

***In-situ* formation of metal nanoparticle/acrylic polymer hybrid and its application to miniemulsion polymerization**

Toshiyuki Tamai, Mitsuru Watanabe, Kimihiro Matsukawa

Osaka Municipal Technical Research Institute, 1-6-50 Morinomiya, Joto-ku, Osaka 536-8553, Japan

Correspondence to: T. Tamai (E-mail: tositama@omtri.or.jp)

ABSTRACT: We present *in-situ* formation of metal nanoparticle/acrylic polymer hybrid and its application to prepare hybrid latex particles by miniemulsion polymerization. On the surface of a silver nanoparticle/silica nanoparticle/acrylic polymer hybrid layer formed *in-situ* on a polyethylene terephthalate (PET) substrate, a copper film is deposited using electroless copper deposition. Silver nanoparticles, which are formed *in-situ* via the reduction of silver ion by radical species and subsequent annealing, work as a catalyst for the electroless deposition. Miniemulsion polymerization via the *in-situ* formation of nanoparticles affords nanoparticle/acrylic polymer hybrid latex particles and polymer particles. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42675.

KEYWORDS: coatings; colloids; emulsion polymerization; surfaces and interfaces

Received 1 May 2015; accepted 29 June 2015

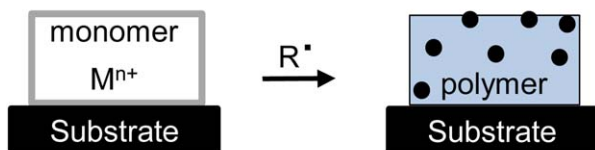
DOI: 10.1002/app.42675

INTRODUCTION

Hybrid materials composed of polymers and nanoparticles, such as metal nanoparticles and metal oxide nanoparticles, are of great scientific and industrial interest, because they derive their unique properties from the nanoparticles, such as catalytic activity^{1,2} and high refractive index.³ Metal nanoparticle/polymer hybrid films can be prepared by means of casting from a solution containing metal nanoparticles and polymers,⁴ by the deposition of metal nanoparticles on the surface of a polymer film,¹ and by *in-situ* formation of metal nanoparticles via the reduction of the metal ions by reducing agents² and photochemically generated radicals.^{5,6} The obtained hybrid films are potentially metallized by means of electroless plating due to the catalytic activity of the metal nanoparticles. Electroless plating is a simple and cost-effective method not only for metallization of polymer substrates but also for fabrication of metallic patterns on polymer substrates used in printed circuits boards. Recently, to fabricate a micropattern, an approach containing direct metallization of photolithographic and printed patterns has attracted much attention.^{1,7,8} We reported the fabrication of micropatterns by direct electroless copper deposition on a pattern of palladium nanoparticle/silica nanoparticle/acrylic polymer hybrid formed by photolithography.⁸ Palladium is a typical precious metal and its nanoparticles are useful as a catalyst, while nanoparticles of a common metal such as silver for a cost effective catalyst are desired. Polymer particles have high surface-to-volume ratio, functional groups at the surface, monodispersity, and simplicity of preparation and are suitable for the

support of nanoparticles. The production of hybrid particles by incorporating nanoparticles into polymer particles has been a field of intense research.⁹⁻¹⁷ The hybrid particles are expected to be used as imaging and sensing materials and catalysts for organic synthesis.^{2,12-16} Electroless plating of the hybrid particles forms the metallic nanoshell, resulting in the formation of polymer-core metal-shell nanoparticles.¹⁸⁻²¹ Thus, immobilizing metal nanoparticles on the surface or inside of polymer particles for producing hybrid particles has been studied intensely. Miniemulsion polymerization is suitable for the incorporation of functional compounds such as dye and nanoparticles into polymer particles.²²⁻³³ The miniemulsion-droplets composed of monomers and nanoparticles are converted to the corresponding polymer particles containing the nanoparticles (hybrid latex particles). Surface-modified nanoparticles and polymers having functional groups, which coordinate to the surface of the nanoparticles, are used for increasing their compatibility and preventing coagulation of the nanoparticles in the polymer component.^{30,31} We reported that, in the miniemulsion polymerization for preparing acrylic polymer particle incorporating ZrO₂ nanoparticle, ZrO₂ nanoparticle modified with methacryl group could be dispersed homogeneously in polymer having phosphoric group.³⁰ It was also reported that nanoparticles could be immobilized to the surface of polymer particle with the aid of the surface functional groups.⁹⁻¹⁵ Such polymer particles having the surface functional group should be designed and prepared by emulsion polymerization or dispersion polymerization carefully, while more simple procedure for preparing hybrid particles is desired. *In-situ* formation of metal

(a) In-situ formation of a hybrid layer on a substrate



M^{n+} : metal ion, R^\bullet : radical,

● : metal nanoparticle

(b) In-situ formation of hybrid particles by miniemulsion polymerization

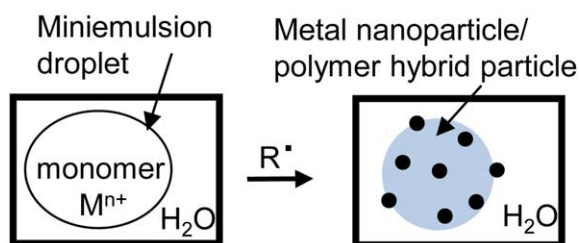


Figure 1. Schematic representation of (a) the *in-situ* formation of a metal nanoparticle/acrylic polymer hybrid layer on a polymer substrate and (b) the *in-situ* formation of metal nanoparticle/polymer hybrid particles by miniemulsion polymerization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

nanoparticles in polymer particles is expected to be simple procedure for preparing hybrid particles.³⁴ We have proposed the *in-situ* formation of a palladium nanoparticle/acrylic polymer hybrid layer on a polymer film [Figure 1(a)].³⁵ The *in-situ* generated radicals induce the radical polymerization of the acrylate and also reduce the palladium ion to form palladium nanoparticles. Radical-induced *in-situ* formation of hybrid is potentially applicable to fabricating hybrid particles by miniemulsion polymerization. We now report *in-situ* formation of a silver nanoparticle/acrylic polymer hybrid layer and electroless Cu deposition on the hybrid surface. A reaction mechanism of formation of silver nanoparticle is discussed. We also report preparing hybrid latex particles by miniemulsion polymerization via *in-situ* formation of metal nanoparticles and discuss the reaction conditions suitable for incorporating the metal nanoparticles into polymer particles [Figure 1(b)].

