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Grafting of Polymer Brushes from Silica Particles Functionalized with Xanthates

Kohji Ohno*[a], Yoshikazu Yahata[a], Motokazu Sakaue[a], Vincent Ladmiral[b]

[a] *Prof. Dr. K. Ohno, Dr. Y. Yahata, M. Sakaue*
Institute for Chemical Research
Kyoto University
Uji, Kyoto 611-0011, Japan
E-mail: ohno@scl.kyoto-u.ac.jp
[b] *Dr. V. Ladmiral*
ICGM, CNRS, UM, ENSCM, Montpellier, France

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Abstract: In this paper, we present the synthesis of polymer brushes using the grafting-from method with silica particles functionalized with xanthate molecules. Monodisperse silica particles (SiPs) were surface-modified with a newly designed silane coupling agent comprising a triethoxy silane and an alkyl halide, 6-(triethoxysilyl)hexyl 2-bromopropionate which was further reacted with potassium *O*-ethyl dithiocarbonate (PEX) to immobilize xanthate molecules on the particle surfaces. Surface-initiated macromolecular design via interchange of xanthates (MADIX) polymerization of vinyl acetate (VAc) was conducted with the xanthate-functionalized SiPs in *N*,*N*-dimethylformamide in the presence of free xanthate molecules and 2,2'-azobis(isobutyronitrile). The polymerization was well-controlled and produced SiPs coated with poly(vinyl acetate) (PVAc) with a well-defined target molar mass and a graft density of around 0.2 chains/nm^2. Dynamic light scattering and transmission electron microscopy measurements reveal that the hybrid particles were highly dispersible in good solvents without any aggregation. The PVAc brushes were hydrolyzed with hydrochloric acid to produce poly(vinyl alcohol) brushes on the SiP surfaces. In addition, the number of xanthate molecules introduced on the SiP surfaces could be successfully controlled by adjusting the concentration of PEX. Thus, the SiPs possessed two functionalities: xanthates able to act as MADIX chain transfer agent and alkyl bromide atom transfer radical polymerization (ATRP) initiation sites. Using these unique bifunctional particles, mixed polymer brushes were constructed on the SiPs by MADIX of VAc followed by ATRP of styrene or methyl methacrylate.

Introduction

Polymer brushes are unique polymeric architectures in which polymer chains are grafted on a solid substrate at high density so that the solvated polymer chains stretch away from the surface.[1-3] Owing to their structural features, polymer brushes have various intriguing physical properties such as strong repulsion against compression, low friction, high biocompatibility, and good antifouling properties.[4] Polymer brushes with controlled graft chain lengths have been fabricated by several surface-initiated living or controlled polymerization techniques including radical, ring-opening, metathesis, and ionic polymerization systems.[5-11] Among them, surface-initiated living radical polymerization (SI-LRP) is the most popular technique because of the robustness, versatility, and simplicity of LRP. Therefore, SI-LRP has been applied to many types of solid substrates of various shapes and materials.[9-11] For instance, fine particles, including silica, gold, iron oxide, carbon, and polymer particles, are commonly used substrates for SI-LRP. Particles can be designed and synthesized using SI-LRP in a bespoke fashion whereby the graft chain length and density, type of graft polymer, and the size and type of core particle can be easily tuned. A variety of hybrid particles grafted with polymer brushes have been synthesized using several SI-LRP techniques, among which nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition-fragmentation chain transfer polymerization (RAFT) systems have been mainly used.[9-11]

We have developed several methods using NMP, ATRP, and RAFT techniques to prepare fine particles having a shell composed of a well-defined, high-density (concentrated) polymer brushes. Importantly, these polymer-grafted fine particles remained colloidally stable (no aggregation) and with a narrow size distribution throughout the preparation procedure.[12-15] We have fabricated two- and three-dimensional colloidal crystals of these particles by utilizing their high dispersibility and monodispersity.[16-19] We have also applied these particles to bio-related materials and investigated the effect of their structures (core particle sizes and brush chain lengths) on their physiological properties such as biodistribution and circulation lifetime in blood after intravenous injection, or as MRI contrast agent (polymer-brush-decorated iron oxide nanoparticles).[20,21]

Macromolecular design via the interchange of xanthates (MADIX) is one of the most promising LRP systems.[22-26] In particular, this is because MADIX can control the polymerization of so-called less-activated monomers (LAM) such as vinyl acetate (VAc), *N*-vinylpyrrolidone (NVP), or *N*-vinylcarbazole. The use of MADIX polymerization has also been reported for the homo- and copolymerization of fluoromonomers such as vinylidene fluoride.[27-30] MADIX polymerization has been applied for the preparation of polymer brushes.[31-36] Wilczewska et al. reported the surface-initiated MADIX polymerization of styrene and butyl acrylate from xanthate-coated iron oxide nanoparticles.[33] The modification of the iron oxide nanoparticles with xanthate moieties proceeded via immobilization of amines on the surface of the particles followed by amide formation with 2-bromopropionyl bromide, and substitution of the bromine atoms with potassium *O*-ethyl dithiocarbonate (PEX). A similar strategy has also been used to introduce xanthate moieties onto graphene oxide, wood fiber, and cellulose nanocrystal surfaces from which surface-initiated MADIX polymerization was carried out.[34-36]

These papers described the preparation of PVAc brushes via SI-MADIX. Poly(vinylalcohol) (PVA) which can be relatively easily be prepared by hydrolysis of PVAc, is an extremely useful polymer with many applications, such as biofunctional materials, adhesives, colloid dispersants, and antifreeze coating agents.[37-45] It is therefore very surprising that well-defined PVA brushes have never been synthesized by any SI polymerization techniques.

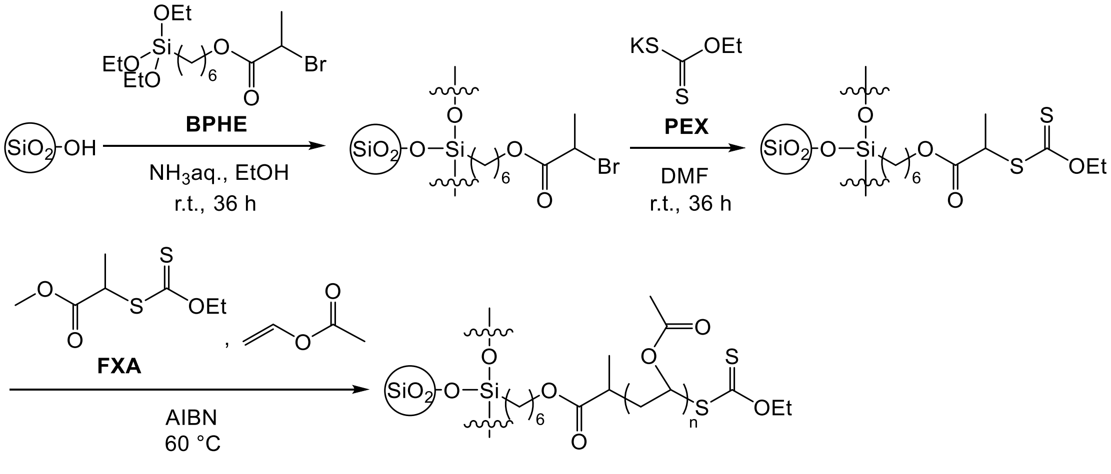
In the present work we report the first preparation and characterization of well-defined concentrated PVA brushes from silica nanoparticles by hydrolysis of PVAc. These hybrid particles were prepared using an original ATRP silane coupling agent that efficiently decorate silica surfaces and which is easily converted into xanthate moieties. Partial conversion of the surface-immobilized brominated moieties into MADIX agent also allowed to combine SI-ATRP and SI-RAFT to prepare unprecedented particles decorated with mixed polymer brush of PVAc/polystyrene and PVAc/poly(methyl methacrylate).

Results and Discussion

Fixation of xanthate moieties on silica particles

In previous studies, we synthesized silane coupling agents having an initiation site for atom transfer radical or nitroxide-mediated polymerizations.[12,13,15] These agents were fixed onto silica particle (SiP) surface in ethanol solution containing ammonia (NH_3) as a basic catalyst. In addition, we also synthesized a silane coupling agent having a trithiocarbonate moiety for SI-RAFT polymerization.[14] To modify the SiP surface with the RAFT silane coupling agent, we could not use the procedure used for SI-ATRP and SI-NMP because NH_3 decomposes the trithiocarbonate moiety via aminolysis. We thus had to use a more complicated procedure for the fixation of trithiocarbonate moieties. It is well known that the xanthate moiety also undergoes aminolysis, just like trithiocarbonate groups;[46-49] therefore, the use of NH_3 should be avoided in the presence of xanthate moieties. In this study, to perform the introduction of a suitable SI-MADIX chain transfer agent on the SiP surface, we adopted another approach in which alkyl bromide groups fixed on the particle surface were converted into xanthate moieties.

