

Postgrafting of vinyl polymers onto hyperbranched poly(amidoamine)-grafted nano-sized silica surface

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Abstract

To prepare polymer-grafted nano-sized silica with hydrophilic core and hydrophobic shell and with higher percentage of grafting, the postgraft polymerization of vinyl polymers onto hyperbranched poly(amidoamine)-grafted (PAMAM-grafted) nano-sized silica initiated by the system consisting of Mo(CO)₆ and terminal trichloroacetyl groups of PAMAM-grafted silica was investigated. The introduction of trichloroacetyl groups onto PAMAM-grafted silica surfaces was readily achieved by the reaction of trichloroacetyl isocyanate with terminal amino groups of PAMAM-grafted silica. It was found that the polymerization of vinyl monomers, such as methyl methacrylate (MMA), styrene, and glycidyl methacrylate (GMA) was successfully initiated by the system consisting of Mo(CO)₆ and terminal trichloroacetyl groups of PAMAM-grafted silica. In the polymerization, the corresponding vinyl polymers were effectively postgrafted onto PAMAM-grafted silica, based on the propagation of polymer from surface radicals formed by the reaction of terminal trichloroacetyl groups with Mo(CO)₆; the percentage of PMMA postgrafting onto PAMAM-grafted silica reached to 400% after 30 min, but the formation of gel was observed after 35 min. The formation of gel tends to decrease by use of hyperbranched PAMAM-grafted silica with higher percentage of grafting. The vinyl polymer-postgrafted nano-sized silica gave a stable colloidal dispersion in various organic solvents.
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1. Introduction

The functionalization of nano-sized particles by grafting of polymers is expected to play an important role in the designing a novel organic/inorganic nano-composite materials. The grafting of polymers onto nano-sized particle surface by ‘grafting from’ and ‘grafting onto’ methods are widely investigated. For example, Advincula et al. have reported the surface initiated polymerization on solid surfaces via anionic mechanism [1]. The grafting of polymers onto the surface by living cationic polymerization and metathesis polymerization were also reported [2,3]. The grafting of polymers and block copolymers with controlled molecular weight onto nano-sized particle

surfaces was successfully achieved by atom transfer polymerization [4–6]. In the system, the surface grafting of polymers with a high grafting density was successfully achieved [5,6]. The grafting of polymers onto solid surface by atom transfer polymerization was also reported by several authors [7–9].

On the other hand, we have reported the grafting of various polymers onto nano-sized particles, such as silica, titanium dioxide, and carbon black, by the polymerization of vinyl monomers initiated by initiating groups previously introduced onto these surfaces [10–12]. For instance, the radical, cationic, and anionic graft polymerization of various monomers was successfully achieved by azo [13], acylium perchlorate [14], and potassium carboxylate [15] groups previously introduced onto the silica surface, respectively.

Recently, we have successfully achieved the grafting of hyperbranched poly(amidoamine) (PAMAM) onto nano-sized silica [16] and carbon black surface [17] by repeating two processes according to poly(amidoamine) dendrimer synthesis methodology [18]: (1) Michael addition of methyl

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acrylate to amino groups introduced onto the surface and (2) terminal amidation of the resulting ester moieties with ethylene diamine (EDA) as shown in Fig. 1. More recently, the scale-up synthesis of hyperbranched PAMAM onto nano-sized silica was also achieved in solvent-free dry-system [19].

It is interesting to note that hyperbranched PAMAM-grafted nano-sized silica has many amino groups as terminal groups of the grafted chain. It is expected that these amino groups can be used as immobilization of various functional groups. We have reported the immobilization of norbornadiene moieties to terminal amino groups of hyperbranched PAMAM-grafted nano-sized silica surface and their application to solar energy conversion and storage materials [20]. In addition, it has been reported that the hyperbranched PAMAM-grafted nano-sized silica has an ability to cure epoxy resins [21].