EXPERIMENTAL

Materials

2,2'-Azobis(2-methylpropionitrile) (AIBN; Wako), 2,2'-azobis(2-methylbutyronitrile) (V-59; Wako), 2,2'-azobis[N-(2-carboxyethyl)-2-methylpropionamide]hydrate (VA-057; Wako), 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (VA-086; Wako), 2,2'-azobis(2-methylpropionamide)dihydrochloride (V-50; Wako), methyl acrylate (MA; TCI), *N*-isopropylacrylamide (NIPAM; Kojin), acetoacetoxyethyl methacrylate (AAEM; Nacalai), ethylene glycol dimethacrylate (EGDMA; TCI), pentaerythritol triacrylate (PETA; Toagosei), $AgBF_4$ (Nacalai), $Pd(CH_3CO_2)_2$

(Nacalai), $Pd(t-C_4H_9CO_2)_2$ (Aldrich), Na_2PdCl_4 (Aldrich), HS-10 (Dai-ichi Kogyo Seiyaku), hexadecane (Nacalai), and propylene glycol 1-monomethyl ether 2-acetate (PGMEA; TCI) were used as received (Figure 2). Butyl methacrylate (BMA; TCI) and *N,N*-diethylaminoethyl methacrylate (DEAEMA; TCI) were distilled under vacuum prior to use. [(Methacryloyloxy)ethyl]dimethyldodecylammonium bromide was synthesized according to a procedure in the literature.³⁶

Preparation of a Silver Nanoparticle/Silica Nanoparticle/Acrylic Polymer Hybrid Layer on a PET Film

A typical hybrid layer was prepared as follows: PETA (monomer, 59 mg), $AgBF_4$ (15 mg), AIBN (radical initiator, 5 mg), and silica nanoparticles (a primary particle size 24 nm, modified by an acrylic group, toluene dispersion, Fuso Chemical, 10 mg) were dissolved in PGMEA (4 mL). From the mixture, a polyethylene terephthalate (PET) film (Toray, Lumirror S10, thickness 250 μm) was spin-coated with a layer composed of PETA/ $AgBF_4$ /AIBN/silica nanoparticle. The coated PET film was

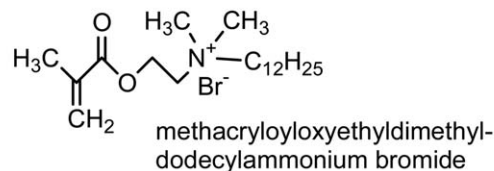
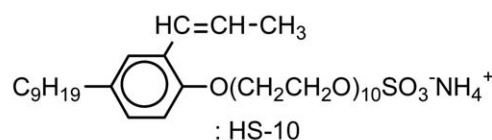
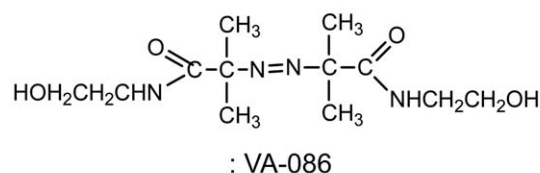
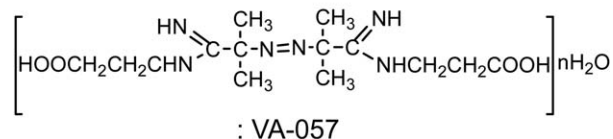
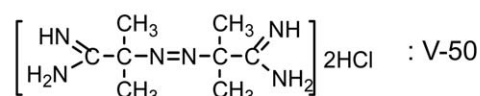
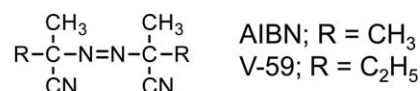


Figure 2. Radical initiators and surfactants.

Table I. Preparation of Hybrid Particles by Miniemulsion Polymerization

Condition ^a	Run	Metal salt/mg	Initiator	Reaction temperature/ °C	Monomer	Polymerization; stability of the emulsion	Products	Diameter of the particles/(nm)
1	1a	Pd(CH ₃ CO ₂) ₂ /9	V-59	67	BMA	Stable	Polymer particle/Hybrid particle	150 ^b
1	1b	Pd(t-C ₄ H ₉ CO ₂) ₂ /12	V-59	67	BMA	Stable	Polymer particle/Hybrid particle	131 ^b
1	1c	Pd(CH ₃ CO ₂) ₂ /45	V-59	67	BMA/MA/EGDMA (100 : 1.6 : 4)	Stable	Polymer particle/Hybrid particle	202 ^c
1	1d	Pd(CH ₃ CO ₂) ₂ /9	AIBN	65	BMA/AAEM (100 : 1)	Stable	Polymer particle/Hybrid particle	186 ^c
1	1e	AgBF ₄ /20	AIBN	65	BMA/NIPAM (100 : 14)	Stable	Polymer particle/Hybrid particle	143 ^c
2	2a	Pd(CH ₃ CO ₂) ₂ /9	VA-057	57	BMA/AAEM (100 : 4)	Stable	Polymer particle/Hybrid particle	164 ^c
2	2b	Pd(CH ₃ CO ₂) ₂ /9	VA-086	86	BMA/MA (100 : 0.3)	Stable	Polymer particle/Hybrid particle	137 ^c
2	2c	Pd(CH ₃ CO ₂) ₂ /9	V-50	56	BMA/DEAEMA (100 : 1.5)	Stable	Polymer particle/Hybrid particle	91 ^c
2	2d	AgBF ₄ /40	VA-057	57	BMA/NIPAM (100 : 14)	Stable	Polymer particle/Hybrid particle	122 ^b
3	3a	Na ₂ PdCl ₄ /37	AIBN	65	BMA/AAEM (100 : 2)	Stable	Polymer particle/Hybrid particle	178 ^c
4	4a	Na ₂ PdCl ₄ /37	VA-057	57	BMA/AAEM (100 : 5)	Unstable	No polymers	-

^a Condition for miniemulsion polymerization is shown in Figure 6(b).