A new type of silane coupling agent was synthesized via the two-step reaction described in the Experimental Section (see Scheme 1). Briefly, 5-hexen-1-ol was acylated with 2-bromopropionyl



Scheme 1. Schematic representation of the reactions for xanthate fixation and surface-initiated MADIX polymerization of vinyl acetate on silica particles.

bromide to obtain 5-hexen-1-yl 2-bromopropionate, which vinyl group was subsequently hydrosilylated with triethoxysilane in the presence of Karstedt's catalyst to obtain 6-(triethoxysilyl)hexyl 2-bromopropionate (BPHE, Scheme 1). The overall yield of this 2-step synthesis was about 30% after distillation, and the purity of BPHE was confirmed to be more than 95% by ^{1}H and ^{13}C NMR and elemental analysis. We selected 2-bromopropionyl group as an alkyl halide because it has been shown to be an excellent precursor for the reaction with potassium *O*-ethyl dithiocarbonate (PEX), and because the resulting xanthate is an excellent chain transfer agent for the MADIX polymerization of various monomers (LAMs).[25] The SiPs were modified with BPHE in the presence of catalytic NH_3 in ethanol, which disperses well both the bare and the reacted SiPs without causing any aggregation (see Experimental Section). To estimate the number of 2-bromopropionyl groups fixed on the SiPs, elemental analysis of the modified SiPs was carried out and the bromine content was determined to be 0.89 wt%, which, along with the known density (1.9 g/cm^3) and diameter (130 nm) of the SiP, indicates a surface density of 2.8 2-bromopropionyl groups/nm^2. Subsequently, the alkyl bromide on the SiP surface was converted to xanthate by reaction with 1.1 equivalent of PEX. Elemental analysis of the resulting xanthate-modified SiPs showed that Br had completely disappeared, and, the sulfur content was estimated to be 0.67 wt%. The density of immobilized xanthate was calculated to be 2.6 groups/nm^2. The small functional group loss (ca. 7%) may be due to measurement uncertainties and to the formation of few carbon-carbon double bond via E1 elimination. The conversion of alkyl bromide into xanthate proceeded almost quantitatively. The xanthate-modified SiPs were pale-yellow and were highly dispersible in various organic solvents such as acetone, tetrahydrofuran (THF), or *N*,*N*-dimethylformamide (DMF). When stored in a refrigerator, a suspension of the modified SiPs remained stable for at least one year.

Surface-initiated MADIX polymerization of vinyl acetate from SiPs

The xanthate-decorated SiPs were subsequently used for the MADIX polymerization of vinyl acetate (VAc). We carried out the polymerization in the presence of a free xanthate chain transfer agent, *O*-

ethyl-*S*-(1-methoxycarbonyl)ethyldithiocarbonate (FXA).

Table 1. Results from the surface-initiated MADIX polymerization of vinyl acetate in the presence of xanthate-modified silica particles.

Run	Polymerization time (*h*)	Monomer conversion (%)	$M_{\mathrm{n,theo}}$	Free polymer		Graft polymer		Graft density (chains/nm^2)
				M_{n}	$M_{\mathrm{w}}/M_{\mathrm{n}}$	M_{n}	$M_{\mathrm{w}}/M_{\mathrm{n}}$	
1[a]	4	6	5370	3200	1.67	–	–	–
2[a]	6	11	9680	8300	1.65	–	–	–
3[a]	12	22	19150	15700	1.60	–	–	–
4[a]	18	30	26030	23600	1.50	–	–	–
5[a]	28	39	33780	31400	1.47	32200	1.39	0.18
6[b]	28	65	5610	4800	1.27	–	–	–

Polymerizations were carried out in *N*,*N*-dimethylformamide (33 wt%) at 60 °C with xanthate-decorated silica nanoparticles (1 wt%): [a] [vinyl acetate (VAc)]$_0$/[free xanthate agent FXA]$_0$/[2,2'-azobis(isobutyronitrile) (AIBN)]$_0$= 1000/1/0.1. [b] [VAc]$_0$/[FXA]$_0$/[AIBN]$_0$= 100/1/1. $M_{\mathrm{n,theo}} = M_{\mathrm{VAc}} \times [\mathrm{VAc}]_0/[\mathrm{FXA}]_0 \times \alpha + M_{\mathrm{FXA}}$ where M_{VAc}, M_{FXA} and α stand for molar masses of VAc , FXA and the VAc conversion, respectively. The difference between Mn, Theo and Mn measured by GPC is due to the difference between, the hydrodynamic volumes of PMMA and PVAc in THF.

The role of the FXA is to allow the efficient exchange reaction between the graft and free polymers, thus controlling the polymerization reaction. In addition, the free polymers produced from FXA are a good measure of the graft polymers produced from the SiP surfaces at the same time. We also added DMF (33 wt%) to the polymerization system to ensure the complete dispersion of the xanthate-decorated SiPs. Indeed, the bulk polymerization of VAc with the xanthate-fixed SiPs yielded some particle aggregates. Thus, we conducted the SI-MADIX polymerization of VAc at a FXA/VAc/AIBN molar ratio of 1/1000/0.1 in the presence of 33 wt% of DMF and 2 wt% of the xanthate-decorated SiPs at 60 °C. The results of the polymerization are summarized in Table 1 (runs 1–5). Figure 1 shows

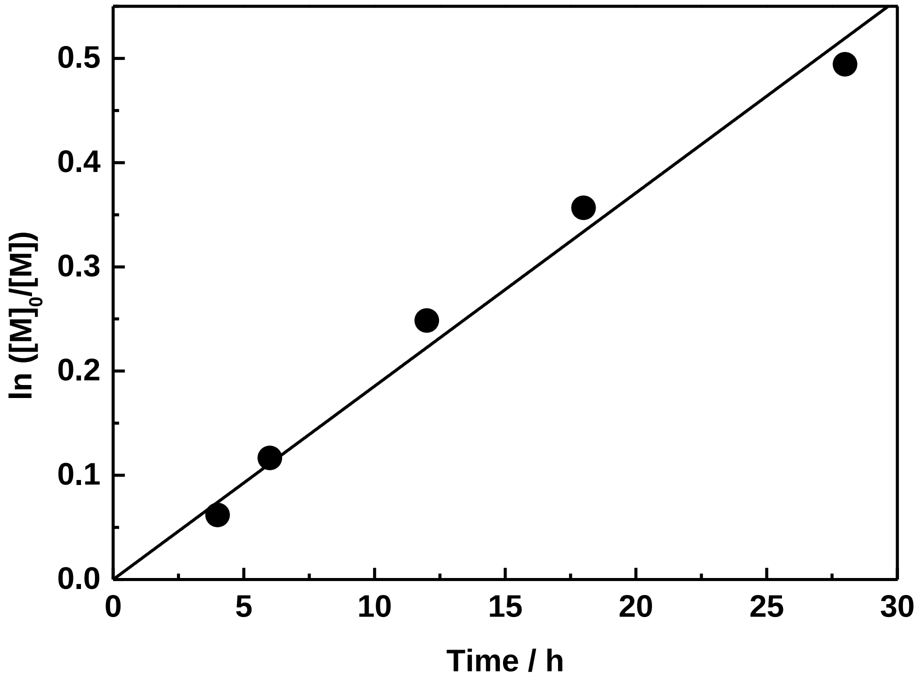


Figure 1. Plot of ln([M]$_0$/[M]) vs. polymerization time, *t*, for the solution polymerization of vinyl acetate (VAc) in *N*,*N*-dimethylformamide (33 wt%) at 60 °C with xanthate-decorated silica nanoparticles (1 wt%): [VAc]$_0$/[free xanthate agent FXA]$_0$/[2,2'-azobis(isobutyronitrile)]$_0$ = 1000/1/0.1.

the kinetic plot for the polymerization of VAc in the presence of xanthate molecules. The plot is approximately linear, which indicates that the number of propagating radical species in the system remains nearly constant throughout the course of polymerization. In the MADIX polymerization of VAc, occasionally an induction period may be observed, but, in the present experimental system, it was not seen.