On the other hand, Bamford et al. have reported that the system consisting of haloalkyl compounds and transition metal carbonyl derivatives, such as $\text{Mo}(\text{CO})_6$, $\text{Mn}_2(\text{CO})_{10}$, and $\text{Re}_2(\text{CO})_{10}$, has an ability to initiate the radical polymerization of vinyl monomers [22,23]. They also reported the preparation of block copolymers by use of the system consisting of $\text{Mo}(\text{CO})_6$ and polymers having terminal trichloroacetyl groups, which were synthesized by the reaction of terminal hydroxyl group of polymer with trichloroacetyl isocyanate [24]. The grafting of vinyl polymers onto glass surface initiated by the system consisting of trichloroacetyl groups on the surface and $\text{Mo}(\text{CO})_6$ has been reported by Eastmond et al. [25]. We have also reported the radical grafting of vinyl polymers onto nano-sized particle surfaces initiated by the system consisting of trichloroacetyl groups on these surfaces and $\text{Mo}(\text{CO})_6$ [26]. We have pointed out that the percentage of grafting in such initiating system was much higher than that initiated by azo groups on the surface, because of no formation of fragment radicals which forms ungrafted polymer [27].

In this paper, to prepare polymer-grafted nano-sized silica with hydrophilic core and hydrophobic shell and with higher percentage of grafting (as shown in Fig. 2), the radical postgraft polymerization of vinyl monomers

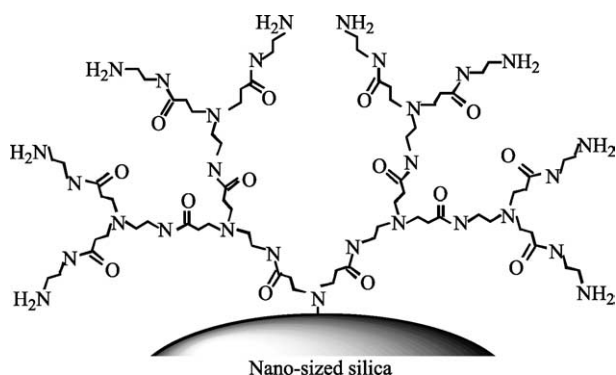


Fig. 1. Schematic illustration of PAMAM-grafted nano-sized silica.

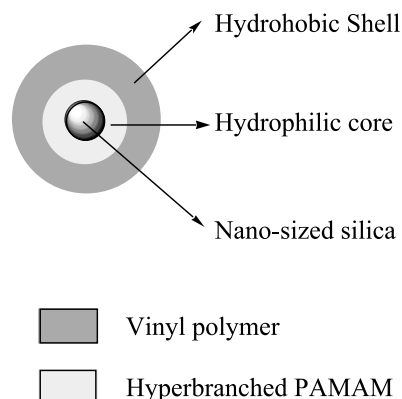


Fig. 2. Schematic illustration of polymer-postgrafted nano-sized silica with hydrophilic core and hydrophobic shell.

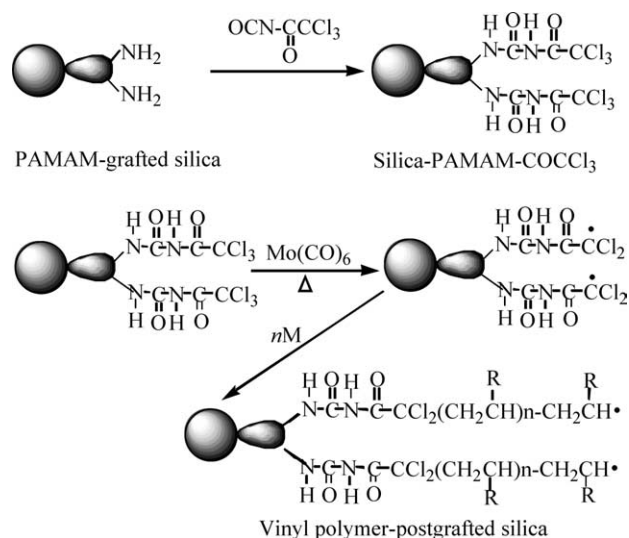
initiated by the system consisting of $\text{Mo}(\text{CO})_6$ and trichloroacetyl groups introduced to terminal amino groups of hyperbranched PAMAM-grafted nano-sized silica was investigated (Scheme 1). In addition, the dispersibility of the polymer-grafted silica will be discussed.