^b Measured by TEM-image.

^c Measured by DLS.

annealed at 150°C for 30 min, which resulted in the formation of a silver nanoparticle/silica nanoparticle/acrylic polymer hybrid layer (thickness 50–100 nm) on its surface. The PET films were immersed in an electroless copper deposition bath (Okuno Chemical Industries) for 2–30 min at 32°C.

Preparation of Hybrid Particles by Miniemulsion Polymerization

Hybrid particles were synthesized by miniemulsion polymerization under reaction conditions **1–4** (see Results and Discussion section). In a typical experiment of anionic emulsion synthesis (Table I, Run **1d**), a 100 mL flask equipped with a condenser and a mechanical stirrer was filled with BMA (3.6 g, 25 mmol), AAEM (53 mg, 0.25 mmol), AIBN (0.1 g, 0.61 mmol, oil-soluble radical initiator), Pd(CH₃CO₂)₂ (9 mg, 0.04 mmol, oil-soluble salt), hexadecane (0.36 g, 1.6 mmol, hydrophobe), HS-10 (0.1 g, 0.12 mmol, surfactant), and water (25 mL). The mixture was stirred for 15 min and ultrasonicated (Branson 450 digital sonifier) for 9 min in an ice bath to obtain the miniemulsion. The miniemulsion was purged with nitrogen gas for 1 h, and then heated to 65°C. The mixture was vigorously stirred at 65°C for 20 h. The obtained emulsion (14 wt % as estimated by gravimetric analysis) consisted of particles having dynamic light scattering (DLS) diameters of 186 nm and a narrow size distribution. AgBF₄ and Na₂PdCl₄ are water-soluble metal salts and were dissolved in water for miniemulsion polymerization under reaction conditions **2–4**. VA-057, VA-086, and V-50, which are water-soluble radical initiators, were dissolved in water and then added to the reaction mixture in the flask heated to 57, 86, and 65°C, respectively. Similarly, cationic emulsions were synthesized using methacryloyloxyethyltrimethylammonium bromide (0.3 g, 0.12 mmol) as a surfactant and V-50 (0.05 g, 0.16 mmol) as an water-soluble radical initiator (Run **2c**).³¹

Characterization

Transmission electron microscopy (TEM) images were obtained using a JEOL model JEM-2100 microscope at an acceleration voltage of 100 kV. The specimens were prepared by dropping the solution of the mixture onto a carbon-coated copper grid and allowing the solvent to evaporate, followed by annealing at 120°C. A field-emission scanning electron microscope (FE-SEM, JEOL model 6700F) were used to observe the film surface. Particle size distributions of the emulsions were measured by dynamic light scattering (DLS) employing Otsuka Electronics DLS-6000HLC. UV-vis absorption spectra were recorded on a JASCO model V-560 spectrophotometer.

RESULTS AND DISCUSSION

In-Situ Formation of a Silver Nanoparticle/Silica Nanoparticle Acrylic Polymer Hybrid Layer and Electroless Cu Deposition on the Hybrid Surface

A layer composed of acrylate monomer (PETA), silver salt (AgBF₄), silica nanoparticles, and radical initiator (AIBN) on a PET substrate was converted to a silver nanoparticle/silica nanoparticle/acrylic polymer hybrid layer (thickness: 50–100 nm) by annealing at 120°C for 30 min. A transmission electron microscopy (TEM) image [Figure 3(a)] of the hybrid shows the silver nanoparticles (diameter: 5–10 nm) and silica nanoparticles

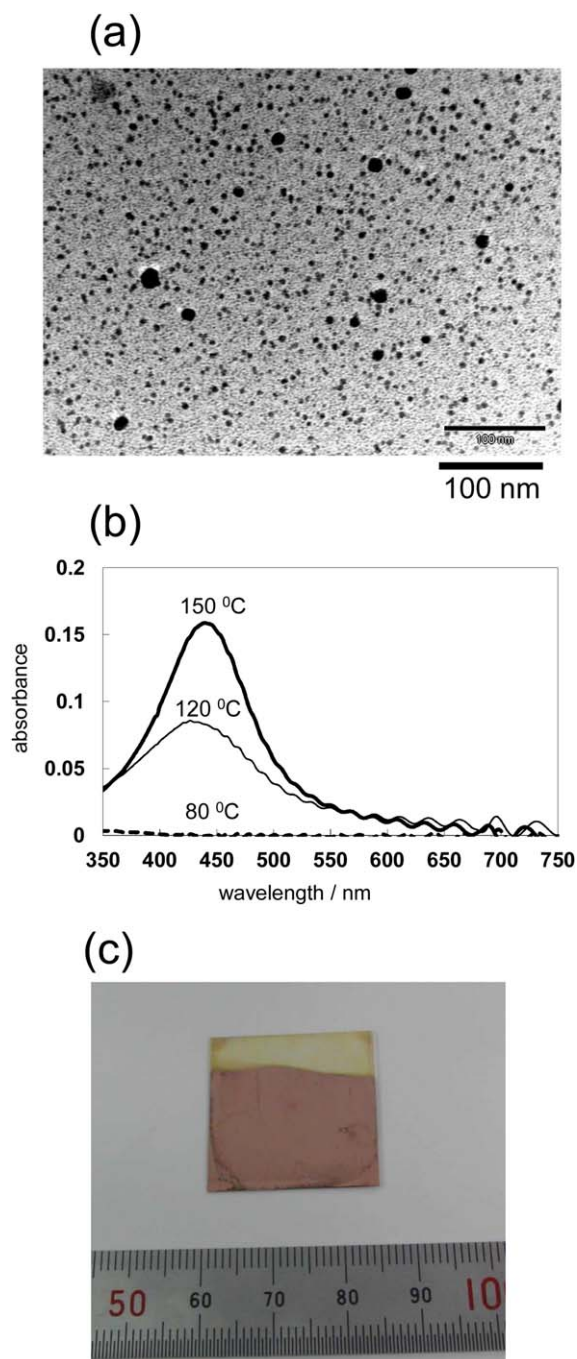


Figure 3. (a) TEM image of the silver nanoparticle/silica nanoparticle/acrylic polymer hybrid layer. (b) UV-vis spectra of the hybrid layers: annealing at 80°C, 120°C, and 150°C. (c) The copper film deposited on the hybrid-coated PET substrate (annealing at 120°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(diameter: 20–30 nm). In the UV-vis absorption spectra of the hybrid layer [Figure 3(b)], the absorption band around 427 nm is attributable to the surface plasmon resonance of silver nanoparticles.³⁷ The layers of the mixture were also annealed at 80 and 150°C. The absorption band around 427 nm was not observed at the hybrid annealed at 80°C. In the hybrid annealed at 150°C, the intensity of the absorption band is higher than