Figure 2 presents the evolution of the molar mass (M_n) and the diversity (M_w/M_n) of the free polymer produced from the FXA as a function of monomer conversion. The M_n values increased linearly with monomer conversion. The M_w/M_n ratio of the free PVAc chains gradually decreased from 1.7 to 1.4 with increasing polymerization time, but remained higher than those obtained in the MADIX polymerization reported previously.[25] This is likely due to the high target PVAc molar mass (i.e. the molar ratio of monomer to FXA at $t = 0$). Indeed, when the target molar mass was lowered ([FXA]$_0$/[VAc]$_0$ = 1/100), the resulting polymers had a M_n = 4,800 g/mol with a low M_w/M_n value of

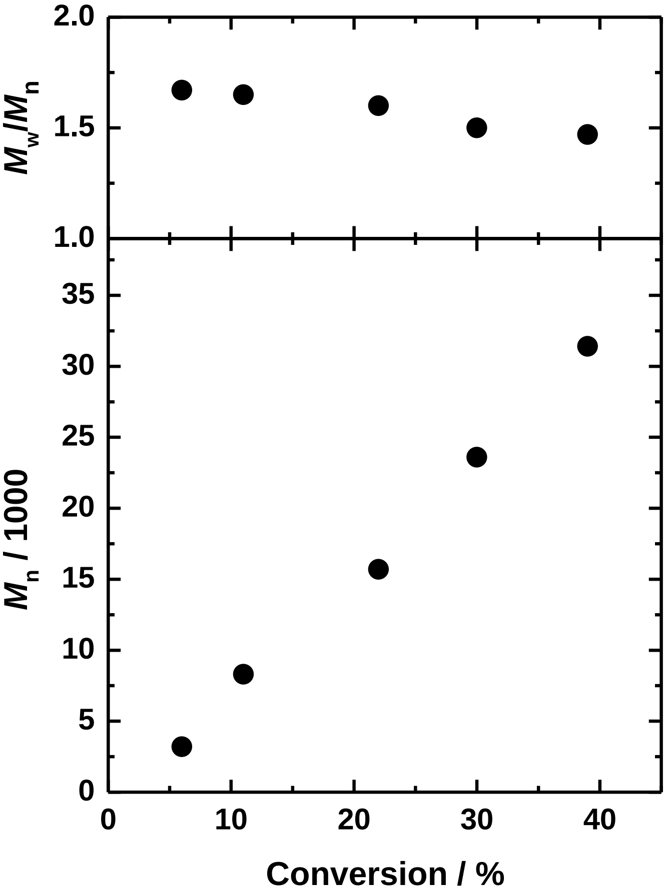


Figure 2. Evolution of the number-average molar mass (M_n) and dispersity (M_w/M_n) of the free polymer as a function of monomer conversion for the solution polymerization of vinyl acetate (VAc) in *N*,*N*-dimethylformamide (33 wt%) at 60 °C with xanthate-decorated silica nanoparticles (1 wt%): $[VAc]_0/[\text{free xanthate agent FXA}]_0/[2,2'\text{-azobis(isobutyronitrile)}]_0 = 1000/1/0.1$.

1.27, similar to that of the system reported previously. The increase in dispersity when high molar masses are targeted is caused by reverse VAc additions generating less reactive xanthate-terminated species (PVAc-CHOAc-CH_2-XA, where XA represents the xanthate moiety). Indeed, these -CH_2-XA-terminated chains only exchange at a meaningful rate with the minority -CH_2-terminated radicals; they accumulate in the reaction medium and lead to a slowdown of the MADIX equilibrium.[50,51] The VAc RAFT polymerization conducted here, thus proceeded with the expected level of control.

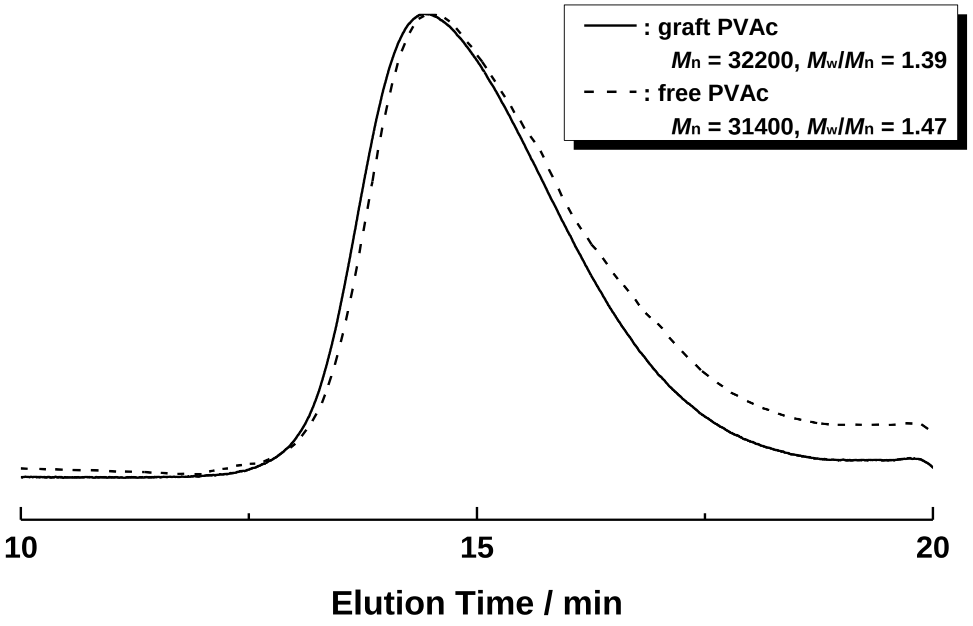


Figure 3. Gel permeation chromatographic traces for the graft (solid curve) and free (broken curve) polymers after 39 h of polymerization of vinyl acetate (VAc) in *N*,*N*-dimethylformamide (33 wt%) at 60 °C with xanthate-decorated silica nanoparticles (1 wt %): [VAc]$_0$/[free xanthate agent FXA]$_0$/[2,2'-azobis(isobutyronitrile)]$_0$ = 1000/1/0.1.

To compare the free and graft polymers, the SiPs purified after the polymerization were treated with hydrofluoric acid (HF) to cleave the graft polymer from the surface for subsequent gel permeation chromatographic (GPC) analysis. Figure 3 shows the GPC traces of the free and graft polymers obtained at the same polymerization time (run 5 in Table 1). Although the two GPC curves have almost the same shape and the obtained molar masses are almost equal, the M_w/M_n value is slightly smaller in the graft polymer; that is, the graft polymer structure was better controlled. The larger dispersity of the free polymer can be explained by the contribution of the initiation reaction of 2,2'-azobis(isobutyronitrile) (AIBN) which creates additional free polymer chains. Nonetheless, these results confirm that the MADIX polymerization of VAc initiated from the surface of the SiPs proceeds in a controlled fashion, producing SiPs with well-defined PVAc brushes (PVAc-SiPs).

Polymer grafting density

Thermogravimetric analyses (TGA) of the xanthate-fixed SiPs and the PVAc-SiPs (run 5 in Table 1) prepared above were carried out to estimate the mass (w) of polymer grafted on the SiPs. Figure 4 shows the TGA curves for both particles. The PVAc-SiPs showed a significant weight loss on heating, indicating that the polymer had been grafted. From the two TGA curves, the degree of grafting (w) was determined, and the graft density (σ) was then calculated using Eq. (1);

$$\sigma = (w/M_{\mathrm{n,graft}})A_{\mathrm{v}}/(\pi d_{\mathrm{c}}^2) \qquad (1)$$

where $M_{\mathrm{n,graft}}$ is the M_{n} of the graft polymer, A_{v} is Avogadro's number, and d_{c} is the diameter of the SiP core. In this estimation, the density of the SiP was set to be 1.9 g/cm^3. The graft density was calculated to be 0.18 chains/nm^2, which means that the number of PVAc chains grown from the SiP

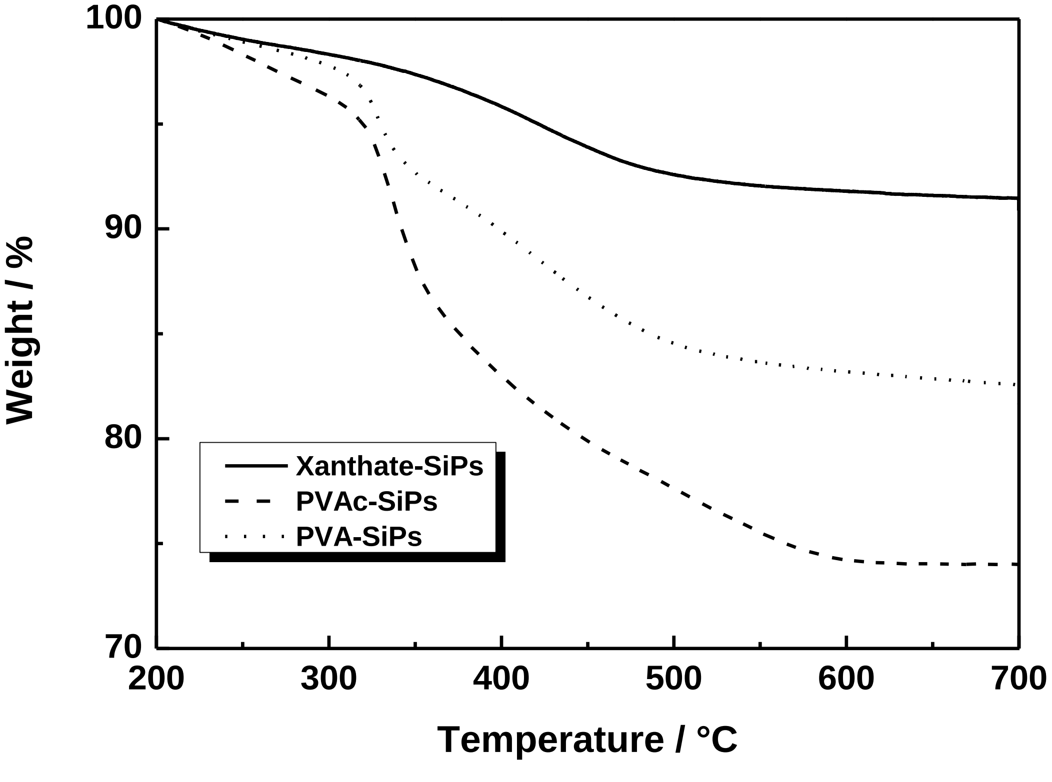


Figure 4. Thermal gravimetric analysis curves of (full line) xanthate-decorated silica particles, (broken line) silica particles grafted with poly(vinyl acetate) brushes, and (dotted line) silica particles grafted with poly(vinyl alcohol) brushes.