2. Experimental

2.1. Materials and reagents

Nano-sized silica used was Aerosil 200 obtained from Nippon Aerosil Co., Ltd, Japan. The specific surface area, average particle size, and silanol group content were $200 \text{ m}^2/\text{g}$, 12 nm and 1.37 mmol/g, respectively. The content of hydroxyl groups was determined by measuring volumetrically the amount of ethane evolved by the reaction with triethylaluminum [27]. The nano-sized silica was dried in vacuo at 110°C before use.

Methyl acrylate (MA) and ethylenediamine (EDA)



Scheme 1.

obtained from Kanto Chemical Co., Inc. Japan were distilled before use. Methyl methacrylate (MMA) was washed with dilute NaHSO_3 solution, dried over sodium sulfate, and distilled under reduced pressure. Styrene was also washed with dilute alkali, dried over barium oxide, and distilled under reduced pressure. *N*-Vinylcarbazole (NVC) was recrystallized from *n*-hexane and dried in vacuo at room temperature. Glycidyl methacrylate (GMA) was distilled under reduced pressure before use.

Trichloroacetyl isocyanate, molybdenum hexacarbonyl ($\text{Mo}(\text{CO})_6$), and γ -aminopropyltriethoxysilane (γ -APS) obtained from Kanto Chemical Co., Ltd, Japan were used without further purification. Other solvents and reagents were purified by ordinary methods.

2.2. Introduction of amino groups onto the silica surface

The introduction of amino groups onto the silica surface was achieved by the treatment of surface silanol groups on silica with γ -APS in the solvent-free dry-system. A typical example is as follows. Into a 500 mL four-necked flask, equipped with a mechanical stirrer having a semicircular blade, a thermometer, a purger of Ar gas and a reflux condenser, 15.0 g of nano-sized silica was charged and atmosphere was replaced with Ar gas. Then, 3.0 g of γ -APS ethanol solution was sprayed onto the silica surface at 150 °C under agitation at 300 rpm. After 30 min, unreacted γ -APS and ethanol were removed under vacuum at 150 °C. The resulting silica was dried in vacuo and stored in vacuo at room temperature. The silica was abbreviated as Silica-NH₂ (RC-0).

2.3. Grafting of hyperbranched PAMAM onto nano-sized silica surface

The grafting of hyperbranched PAMAM from the silica surface was achieved by repeating two steps: (1) Michael addition of MA to amino groups on the surface and (2) amidation of terminal groups with EDA in solvent-free dry-system [19] as shown in Scheme 2.

Hyperbranched PAMAM-grafted silica obtained from repeated reaction cycles of *n*-times was abbreviated as Silica-PAMAM (RC-*n*). The percentage of PAMAM grafting was determined by the following equation:

$$\text{PAMAM grafting(\%)} = (A/B) \times 100$$

where *A* is weight of PAMAM grafted and *B* is weight of nano-sized silica charged. The weight of PAMAM grafted onto the surface was determined by weight loss when PAMAM-grafted silica was heated at 800 °C by use of a thermal analyzer (Thermogravimetric Analyzer TGA-50, Shimadzu Manufacturing Co., Ltd).