that at 120°C and the band maximum red-shifts to 440 nm. The density of silver nanoparticles is estimated from the intensity of the absorption band at 150°C > at 120°C > at 80°C [Figure 3(b)]. The red-shift of the band maximum shows that the hybrid annealed at 150°C contains larger size silver nanoparticles than that annealed at 120°C. A field-emission scanning electron microscope (FE-SEM) image of the surface of the hybrid annealed at 150°C shows silica nanoparticles (diameter: ca. 100 nm) and silver nanoparticles (diameter: ca. 10 nm) definitely [Figure 4(c)]. In contrast FE-SEM images of the hybrid annealed at 80 and 120°C show silica nanoparticles (diameter: ca. 100 nm) and ambiguous particles [Figure 4(a,b)]. These results show that the hybrid annealed at 150°C contains silver nanoparticles whose size and density are higher than those at 120°C. Using electroless copper deposition for 2 min, a copper film was deposited on the surface of the hybrid-coated PET substrate. The copper films (thickness ca. 150 nm) on the hybrids annealed at 120°C [Figure 3(c)] and 150°C were free of cracks and defects. The adhesion between the copper film and the PET substrate was evaluated through a peel adhesion test using 3M tape. When the test was performed, the copper film on the PET substrate coated with the hybrid containing silica nanoparticles was completely undamaged, whereas most of the copper film on the substrate coated with the hybrid containing no silica nanoparticles was damaged. This shows that silica nanoparticles promote the adhesion between the copper film and the hybrid (copper/hybrid interface). It was reported that nanometer-scale roughness (<ca. 50 nm) on the surface of the hybrid due to silica nanoparticles promote the adhesion through nanoscale mechanical interlocking effects.³⁵ In the hybrid annealed at 80°C, copper film was formed only at small area of its surface even after the electroless deposition for 30 min. The hybrid layer would be formed as shown in Figure 5. Radicals from AIBN initiate radical polymerization of the acrylate monomer and also reduce silver ion to silver atom, which forms silver-nanoparticles during the annealing at 120 and 150°C.^{6,34,35} The half-life time of AIBN at 65°C is 10 h, and AIBN is estimated to decompose within a minute at 120 and 150°C. During the annealing, the silver nanoparticles would be formed after completion of the formation of the radicals. In the initial period of the annealing, the radical co-polymerization of the acrylic group of the monomer and the silica nanoparticles forms the cross-linking network composed of acrylic polymer chain and the silica nanoparticles. Subsequently, silver atoms diffuse in the crosslinking network to form the silver-nanoparticles having the catalytic activity, but do not grow into larger size particles that do not have the catalytic activity. The density and size of the silver nanoparticle depends on the degree of the diffusion of silver atoms. The silver nanoparticles formed on the hybrid surface at 120°C, of which density is smaller than at 150°C, work as the catalyst for electroless copper deposition, while the density of the silver nanoparticles formed at 80°C is not sufficient to work as the catalyst. In summary, the hybrid layer is formed *in-situ* by annealing on a PET substrate and a copper film is deposited on the surface of the hybrid using electroless copper deposition. For fabricating metallic pattern on a polymer substrate used in printed circuits boards, the temperature for the