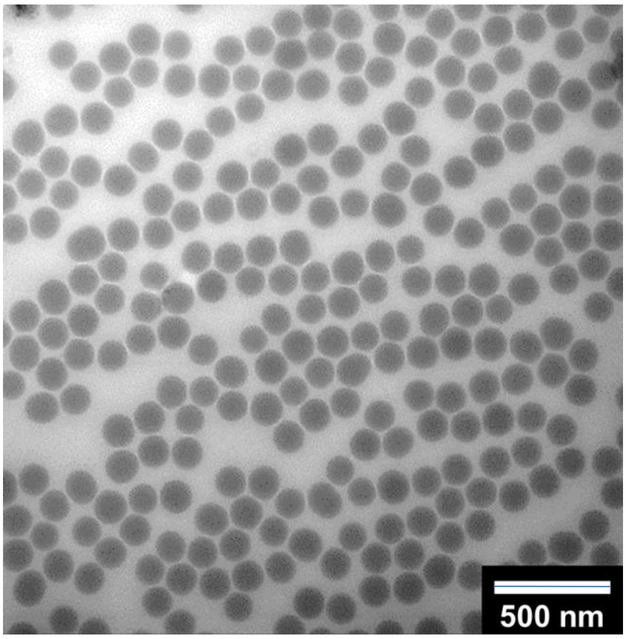


Figure 5. Transmission electron microscopic image of silica particles grafted with poly(vinyl acetate) brushes (PVAc-SiP). The average diameter of the silica particle cores is 130 nm. The number-averaged molar mass of the graft PVAc is 32,200 g/mol.

surface is about one-order of magnitude lower than that of the xanthate moieties fixed on the same surface. This difference is often observed in surface-initiated polymerization.[12-14] Importantly, the polymer graft density is high enough to demonstrate that the layer of polymer grafts is in the concentrated-brush regime.

Dynamic light scattering measurements of the PVAc-SiPs

As shown in the transmission electron microscopic (TEM) image in Figure 5, the PVAc-SiPs are well dispersed without any aggregation. The PVAc-SiPs were well dispersed in good solvents for PVAc, such as THF or acetone. To evaluate the dispersion state and the hydrodynamic size of the PVAc-SiPs in solution in more details, dynamic light scattering (DLS) measurements were conducted on a series of dilute dispersion of PVAc-SiPs in DMF. Figure 6 shows the hydrodynamic diameters, D_h, for the hybrid PVAc-SiPs as a function of M_n of the PVAc grafts. The diameters of the compact-core shell model, consisting of a SiP core and a PVAc shell of bulk density, and the fully stretched core-shell

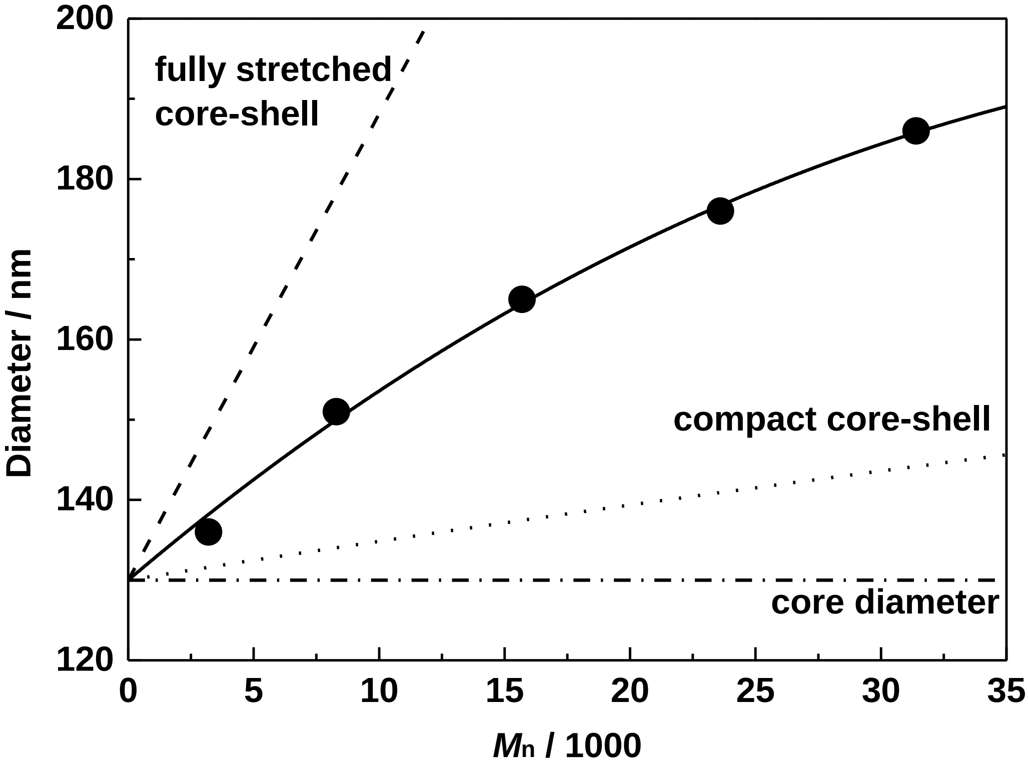


Figure 6. Plot of the average hydrodynamic diameter, D_h, of the silica particles grafted with poly(vinyl acetate) brushes (PVAc-SiPs) as a function of number-average molar mass M_n of the PVAc graft chains. The D_h values were determined by dynamic light scattering in dilute DMF suspension at 25 °C. The diameters of the SiP cores are 130 nm. The broken and dotted lines represent the diameters of the fully stretched and compact core-shell models, respectively (see text).

model, consisting of a SiP core and a PVAc shell whose size is equal to that of the PVAc chains radially stretched in an all-trans conformation, are also shown. The D_h value increased with increasing M_n, and remained intermediate between the diameters of the two models.

Synthesis of poly(vinyl alcohol) brushes

PVAc was used as a precursor of poly(vinyl alcohol) (PVA), an important general-purpose polymers. PVA is widely used for various applications, such as biocompatible materials, colloidal dispersion stabilizers, adhesives, and antifreeze agents.[37-45] Although some studies concerning PVA brushes have been reported,[52] there are still no reports on the synthesis of PVA brushes with a well-defined structure and a narrow molar mass distribution because the methods for the preparation of the precursor PVAc are ATRP and iodine-mediated systems, which are not suitable for obtaining well-defined PVAc. In addition, an analysis of the characteristics of the obtained PVA brushes has been insufficient. PVA is generally synthesized by hydrolyzing PVAc under alkaline conditions. Therefore, it seems that PVA brushes can be easily synthesized by treating PVAc brushes under the same conditions; however, surprisingly, as mentioned above, PVA brushes are rarely reported. The primary reason for the difficulty in the synthesis of PVA brushes is that, during the hydrolysis of the PVAc side chains under alkaline conditions, the covalent bonds of the ester linkages (in most cases, bonding the substrate and the PVAc brush) are cleaved at the same time; thus, the graft polymers are cleaved from the substrate surfaces. We attempted the hydrolysis of PVAc under alkaline conditions, but, as expected, the ester bonds connecting the polymers with the particle surface were cleaved at the same time, resulting in the degrafting of the polymers. Therefore, the hydrolysis conditions were extensively studied to achieve the hydrolysis of the PVAc brushes without degrafting. This was achieved under certain acidic conditions, as described below.

