.

CONCLUSIONS

In this study, we found that Ag(0) metal reduced by HCOOH served as a promising catalyst for the hydrolysis reaction of the PVAc matrix. The reduced Ag(0) interacted with the oxygen species of the ester groups of the PVAc matrix to act for active sites, and then, the ester groups associated with Ag(0) metal was accelerated to hydrolyze in the presence of HCOOH. These partially hydrolyzed PVOH–PVAc polymer chains exhibited various self-assembly behaviors in selective solvent. When the polar solvent H₂O was introduced, Ag-containing normal micelles were obtained, but when the nonpolar solvent *p*-xylene was added, Ag-containing reverse micelles were formed. The microstructure of the normal micelles was a Ag shell corona, and that of the reverse micelles was a Ag cluster core.

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