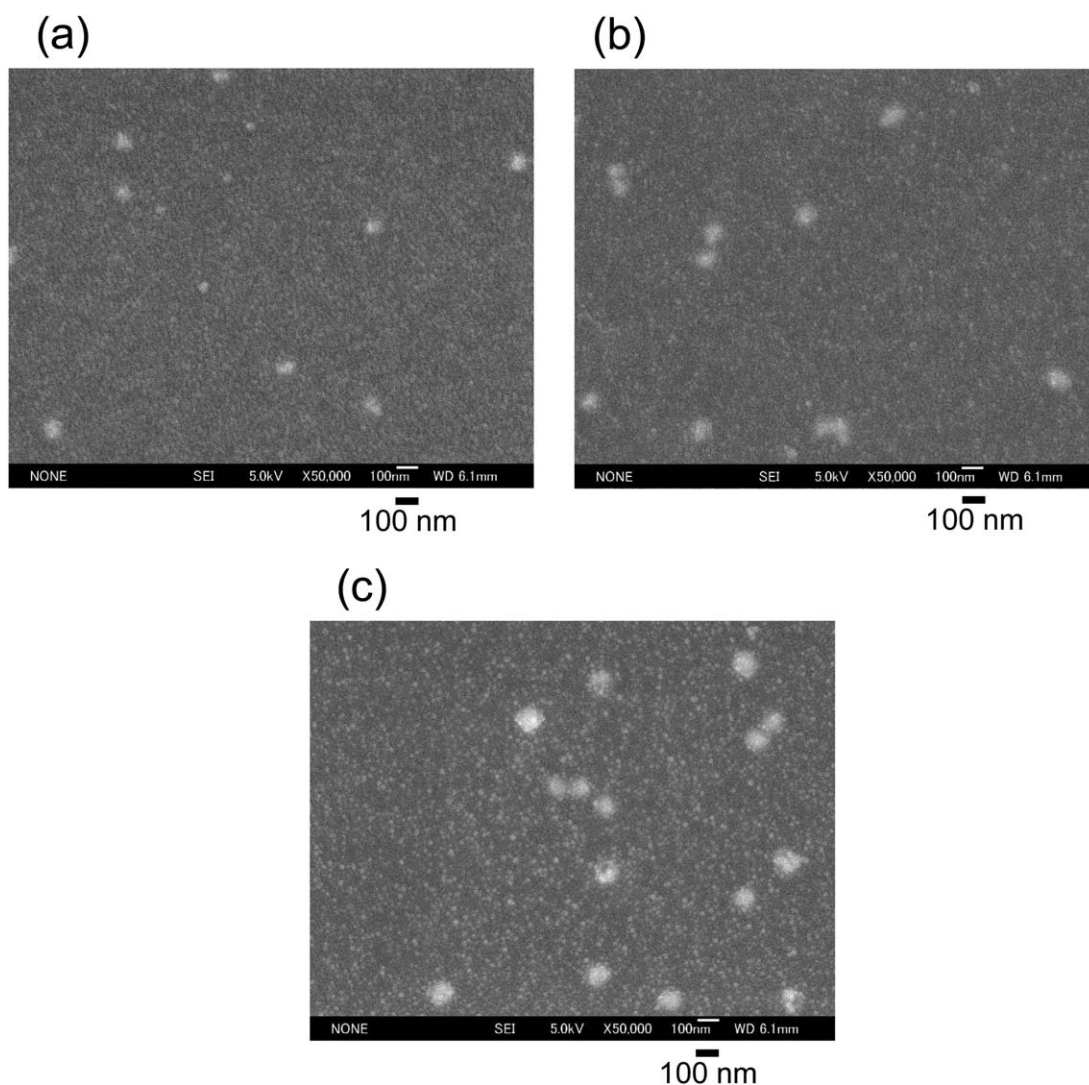


Figure 4. FE-SEM images of the surface of the hybrid layer: annealing at (a) 80°C, (b) 120°C, and 150°C.

annealing is desired to be lower to inhibit thermal degradation of the polymer. The minimum temperature for the annealing in the present process is around 120°C. In the case of heat resistant polymer substrates, the temperature for the annealing above 150°C is available.

***In-Situ* Formation of Hybrid Latex Particles by Miniemulsion Polymerization**

Miniemulsion polymerization is suitable for the incorporation of functional compounds such as nanoparticles into polymer particles.^{22–24} Radicals initiate polymerization in the miniemulsion-droplets composed of monomers and nanoparticles and then the miniemulsion-droplets are converted to the corresponding polymer particles containing the nanoparticles (hybrid latex particles).^{30,31} It is expected that *in-situ* formation of the hybrid in the miniemulsion-droplets can form metal nanoparticle/polymer hybrid particles [Figure 6(a-i)]. For *in-situ* formation of metal nanoparticles, metal ions and radicals should be incorporated into the miniemulsion-droplets, where the metal ions are reduced by the radicals to form metal nano-

particles. It is known that, in miniemulsion polymerization, both oil-soluble and water-soluble radical-initiators can initiate polymerization.³⁸ In the case of the oil-soluble radical-initiators, radicals are formed and initiate the polymerization in the miniemulsion-droplets. In contrast, radicals formed from the water-soluble radical-initiators in the water phase move into the miniemulsion-droplets and then initiate the polymerization. In a similar manner, both oil-soluble and water-soluble metal salts are expected to supply metal ions in the miniemulsion-droplets. Thus, for *in-situ* formation of the hybrid latex particles by miniemulsion polymerization, we propose reaction conditions 1–4, which use combinations of different types of radical initiators and metal salts [Figure 6(b)]. For *in-situ* formation of the metal nanoparticles, the metal ions and the radicals should stay in the miniemulsion-droplet or move from the water phase into the miniemulsion-droplets. Then the metal nanoparticles formed via the reduction of the metal ions stay at the surface or the inside of the polymer particles to form hybrid particles. The leakage of the metal ions, the radicals, and the metal nanoparticles from the miniemulsion-droplets and the polymer particles

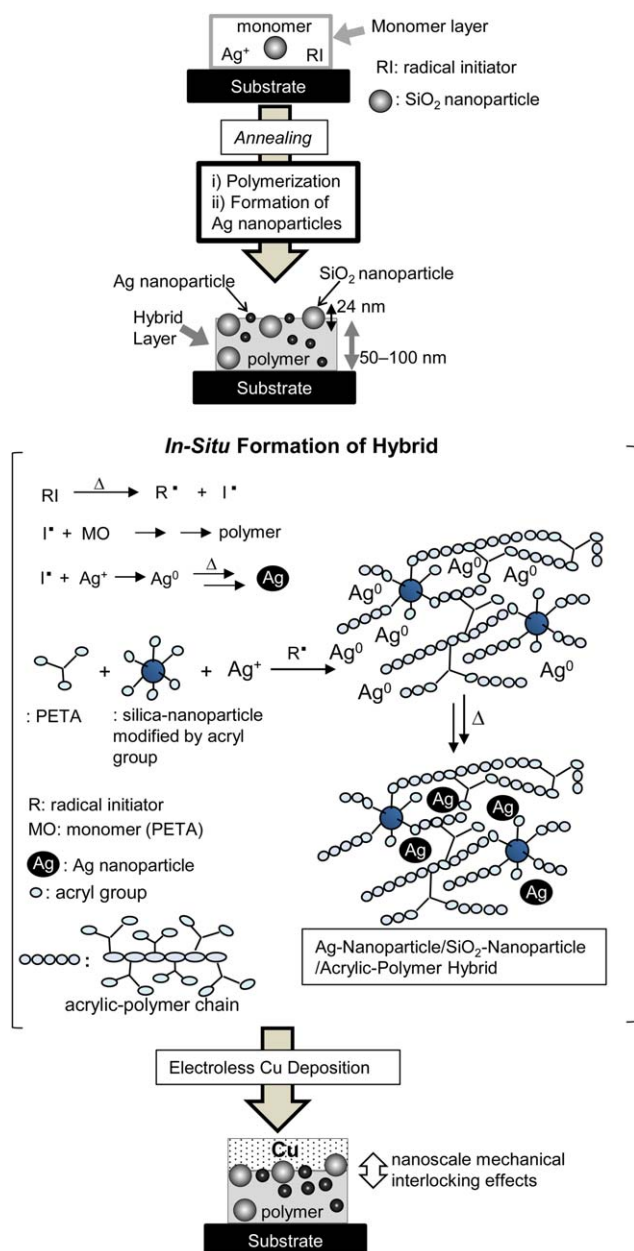
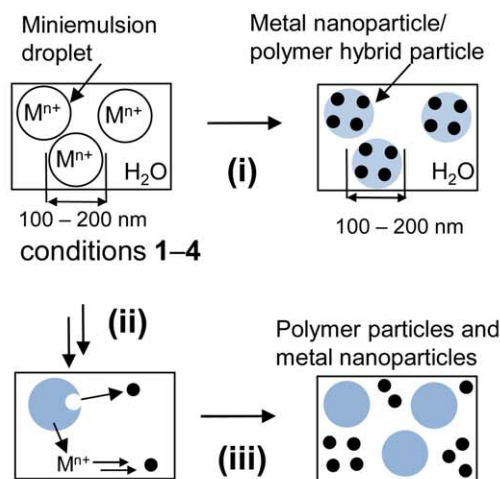