To hydrolyze the PVAc brushes on the SiP surfaces, the hybrid particles (run 5 in Table 1) were stirred in methanol containing 1.5 N aqueous HCl solution at 50 °C for 2 days. Washing/redispersion cycles in methanol and water provided stable dispersion of the resulting PVA-grafted silica nanoparticles. Figure S1a shows a TEM image of these PVA-grafted nanoparticles. Figure S2 shows that the PVAc-SIPs aggregate and sediment in water whereas PVA-SIPs form stable colloidal suspension in water. Figure 7 shows the Fourier transform infrared (FT-IR) spectra of the hybrid particles before and after hydrolysis. Prior to the HCl treatment, a peak at 1740 cm^{-1} ascribed to the stretching vibration of the C═O bond of the acetyl group was observed, whereas that peak almost completely disappeared after the treatment. Thus, the deacetylation reaction had progressed almost completely. In addition, using TGA, the amount of grafted polymer on the hybrid particles before and after deacetylation by the HCl treatment was measured. These measurements indicated that the ratio of the amount of grafted polymers before and after deacetylation was 86/47 (the weight

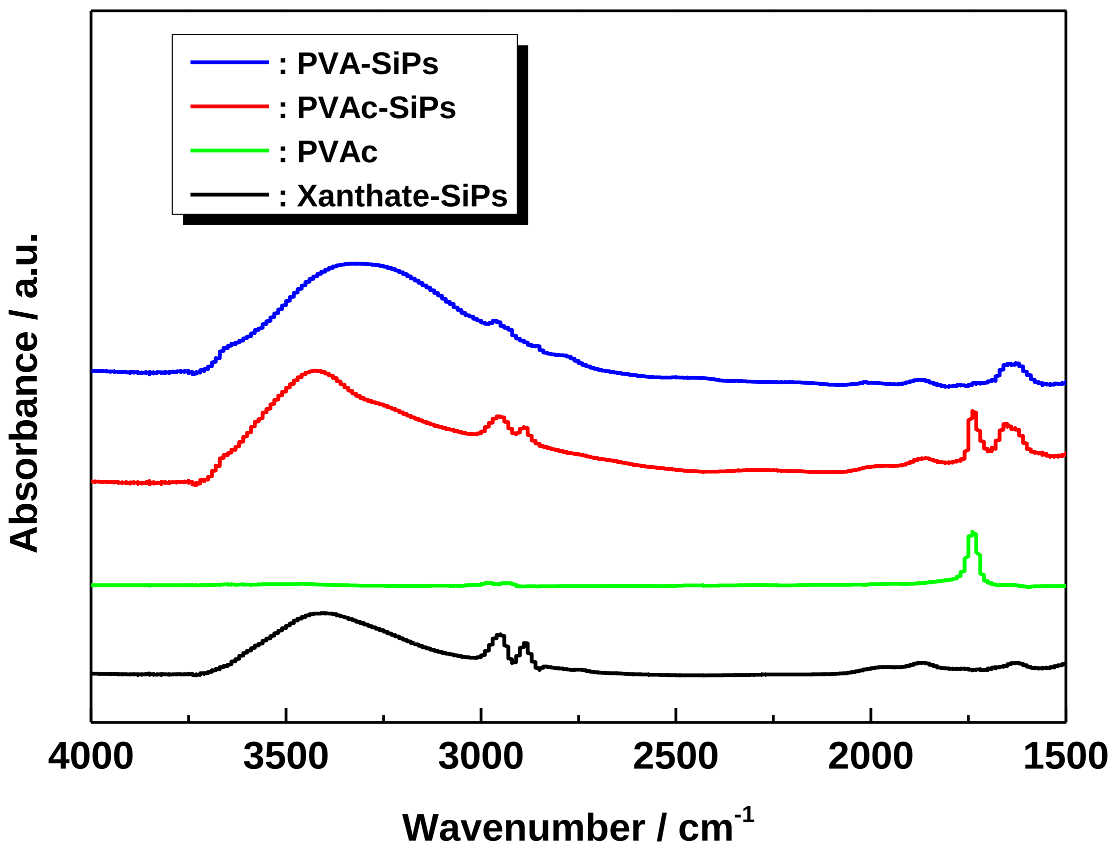


Figure 7. Infrared spectra of (black) xanthate-decorated silica particles, (green) poly(vinyl acetate), (red) silica particles grafted with poly(vinyl acetate) brush, and (blue) silica particles grafted with poly(vinyl alcohol) brushes.

ratio of the amount of PVAc and PVA graft polymers), as shown in Figure 4. This ratio is approximately equal to the weight ratio of the monomer units of PVAc and PVA, i.e., 86/44 for VAc/VA. These results confirmed that the deacetylation reaction proceeded almost completely and that no degrafting reaction occurred under the acidic hydrolysis conditions used in this study. It should be emphasized here that we demonstrate, for the first time, that well-defined PVA brushes can be synthesized by combining the SI-MADIX polymerization of VAc and a subsequent hydrolysis reaction in a mixture of methanol and water with an appropriate concentration of HCl.

Formation of mixed polymer brushes

Mixed polymer brushes are a unique polymeric architecture in which two or more kinds of polymers are grafted onto the same substrate.[53,54] They have attracted attention for both fundamental and applied aspects because they show interesting physicochemical properties such as characteristic phase-separation behaviors in both bulk and solution systems. Several synthetic methods for mixed polymer brushes using SI-LRP have been reported so far. Zhao et al. synthesized mixed polymer brushes by modifying the substrate surface with a Y-shape fixed initiator having NMP- and ATRP-type initiation sites in the same molecule.[53] Benicewicz et al. synthesized mixed polymer brushes in two different approaches on the basis of SI-RAFT polymerization.[55,56] Meanwhile, Matyjaszewski et al. and Li et al. independently developed a new method for the synthesis of block copolymers in solution using haloxanthate inifers, in which xanthate and ATRP-initiating groups are present in the same molecule, by conducting the MADIX polymerization of *N*-vinylpyrrolidone (NVP) or VAc followed by the ATRP of styrene (S) or methyl methacrylate (MMA).[57,58] In this MADIX/ATRP polymerization system, they took advantage of the fact that PS or PMMA radicals hardly chain-transfer to the xanthate moietes; in other words, xanthate is a poor chain transfer agent in the MADIX polymerization of S or MMA. Inspired by their findings, in the present study, we decided to apply this MADIX/ATRP polymerization approach to surface-initiated polymerization to synthesize a mixed polymer brush.

Scheme 2 shows the synthesis strategy for the mixed polymer brushes used in this study. First, by reacting some of the 2-bromopropionyl groups on the SiP surface with an appropriate amount of PEX, SiPs having both alkyl bromide groups and xanthate groups on the surface were prepared. Then, using these modified particles, we carried out the SI-MADIX polymerization of VAc followed by the SI-ATRP of S or MMA for the fabrication of a mixed polymer brush on the SiP surface. In this strategy, SI-MADIX polymerization was conducted first because the reaction requires more space for the reversible addition-fragmentation chain transfer process between the polymer chains than ATRP. In addition, the composition of the mixed polymer brush, i.e., the ratio of the amount of grafted

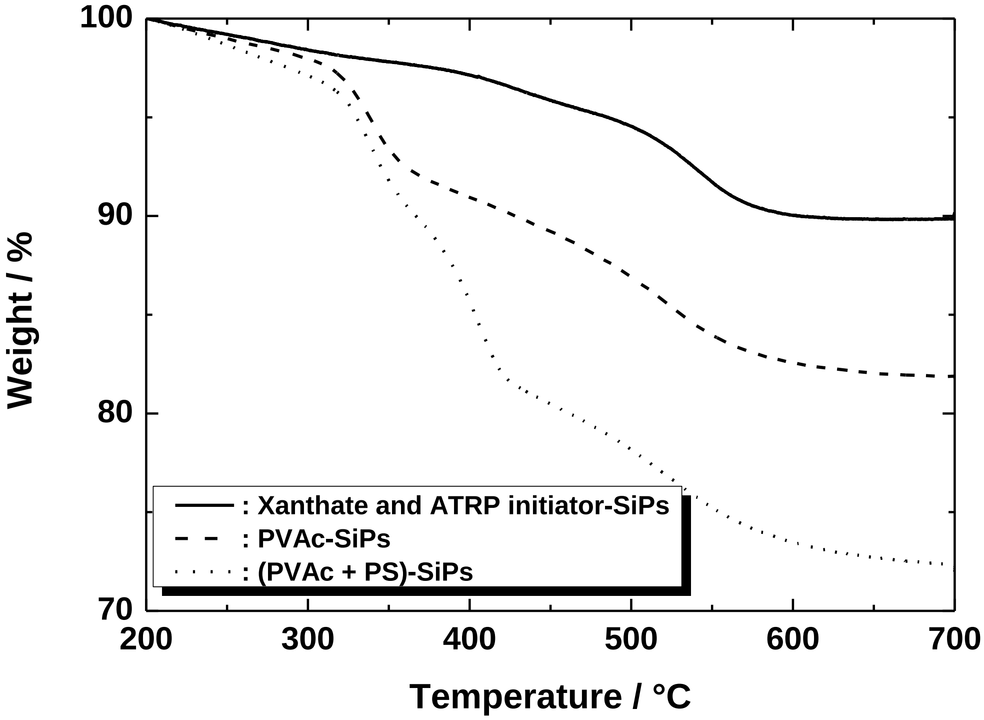


Figure 8. Thermal gravimetric analysis curves of (full line) xanthate and ATRP initiator-decorated silica particles, (broken line) silica particles grafted with poly(vinyl acetate) brushes, and (dotted line) silica particles grafted with mixed polymer brushes composed of poly(vinyl acetate) and polystyrene homopolymers.