2.4. Immobilization of trichloroacetyl groups to terminal amino groups of hyperbranched PAMAM-grafted nano-sized silica

The immobilization of trichloroacetyl groups to terminal amino groups of hyperbranched PAMAM-grafted silica was achieved by the reaction of trichloroacetyl isocyanate with terminal amino groups of grafted chains (Scheme 1 (1)). A typical example was as follows. Into a flask, 1.0 g of hyperbranched PAMAM-grafted silica, 1.0 g of trichloroacetyl isocyanate, and 150 mL of toluene were charged and the mixture was stirred at 80 °C for 8 h under nitrogen. After the reaction, the resulting silica was centrifuged at 1.5×10^4 rpm and supernatant solution containing unreacted trichloroacetyl isocyanate was removed. The silica precipitated was dispersed in THF and centrifuged again. The procedures were repeated until no more trichloroacetyl isocyanate could be detected in the supernatant solution. The treated silica having trichloroacetyl groups was stored in vacuo at room temperature in the dark. The silica having terminal trichloroacetyl groups was abbreviated as Silica-PAMAM-COCCl₃.

2.5. Polymerization procedures of vinyl monomers in the system consisting of hyperbranched PAMAM-grafted silica having trichloroacetyl groups and $\text{Mo}(\text{CO})_6$

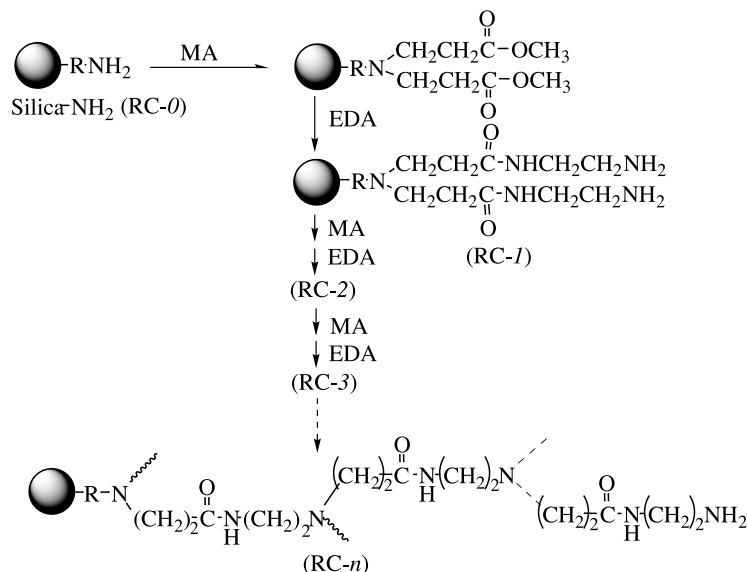
Into a polymerization tube, 0.10 g of Silica-PAMAM-COCCl₃, 0.01 g of $\text{Mo}(\text{CO})_6$, and 10.0 mL of vinyl monomer were charged. The tube was cooled with a liquid nitrogen bath, thawed three times, and sealed under high vacuum. The polymerization was conducted at 70 °C under stirring with a magnetic stirrer. After the polymerization, the contents of the polymerization tube were poured into a large excess of methanol to precipitate polymer-postgrafted silica and ungrafted polymer. The precipitate was filtered and dried in vacuo at 50 °C. The conversion was determined by the following equation:

$$\text{Conversion(\%)} = (C - D)/E \times 100,$$

where *C* is weight of precipitate, *D* is weight of Silica-PAMAM-COCCl₃ charged, and *E* is weight of monomer charged.

2.6. Determination of postgrafting and overall grafting

To separate the polymer-postgrafted nano-sized silica from the reaction mixture, the product was dispersed in THF and the dispersion was centrifuged at 1.5×10^4 rpm. The supernatant solution containing ungrafted polymer was removed and the nano-sized silica precipitated was dispersed again in THF and centrifuged. The procedures were repeated until no more polymers could be detected in the supernatant solution. The percentage of postgrafting and overall grafting were calculated by the following equations



Scheme 2.

$$\text{Postgrafting (\%)} = (F/G) \times 100$$

$$\text{Overall grafting (\%)} = (H/I) \times 100$$

where F is weight of the postgrafted vinyl polymer, G is weight of PAMAM-grafted silica charged, H is weight of total polymer (PAMAM grafted + vinyl polymer postgrafted), and I is net weight of nano-sized silica. The weight of polymer postgrafted onto nano-sized silica was determined from the weight loss of the polymer-postgrafted silica when the silica was heated at 800 °C by using of a thermogravimetric analyzer.