Figure 5. Proposed mechanism for the *in-situ* formation of the silver nanoparticle/silica nanoparticle/acrylic polymer hybrid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

prevents the formation of the hybrid particles [Figure 6(a-ii, iii)]. For avoiding the leakage, we used a variety of metal salts, radical initiators, and monomers as shown in Table I. Oil-soluble metal salts and radical initiators having hydrophobic groups could be favorable for holding them in the miniemulsion-droplets. Pd(*t*-C₄H₉CO₂)₂ and V-59 are more hydrophobic than Pd(CH₃CO₂)₂ and AIBN, respectively. The monomers AAEM, NIPAM, and DEAEMA have acetoacetoxy, amide, and diethylamino groups, respectively. Such functional groups can coordinate to metal ions and are expected to contribute to hold the metal ions and metal nanoparticles in the

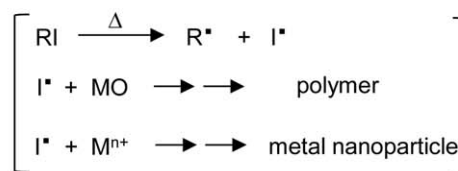
miniemulsion-droplets.^{9,14,29,34,39} Monomer MA, which has carboxylic group, is also expected to interact with metal ion. The compatibility between the polymer component and the metal

(a) In-situ formation of hybrid particles by miniemulsion polymerization under conditions 1–4



(b) Miniemulsion droplet under reaction conditions 1–4

	oil-soluble radical-initiator	water-soluble radical-initiator
oil-soluble salt	Condition 1 	Condition 2
water-soluble salt	Condition 3 	Condition 4



Mⁿ⁺ : metal ion, MO: monomer
 R[•] : radical, RI : radical initiator
 ● : metal nanoparticle

Figure 6. Proposed reaction conditions 1–4 for the *in-situ* formation of hybrid latex particles by miniemulsion polymerization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

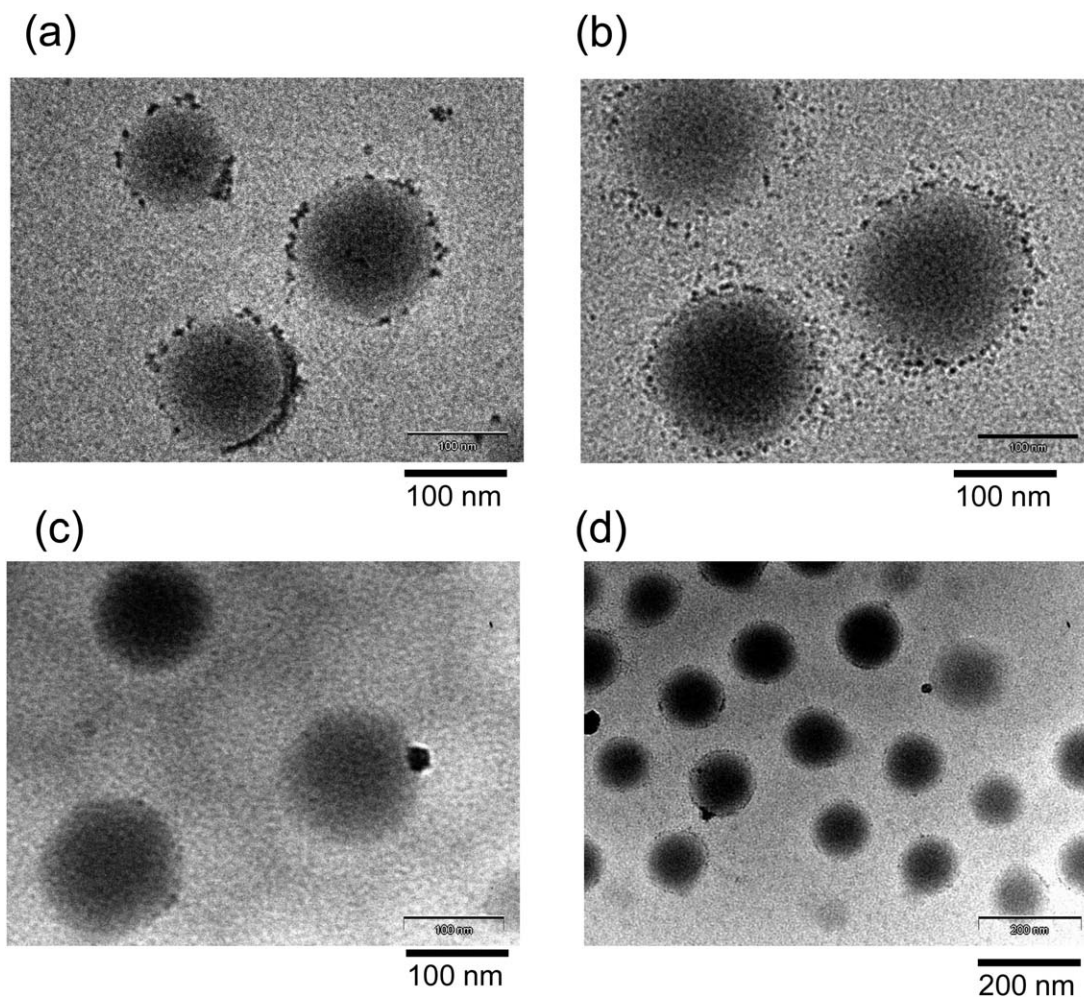


Figure 7. TEM images of the particles prepared by miniemulsion polymerization from the mixture of (a) BMA/AAEM/AIBN/Pd(CH₃CO₂)₂ (Table I, Run 1d), (b) BMA/AAEM/VA-057/Pd(CH₃CO₂)₂ (Run 2a), and (c)–(d) BMA/NIPAM/VA-057/AgBF₄ (Run 2d).