PVAc and PS, can be controlled by the amount of PEX added. That is, when the amount of added PEX was high, the surface density of xanthate introduced increased, resulting in a higher amount of PVAc graft chains, and vice versa. As a representative example, when 0.05 equivalents of PEX with respect to the 2-bromopropionyl group (2.8 groups/nm^2) on the SiP surface were used, the surface densities of 2-bromopropionyl and xanthate groups were 2.3 and 0.14 groups/nm^2, respectively, as determined by elemental analysis of the particles. Next, SI-MADIX polymerization of VAc was carried out in DMF at 60 °C for 36 h, using VAc (1000 eq.), FXA (1 eq.), and AIBN (0.1 eq.) in the presence of the SiPs bearing both xanthate and ATRP-initiating groups. The polymerization resulted in a free PVAc having an M_n of 38,800 g/mol and M_w/M_n of 1.58 at a monomer conversion of 49%. After the polymerization, the SiPs were washed, collected, and then used as a substrate for the SI-ATRP of S in DMF at 100 °C for 24 h using S (500 eq.), ethyl 2-bromoisobutyrate as a free ATRP initiator (1 eq.), Cu(I)Cl (2.5 eq.), and dNbipy (5 eq.). The polymerization resulted in a free PS having an M_n of 51,800 g/mol and M_w/M_n of 1.14 at a monomer conversion of 98%. Figure 8 shows the results of the TGA measurements of the particles after treatment in each reaction step described above. The increasing weight loss shown in the thermograms after each polymerization step (SI-MADIX polymerization and SI-ATRP) compared to that of the xanthate-decorated SiPs indicate that PVAc and PS chains were effectively grown on the particle surfaces. The grafting densities of the PVAc and PS brushes were both determined to be 0.07 chains/nm^2 on the basis of the TGA results and the molar masses of the free polymers produced in each polymerization. Figure 9 shows the GPC traces of the grafted PVAc, of the mixture of grafted PVAc and PS grown from the particles surfaces, and of the free PS simultaneously produced in the second polymerization. The GPC trace of the mixture of grafted PVAc and PS is clearly composed of the PVAc peak and a sharp PS peak. The PS peak shape and position observed in this GPC trace nicely corresponds to that of the free PS simultaneously produced by the SI-ATRP of S. Note that the peak derived from PS is more intense than that of PVAc, because the differential refractive index of PS with respect to THF is much higher than that of PVAc.

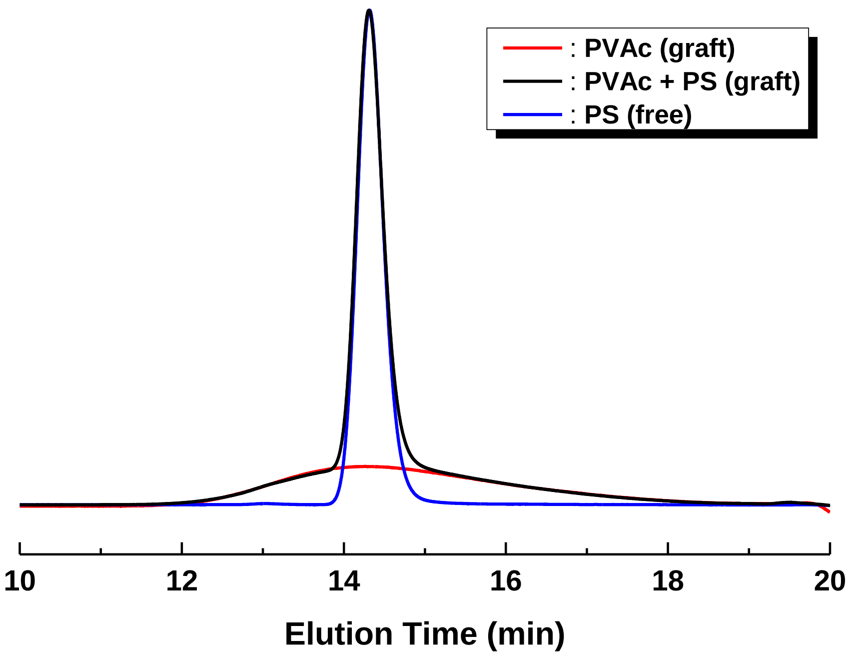


Figure 9. Gel permeation chromatographic traces for (red) poly(vinyl acetate) graft polymer produced by SI-MADIX polymerization, (black) the mixture of poly(vinyl acetate) and polystyrene graft polymers produced by SI-MADIX polymerization followed by SI-ATRP, and (blue) polystyrene free polymer produced by SI-ATRP.

These results suggested that the SI-ATRP of S proceeded from the 2-bromopropionyl groups fixed on the SiP surfaces and that the xanthate moieties, present at the chain ends of the PVAc graft polymers, did not affect the SI-ATRP reaction, as expected. Furthermore, the IR spectrum of the hybrid particles after SI-MADIX and SI-ATRP is shown in Figure 10 along with the IR spectra of PVAc and PS for comparison. A peak at 1740 cm^{-1} attributed to the C=O stretching of PVAc and a peak around 3000–3140 cm^{-1} assigned to the C–H stretching of the aromatic ring of PS clearly appear in the spectrum of the polymer brush-grafted SiPs, confirming that both PVAc and PS chains were present on the surface of the particles. Together with the GPC results described above, there is strong evidence that a mixed polymer brush composed of PVAc and PS homopolymers was formed on the SiP surface without the formation of any PVAc-*b*-PS block copolymer.

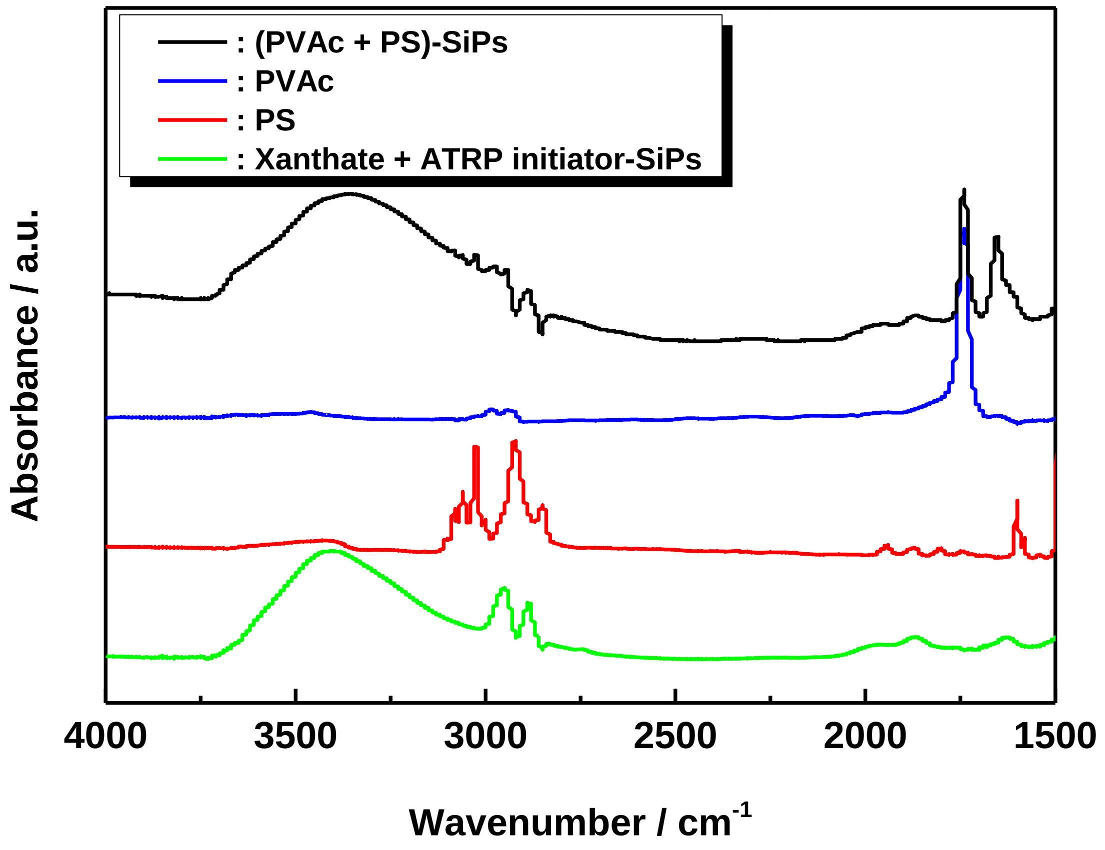


Figure 10. Infrared spectra of (green) xanthate and ATRP initiator-decorated silica particles, (red) polystyrene, (blue) poly(vinyl acetate), and (black) silica particles grafted with mixed polymer brushes composed of poly(vinyl acetate) and polystyrene homopolymers.