2.7. Surface wettability of hyperbranched PAMAM-grafted and PMMA-postgrafted silica

The wettability of PAMAM-grafted and PMMA-postgrafted silica of water was estimated by the penetrating rate of water through a column packed with polymer-grafted silica. Into a glass column (inside diameter 2 mm), 0.10 g of polymer-grafted silica was packed, and water was added from the top of the column. Then the penetrating rate of water through the column was determined.

3. Results and discussion

3.1. Grafting of hyperbranched PAMAM from silica surface

The grafting of hyperbranched PAMAM onto nano-sized silica surface was examined by repeating two processes: (1) Michael addition of surface amino groups as an initiator site to MA and (2) amidation of resulting ester with large excesses of EDA in solvent-free dry system as shown in Scheme 2.

Table 1 shows the property of hyperbranched PAMAM-grafted nano-sized silica used in this study. Silica-PAMAM (RC- n) means hyperbranched PAMAM-grafted silica and RC-4, RC-6 and RC-8 in parenthesis mean 4-times, 6-times and 8-times reaction cycles for the PAMAM grafting (Scheme 2). It was found that PAMAM was successfully grafted using the methodology of PAMAM dendrimer synthesis. The percentage of PAMAM grafting and amino group content increased with increasing reaction cycles. However, the percentage of PAMAM grafting and the amino group content were considerably smaller than those of calculated value. Therefore, the result indicates that the theoretical propagation of PAMAM from silica surface was hardly achieved, but hyperbranched PAMAM was successfully grafted onto the silica surface as mentioned in the previous papers [16,19].

The grafting of hyperbranched PAMAM onto the surface was confirmed by infrared spectra of the PAMAM-grafted silica. The infrared spectra show new absorptions at 1650 and 1550 cm⁻¹, which are characteristic of amide bond and amino group, respectively, of hyperbranched PAMAM.

3.2. Introduction of trichloroacetyl groups onto PAMAM-grafted silica surfaces

The introduction of trichloroacetyl groups onto

Table 1
Properties of PAMAM-grafted silica

Reaction cycles	Grafting (%)	Amino groups (mmol/g)	Trichloro acetyl groups (mmol/g)
RC-0	–	0.8	0.5
RC-4	51.8	2.0	1.6
RC-6	102.8	3.0	2.4
RC-8	107.1	3.8	2.9

PAMAM-grafted nano-sized silica by the reaction of terminal amino groups of grafted PAMAM with trichloroacetyl isocyanate was examined as shown in Scheme 1 (1). The content of trichloroacetyl groups, which was estimated from remaining amino groups after the treatment with trichloroacetyl isocyanate was also shown in Table 1.

It was found that about 75–80% of terminal amino groups of PAMAM-grafted silica were reacted with trichloroacetyl isocyanate. The hyperbranched PAMAM-grafted silica having trichloroacetyl groups were abbreviated as Silica–PAMAM–COCCl₃.

3.3. Initiating activity of polymerization by the system consisting of trichloroacetyl groups on PAMAM-grafted silica and Mo(CO)₆

The polymerization of GMA initiated by the system consisting of Silica–PAMAM (RC-6)–COCCl₃ and Mo(CO)₆ was investigated. The results are shown in Table 2. No polymerization of GMA was initiated in the presence of untreated silica (Run 2). Molybdenum hexacarbonyl (Run 1) and Silica–PAMAM–COCCl₃ (Run 4) alone have no ability to initiate the polymerization. In addition, no polymerization was initiated by the system consisting of untreated silica and Mo(CO)₆ (Run 3).