component is considered to play an important role in formation of the metal nanoparticles. EGDMA were used as a cross-linking agent to harden the polymer particles and to prevent the leakage of the metal nanoparticles.²⁶ In addition, the miniemulsion-droplets should be dispersed in water without coagulation, while the miniemulsion-droplets are destabilized by the excess amount of polar components such as the monomers having functional groups. All polymer particles prepared by miniemulsion polymerization except those prepared in Run 2c (Table I) have negative charge derived from an anionic surfactant and radical initiators. In contrast, polymer particles prepared in Run 2c have positive charge. Miniemulsion polymerization was performed under reaction conditions 1–4 as shown in Table I and Figure 6(b). We used oil-soluble metal salts and radical initiators in condition 1, which corresponds to that of the *in-situ* formation of the hybrid layer as described in the preceding section. Miniemulsion polymerization using the mixture of BMA/Pd(CH₃CO₂)₂/V-59 afforded palladium nanoparticle/polymer hybrid particles and polymer particles (Run 1a–b). TEM image of the particles shows some metal nanoparticles on the surface of polymer particles and also outside the polymer particles (data not shown). Similar miniemulsion poly-

merization using MA and AAEM, which have functional groups, also afforded a mixture of hybrid particles and polymer particles (Run 1c–d). Miniemulsion polymerization using AgBF₄ also afforded hybrid particles and polymer particles (Run 1e). Miniemulsion polymerization under condition 2 (Run 2a–d), in which we used oil-soluble metal salts and water-soluble radical initiators, and that under condition 3 (Run 3a), in which we used a water-soluble metal salt and an oil-soluble radical initiator, also gave hybrid particles and polymer particles. Hybrid particles and polymer particles were also obtained by cationic miniemulsion polymerization (Run 2c). TEM images of particles prepared in Run 1d, 2a, and 2d are shown in Figure 7. TEM images of the particles prepared under other conditions also showed the formation of both hybrid particles and polymer particles (data not shown). Under condition 4 (Run 4a), in which we used water-soluble metal salt and radical initiator, the miniemulsion was unstable and coagulated during the polymerization. Results shown above indicate that *in-situ* formation of metal nanoparticle/acrylic polymer hybrid occurs in the miniemulsion-droplets during the polymerization under conditions 1–3. Radicals formed both in the miniemulsion-droplets (conditions 1, 3) and in water (condition 2) initiate the

polymerization. Radical species reduce metal ions in the miniemulsion-droplets (conditions 1, 2) to form the metal nanoparticles. Metal ions derived from the water-soluble salt are also reduced to form the metal nanoparticles at the surface of the miniemulsion-droplets (condition 3). In some of the droplets, the metal nanoparticles leak out to the water phase, resulting in the formation of polymer particles containing no metal nanoparticles [Figure 6(a-ii, iii)]. It is known that the surface of latex particles is hydrophilic for the functional groups derived from the surfactants and the radical initiators. The surface of the metal nanoparticles could be hydrophilic, therefore, the metal nanoparticles are located at the periphery of the surface of the polymer particles or leak out of the polymer particles. Alternatively, the metal ions and the radical species leak out of the miniemulsion-droplets and then react to form the metal nanoparticles in water. Under condition 4, radical species react with metal ions in water to form larger size metal particles, which could destabilize the miniemulsion and result in coagulation. In miniemulsion polymerization via *in-situ* formation of metal nanoparticles, it is thought that the metal nanoparticles are formed in the miniemulsion droplets and some of them leak out to the water phase under all reaction conditions, although their detailed mechanism is not known at the present. The compatibility between the polymer component and the metal component is considered to play an important role in the morphology of the hybrid particle.³³ Functional groups of the polymer component could affect the compatibility. Investigations of the reaction conditions of the miniemulsion polymerization in which no metal nanoparticles leak out of the miniemulsion-droplets and the polymer particles and the evaluation of catalytic activity of the hybrid particles are currently underway.

CONCLUSIONS

A silver nanoparticle/acrylic polymer hybrid layer was formed on a PET substrate by annealing and then a copper film was deposited on the surface of the hybrid using electroless copper deposition. Silver nanoparticles, which are formed *in-situ* via the reduction of silver ion by radical species and subsequent annealing, work as a catalyst for electroless copper deposition. Silver is a common metal and its nanoparticle is expected to be a cost effective catalyst. Metal nanoparticle/acrylic polymer hybrid latex particles were prepared by miniemulsion polymerization via the *in-situ* formation of palladium and silver nanoparticles in the miniemulsion-droplets. The hybrid latex particles are potentially converted to metallodielectric composite particles via electroless metal deposition on their surface^{19,34} and also applicable to coating materials whose surface can be metallized by electroless plating.

ACKNOWLEDGMENTS

This study was partly supported by JSPS KAKENHI Grant Number 25410135. We would also like to thank Okuno Chemical Industries Co., Fuso Chemical Co., and Dai-ichi Kogyo Seiyaku Co. for gift of copper deposition bath, silica nanoparticles (organo silica sol), and a surfactant, respectively.