Mixed polymer bushes have been reported to exhibit a unique phase-separated structure.[55,59,60] Inspired by this, the structural analysis of the above-mentioned mixed polymer brush-decorated SiPs was carried out using TEM. In the experiment, first, a suspension of the hybrid particles in dichloromethane was cast onto a carbon-coated copper TEM microgrid, and the sample grid was treated with RuO_4 to selectively stain the PS fraction of the hybrid particles. Figure 11 shows a TEM photograph of the mixed polymer brush-decorated SiPs after staining. A characteristic pattern consisting of dark and bright regions of several tens of nanometers is visible. As a comparison, when SiPs grafted with PS brushes or PVAc brushes alone were treated under the same staining conditions,

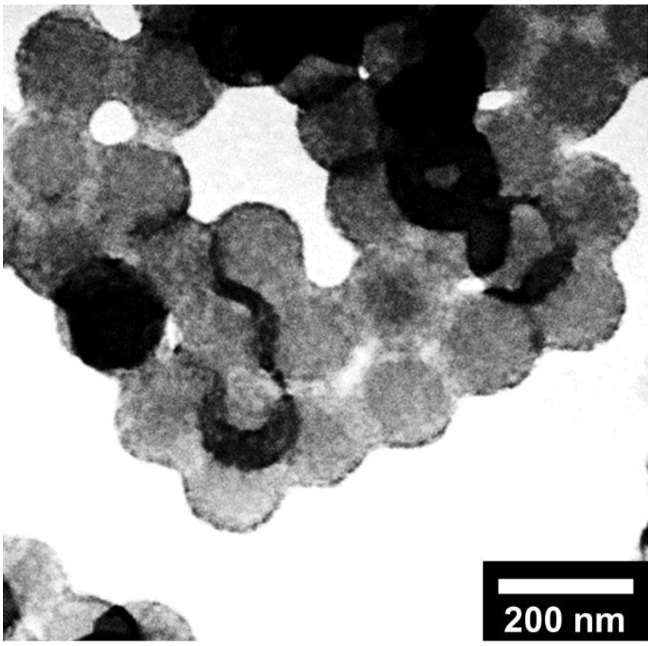


Figure 11. Transmission electron microscopic image of silica particles grafted with mixed polymer brushes composed of poly(vinyl acetate) and polystyrene homopolymers. The average diameter of the silica particle core is 130 nm. The number-averaged molar masses of the graft poly(vinyl acetate) and polystyrene homopolymers are 38,800 g/mol and 51,800 g/mol, respectively. The sample grid was treated with RuO_4 to stain the polystyrene fraction of the hybrid particles selectively.

the PS and PVAc brushes were observed to be dark and blurry, respectively (Figure S1). Judging from these results, the pattern shown in Figure 11 is likely due to the fact that the PVAc and PS brushes on the SiP surface formed a phase-separated structure at the nanometer scale.

We also examined the versatility of this synthetic method for mixed polymer brushes by using MMA as a monomer for SI-ATRP instead of S. The experiment provided similar results as in the case of S, as shown by the TGA and GPC results, which revealed that mixed polymer brushes consisting of PVAc and PMMA homopolymers were formed on the SiP surface (Figure S3). These experiments demonstrated the high versatility of this method, and thus, the synthesis of mixed polymer brushes composed of other combinations of homopolymers using this method is highly probable.

Conclusions

Monodisperse SiPs were surface-modified with a newly designed triethoxysilane derivative having 2-bromopropionyl group. The modified particles were further treated with PEX to yield xanthate moieties on their surfaces. The SI-MADIX polymerization of VAc from the xanthate-modified SiPs proceeded with good control over the molar mass and dispersity of the graft polymer and with a high graft density of around 0.2 chains/nm^2, resulting in hybrid particles grafted with well-defined PVAc brushes. Hydrolysis of the PVAc brushes with an appropriate concentration of HCl generated well-defined PVA brushes without causing any degrafting, i.e., reduction in the graft density. This is the first report of the synthesis of well-defined, concentrated PVA brushes. A novel strategy has also been developed for fabricating mixed polymer brushes: SI-MADIX polymerization of VAc followed by SI-ATRP of S or MMA from SiPs functionalized with a controlled number of xanthate moieties and ATRP-initiating sites. Owing to its simplicity and versatility, this method can be easily applied to many other monomers and solid substrates. In addition, combined with the rich chemistry of xanthate molecules, such as chain-end functionalization, the present system will undoubtedly find unique applications.

Experimental Section

The list of reagents and general measurements used in this study are provided in the supporting information.

Synthesis of alkyl bromide-carrying silane coupling agent, 6-(triethoxysilyl)hexyl 2-bromopropionate (BPHE, Scheme 1)

A two-step reaction was conducted for the synthesis of BPHE. First step: 2-bromopropionyl bromide (25 g, 115.8 mmol) was added dropwise to a cooled mixture of 5-hexen-1-ol (12 g, 121 mmol), triethylamine (12.3 g, 122 mmol), and dry dichloromethane (100 mL) at 0 °C under Ar atmosphere. The reaction mixture was magnetically stirred for 2 h at 0 °C and then for another 24 h at room temperature. The mixture was washed three times with water (3 × 200 mL). The organic layer was dried over $\mathrm{Na_2SO_4}$ and filtered. The solvent was removed to obtain a brown oil, which was distilled to yield 5-hexen-1-yl 2-bromopropionate (BPH) as a transparent liquid collected at 1 mmHg and 32−35 °C (17.8 g, 65% yield). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.47 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_2CH{=}CH_2}$), 1.68 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CH{=}CH_2}$), 1.81 (d, 3H, $\mathrm{C}\mathit{H}_3\mathrm{CH}$), 2.08 (q, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH{=}CH_2}$), 4.15 (t, 2H, $\mathrm{C}\mathit{H}_2\mathrm{OOC}$), 4.36 (q, 1H, $\mathrm{C}\mathit{H}\mathrm{CH_3}$), 4.68 (d, 2H, $\mathrm{C}\mathit{H}_2\mathrm{O}$), 4.95–5.03 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{{=}CH}$), 5.78 (m, 1H, $\mathrm{CH_2{=}C}\mathit{H}$). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 21.7 ($\mathrm{CH}\mathit{C}\mathrm{H_3}$), 25.0 ($\mathit{C}\mathrm{H_2CH_2CH_2CH{=}CH_2}$), 27.9 ($\mathit{C}\mathrm{H_2CH_2CH{=}CH_2}$), 33.3 ($\mathit{C}\mathrm{H_2CH{=}CH_2}$), 40.3 ($\mathit{C}\mathrm{HBr}$), 65.9 ($\mathit{C}\mathrm{H_2O}$), 115.0 ($\mathit{C}\mathrm{H_2{=}CH}$), 138.3 ($\mathrm{CH_2{=}}\mathit{C}\mathrm{H}$), 170.4 ($\mathit{C}\mathrm{{=}O}$). Anal. Calcd for $\mathrm{C_9H_{15}O_2Br}$: C, 45.97; H, 6.43; O, 13.62; Br, 33.98. Found: C, 46.21; H, 6.61; O, 13.42; Br, 33.76.

Second step: a two-necked round-bottom flask was charged with BPH (9.48 g, 40 mmol) and toluene (40 mL), and equipped with a magnetic stirring bar and a rubber septum. After bubbling the mixture with argon, triethoxysilane (9.86 g, 60 mmol) that had been purged with argon beforehand was added into the flask in a glove box purged with argon, and subsequently Karstedt's catalyst solution (80 mg) was added to the reaction mixture using a syringe. The reaction mixture was magnetically stirred under an argon atmosphere for 48 h at 65 °C. The progress of the reaction (disappearance of BPH) was monitored by ^{1}H NMR spectroscopy. The volatile components were removed under vacuum using rotary evaporator. The remaining liquid was purified by distillation under reduced pressure, and the silane coupling agent BPHE was collected at 0.5 mmHg and 157−162 °C as a transparent liquid (8.1 g, 51% yield). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.63 (t, 2H, $\mathrm{C}\mathit{H}_2\mathrm{Si(OCH_2CH_3)_3}$), 1.23 (t, 9H, $\mathrm{(C}\mathit{H}_3\mathrm{CH_2O)_3Si}$), 1.29-1.50 (br, 6H, $\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2Si}$), 1.50-1.73 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2O}$), 1.82 (d, 3H, $\mathrm{C}\mathit{H}_3\mathrm{CH}$), 3.81 (q, 6H, $\mathrm{OC}\mathit{H}_2\mathrm{CH_3}$), 4.16 (t, 2H, $\mathrm{C}\mathit{H}_2\mathrm{O}$), 4.36 (q, 1H, $\mathrm{C}\mathit{H}\mathrm{CH_3}$). ^{13}C NMR: 10.4 ($\mathit{C}\mathrm{H_2Si}$), 18.4 ($\mathrm{((}\mathit{C}\mathrm{H_3CH_2O)_3Si)}$), 21.7 ($\mathit{C}\mathrm{H_2CH_2Si}$), 22.8, 25.5, 28.4, 32.7 ($\mathit{C}\mathrm{H_2}$), 40.3 ($\mathit{C}\mathrm{Br}$), 58.4 ($\mathrm{O}\mathit{C}\mathrm{H_2CH_3}$), 66.2 ($\mathit{C}\mathrm{H_2O}$), 170.4 ($\mathit{C}\mathrm{{=}O}$). Anal. Calcd for $\mathrm{C_{15}H_{31}BrO_5Si}$: C, 45.11; H, 7.82; Br, 20.01. Found: C, 44.96; H, 7.99; Br, 19.90.