REFERENCES

1. Zabetakis, D.; Dressick, W. J. *ACS Appl. Mater. Interfaces* **2009**, *1*, 4.
2. Fujii, S.; Matsuzawa, S.; Nakamura, Y.; Ohtaka, A.; Teratani, T.; Akamatsu, K.; Tsuruoka, T.; Nawafune, H. *Langmuir* **2010**, *26*, 6230.
3. Inkyo, M.; Tokunaga, Y.; Tahara, T.; Iwaki, T.; Iskandar, F.; Hogan, C. J., Jr.; Okuyama, K. *Ind. Eng. Chem. Res.* **2008**, *47*, 2597.
4. Qi, L.; Lee, B. I.; Chen, S.; Samuels, W. D.; Exarhos, G. J. *Adv. Mater.* **2005**, *17*, 1777.
5. Cook, W. D.; Nghiem, Q. D.; Chen, Q.; Chen, F.; Sangermano, M. *Macromolecules* **2011**, *44*, 4065.
6. Sakamoto, M.; Majima, T. *Bull. Chem. Soc. Jpn.* **2010**, *83*, 1133.
7. Lancaster, J. R.; Jehani, J.; Carroll, G. T.; Chen, Y.; Turro, N. J.; Koberstein, J. T. *Chem. Mater.* **2008**, *20*, 6583.
8. Tamai, T.; Watanabe, M.; Watase, S.; Nishioka, N.; Matsukawa, K. *Trans. JIEP* **2011**, *4*, 110.
9. Dokoutchaev, A.; James, J. T.; Koene, S. C.; Pathak, S.; Prakash, G. K. S.; Thompson, M. E. *Chem. Mater.* **1999**, *11*, 2389.
10. Shi, W.; Sahoo, Y.; Swihart, M. T.; Prasad, P. N. *Langmuir* **2005**, *21*, 1610.
11. Kim, H.; Daniels, E. S.; Dimonie, V. L.; Klein, A. J. *Polym. Sci. Part A: Polym. Chem.* **2007**, *46*, 912.
12. Khan, M. A.; Perruchot, C.; Armes, S. P.; Randall, D. P. *J. Mater. Chem.* **2001**, *11*, 2363.
13. Pathak, S.; Greci, M. T.; Kwong, R. C.; Mercado, K.; Prakash, G. K. S.; Olah, G. A.; Thompson, M. E. *Chem. Mater.* **2000**, *12*, 1985.
14. Mei, Y.; Lu, Y.; Polzer, F.; Ballauf, M.; Drechsler, M. *Chem. Mater.* **2007**, *19*, 1062.
15. Wen, F.; Zhang, W.; Wei, G.; Wang, Y.; Zhang, J.; Zhang, M.; Shi, L. *Chem. Mater.* **2008**, *20*, 2144.
16. Mayer, A. B. R.; Mark, J. E. *Angew. Makromol. Chem.* **1999**, *268*, 52.
17. Voorn, D. J.; Ming, W.; van Herk, A. M. *Macromolecules* **2006**, *39*, 4654.
18. Wang, P. H.; Pan, C.-Y. *J. Appl. Polym. Sci.* **2000**, *75*, 1693.
19. Kim, H.; Daniels, E. S.; Dimonie, V. L.; Klein, A. J. *Appl. Polym. Sci.* **2009**, *112*, 843.
20. Liu, J. B.; Zhan, P.; Wang, S. Z.; Zhang, J. H.; Wang, Z. L. *Langmuir* **2005**, *21*, 1683.
21. Fujii, S.; Hamasaki, H.; Takeoka, H.; Tsuruoka, T.; Akamatsu, K.; Nakamura, Y. *J. Colloid Interface Sci.* **2014**, *430*, 47.
22. Landfester, K. *Angew. Chem. Int. Ed.* **2009**, *48*, 4488.
23. Van Herk, A. M.; Landfester, K., Eds. *Hybrid Latex Particles: Preparation with (Mini)emulsion Polymerization*; Springer: Heidelberg, **2010**.
24. Paulis, M.; Leiza, J. R. In *Encapsulation with Miniemulsion Polymerization*; Kobayashi, S.; Mullen, K., Eds.; Springer: Heidelberg, **2014**; p 1.
25. Schreiber, E.; Ziener, U.; Manzke, A.; Plettl, A.; Ziemann, P.; Landfester, K. *Chem. Mater.* **2009**, *21*, 1750.

26. Ando, K.; Kawaguchi, H. *J. Colloid Interface Sci.* **2005**, *285*, 619.
27. Yamauchi, N.; Nagao, D.; Konno, M. *Colloid Polym. Sci.* **2010**, *288*, 55.
28. Tamai, T.; Watanabe, M.; Maeda, H.; Mizuno, K. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 1470.
29. Tamai, T.; Watanabe, M.; Hatanaka, Y.; Tsujiwaki, H.; Nishioka, N.; Matsukawa, K. *Langmuir* **2008**, *24*, 14203.
30. Tamai, T.; Watanabe, M.; Minami, Y.; Okazaki, S.; Masuyama, A.; Matsukawa, K. *Chem. Lett.* **2011**, *40*, 37.
31. Berkel, K. Y.; Piekarski, A. M.; Kierstead, P. H.; Pressly, E. D.; Ray, P. C.; Hawker, C. J. *Macromolecules* **2009**, *42*, 1425.
32. Diaconu, G.; Micusik, M.; Bonnefond, A.; Paulis, M.; Leiza, J. R. *Macromolecules* **2009**, *42*, 3316.
33. Reyes, Y.; Paulis, M.; Leiza, J. R. *J. Colloid Interface Sci.* **2010**, *352*, 359.
34. Chen, C.-W.; Serizawa, T.; Akashi, M. *Langmuir* **1999**, *15*, 7998.
35. Tamai, T.; Watanabe, M.; Ikeda, S.; Kobayashi, Y.; Fujiwara, Y.; Matsukawa, K. *Chem. Lett.* **2012**, *41*, 277.
36. Nagai, K.; Ohishi, Y.; Inaba, H.; Kudo, S. *J. Polym. Sci. Polym. Chem. Ed.* **1985**, *23*, 1221.
37. Mayer, A. B. R.; Grebner, W.; Wannemacher, R. *J. Polym. Sci. Part B: Polym. Phys.* **2000**, *104*, 7278.
38. Taniguchi, T.; Takeuchi, N.; Kobaru, S.; Nakahira, T. *J. Colloid Interface Sci.* **2008**, *327*, 58.
39. Taniguchi, T.; Inada, T.; Kashiwakura, T.; Murakami, F.; Kohri, M.; Nakahira, T. *Colloids Surf. A* **2011**, *377*, 63.