Fixation of the silane coupling agent BPHE on silica particles

A suspension of silica particles (SiPs, diameter = 130 nm) in ethylene glycol was diluted with ethanol and centrifuged, and the collected SiPs were then redispersed in ethanol and centrifuged. By repeating this operation three times, a SiP (4 g, solid) suspension in ethanol (200 mL) was obtained. Then, BPHE (2 g) was added to this ethanolic SiP suspension. After 1 h, a mixture of 28% NH_3 aqueous solution (19.2 g) and ethanol (200 mL) was added to the suspension under stirring, and the reaction was left to stir for 20 h at 25 °C. The modified SiPs were washed by three successive cycles of centrifugation and redispersion in ethanol.

Introduction of xanthate moieties on silica particles

Xanthate moieties were introduced as follows: potassium *O*-ethyl dithiocarbonate (PEX, 3.8 mg) dissolved in ethanol (100 mL) was added to a suspension of the alkyl bromide-decorated SiPs (2 g, solid) in ethanol (100 mL), and the mixture was magnetically stirred at room temperature for 36 h. The xanthate-decorated SiPs were washed by repeated centrifugation/redispersion in ethanol/water of 1/1 v/v twice and in *N*,*N*-dimethylformamide (DMF) twice. The particles were finally dispersed in DMF for stock.

Surface-initiated MADIX polymerization on SiPs

The xanthate-decorated SiPs were used for polymerization of VAc as follows. The xanthate-decorated SiPs in DMF were mixed with a VAc solution containing a predetermined amount of the free xanthate chain transfer agent, *O*-ethyl-*S*-(1-methoxycarbonyl)ethyldithiocarbonate (FXA), and a radical initiator, 2,2'-azobis(isobutyronitrile) (AIBN), in a Pyrex glass tube containing a magnetic stirrer and equipped with a three-way cock. The mixture was deoxygenated by Ar bubbling for 15 min at 0 °C and then placed in an oil bath. The bath was heated at 60 °C to start the polymerization. A part of the polymerization solution was taken out and cooled to room temperature after a predetermined time *t*. Some of the solution was used for NMR measurement to determine the monomer conversion. Tetrahydrofuran (THF) was added to the remaining solution, and the solution was centrifuged to collect the SiPs grafted with polymers. The supernatant obtained by the centrifugation was subjected to gel permeation chromatographic (GPC, PMMA-calibrated) measurement to determine the molar mass and molar mass distribution of the free polymers. By repeating the operations of centrifugation and redispersion five times, polymer-grafted SiPs were obtained without any unbound (free) polymer. The PVAc graft polymers were cleaved from the SiP surface as follows. The polymer-grafted SiPs (50 mg) were dispersed in toluene (2 mL) containing tetraoctylammonium bromide (50 mg), which was used as a phase transfer catalyst, and 10% aqueous solution of hydrofluoric acid (2 mL) was added. The two-phase mixture was vigorously stirred for 3 h. The organic layer containing the cleaved polymer was subjected to GPC analysis to determine the molar mass of the polymer. Dried polymer-grafted SiPs were subjected to thermal gravimetric analysis (TGA) to determine the amount of graft polymer.

A typical condition for polymerization is shown below. The polymerization of VAc was conducted at 60 °C for 28 h with VAc (25.8 g, 300 mmol), FXA (68 mg, 0.3 mmol), AIBN (5 mg, 0.03 mmol), xanthate-fixed SiPs (1.2 g) as starting materials in DMF (14.5 g). The conversion of the monomer was 39 %. M_n and M_w/M_n of free polymer and graft polymer was 31,400 g/mol and 1.47 and 32,200 g/mol and 1.39, where M_n and M_w are the number- and weight-average molar masses, respectively, and M_w/M_n is the dispersity.

Hydrolysis of PVAc chains grafted on silica particles

PVAc-SiPs (1 g) were dispersed in methanol (5 mL) containing 1.5 N aqueous HCl (4 mL). The suspension was magnetically stirred at 50 °C for 48 h. The treated particles were washed by repeated centrifugation/redispersion in methanol three times and in water twice.

Synthesis of mixed polymer brushes on the SiP surfaces

BPHE-coated SiPs (0.2 g) were reacted with a mixture of PEX (0.019 mg, 0.05 equivalent relative to bromine atoms on the SiP surface) and ethanol (20 mL), and the solution was magnetically stirred at room temperature for 36 h and subsequently passed through a filter membrane. The modified SiPs were washed by repeated centrifugation/redispersion to obtain a DMF stock suspension. Using these modified SiPs (100 mg), SI-MADIX polymerization of VAc (8.6 g, 10 mmol) was conducted in the presence of FXA (22.5 mg, 0.1 mmol) and AIBN (1.6 mg, 0.01 mmol) in DMF (4.3 g) at 60 °C for 36 h, as described above. After the polymerization, the particles were washed by repeated centrifugation/redispersion in DMF five times to obtain a DMF stock suspension. The resulting PVAc-grafted SiPs (50 mg) in DMF (0.9 g) were mixed with styrene (S, 2.76 g, 27.6 mmol) containing ethyl 2-bromoisobutyrate (2-(EiB)Br, 10 mg, 0.055 mmol) and 4,4'-dinonyl-2,2'-dipyridyl (dNbipy, 115 mg, 0.282 mmol), and the mixture was quickly added to a Pyrex glass tube charged with copper(I) chloride (Cu(I)Cl, 13.7 mg, 0.138 mmol). The tube was immediately connected to a vacuum line to degas the reaction mixture by three freeze–pump–thaw cycles, and finally sealed under vacuum. The sealed tube was placed in a shaking oil bath (TAITEC Corp., Japan, Personal H-10) and polymerization was carried out at 100 °C for 24 h. After the polymerization, the particles were washed by repeated centrifugation/redispersion in toluene five times to obtain a toluene stock suspension. The resulting free and graft polymers were characterized by similar methods to those used for the PVAc-SiPs described above. Similarly, polymerization was carried out using the PVAc-grafted SiNPs (50 mg) in DMF (0.9 g) containing methyl methacrylate (MMA, 2.76 g, 27.6 mmol), 2-(EiB)Br (10 mg, 0.055 mmol), dNbipy (115 mg, 0.282 mmol), and Cu(I)Cl (13.7 mg, 0.138 mmol) at 60 °C for 21 h.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: Colloids • Nanoparticles • Polymerization • Polymers • Surface chemistry

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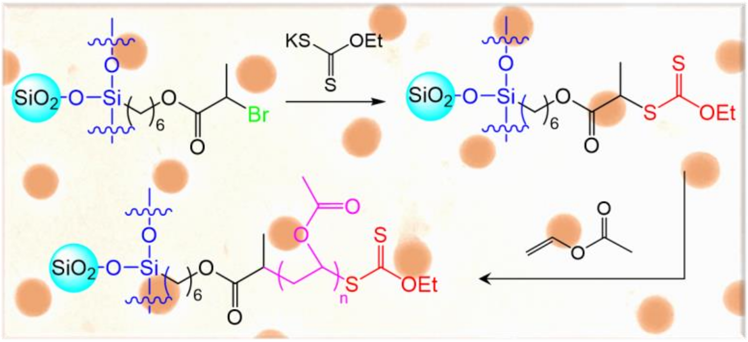
Graphical abstract

Grafting of Polymer Brushes from Silica Particles Functionalized with Xanthates

Kohji Ohno, Yoshikazu Yahata, Motokazu Sakaue, Vincent Ladmiral



Surface-initiated polymerization of vinyl acetate (VAc) from xanthate-modified silica particles resulted in hybrid particles grafted with well-defined PVAc brushes. Hydrolysis of the PVAc brushes generated well-defined poly(vinyl alcohol) (PVA) brushes. This is the first report of the synthesis of well-defined, concentrated PVA brushes. A novel strategy has also been developed for fabricating mixed polymer brushes.