On the contrary, the polymerization of GMA was successfully initiated in the coexistence of Silica–PAMAM–COCCl₃ and Mo(CO)₆ and polyGMA was postgrafted onto the PAMAM-grafted silica (Run 5) without formation of gel: the percentage of polyGMA postgrafting reached 352.2%: this means that 3.52 g of polyGMA was postgrafted onto 1.0 g of PAMAM-grafted nano-sized silica surface.

The results suggest that postgrafted polyGMA propagated from the radicals formed by the reaction of terminal trichloroacetyl groups of PAMAM-grafted silica with Mo(CO)₆, as shown in Scheme 2, to give polymer-grafted nano-sized silica with hydrophilic core and hydrophobic shell as shown in Fig. 2.

Fig. 3 shows the effect of polymerization time on the postgrafting of GMA initiated by the system consisting of Silica–PAMAM(RC-4)–COCCl₃ and Mo(CO)₆ system. The percentage of polyGMA postgrafting exceeded 350% in spite of short polymerization time (15 min), but the formation of gel was observed after 20 min.

Fig. 4 shows the infrared spectra of (A) Silica–PAMAM(RC-4)–COCCl₃ and (B) polyGMA-postgrafted

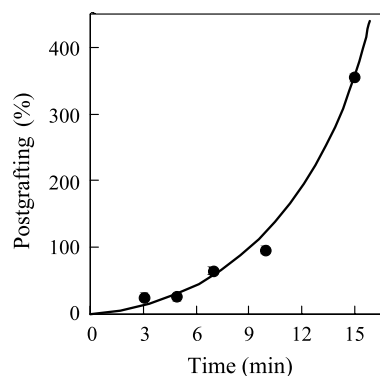


Fig. 3. Postpolymerization of GMA initiated by the system consisting of Silica–PAMAM–COCCl₃ and Mo(CO)₆. Silica–PAMAM–COCCl₃ (RC-4, grafting = 51.8%), 0.10 g; Mo(CO)₆, 0.01 g; GMA, 10.0 mL; 70 °C.

PAMAM-grafted silica obtained from the above polymerization. Infrared spectra of polyGMA-postgrafted PAMAM-grafted silica show new absorptions, which agreed with those of polyGMA (C).

3.4. Effect of PAMAM grafting on the PMMA postgrafting and gelation

Fig. 5 shows the time-conversion and time-percentage of postgrafting curves in the postgraft polymerization of MMA initiated by the system consisting of Silica–PAMAM–COCCl₃ (RC-4) and Mo(CO)₆ at 70 °C. It was found that conversion and percentage of grafting increased with progress of the polymerization. The percentage of postgrafting exceeded over 200% after 30 min, but the formation of gel was observed after 35 min.

Fig. 6 shows the time-conversion and time-percentage of postgrafting curves in the postgraft polymerization of MMA initiated by the system consisting of Silica–PAMAM(RC-6)–COCCl₃ and Mo(CO)₆ at 70 °C. It is interesting to note that in the system no gelation was observed even after 40 min. The percentage of PMMA grafting exceeded 600%. The value was extremely higher than that obtained from the graft polymerization initiated by azo groups introduced onto nano-sized silica surface.

Based on the above results, it is concluded that the system consisting of silica having Silica–PAMAM–COCCl₃ and Mo(CO)₆ has an ability to initiate the polymerization of MMA to give PMMA-postgrafted nano-sized silica with extremely high percentage of grafting. The gelation of the

Table 2

Polymerization of GMA initiated by the system consisting of Silica–PAMAM(RC-6)–COCCl₃ and Mo(CO)₆

Run	Silica	Mo(CO) ₆ (g)	Conversion (%)	Postgrafting (%)
1	None	0.01	0	–
2	Untreated	0.01	0	–
3	Silica–PAMAM	0.01	0	–
4	Silica–PAMAM–COCCl ₃	–	0	–
5	Silica–PAAMM–COCCl ₃	0.01	14.7	352.2

Silica, 0.01 g; Mo(CO)₆, 0.01 g; GMA, 10.0 mL; 70 °C; 15 min.

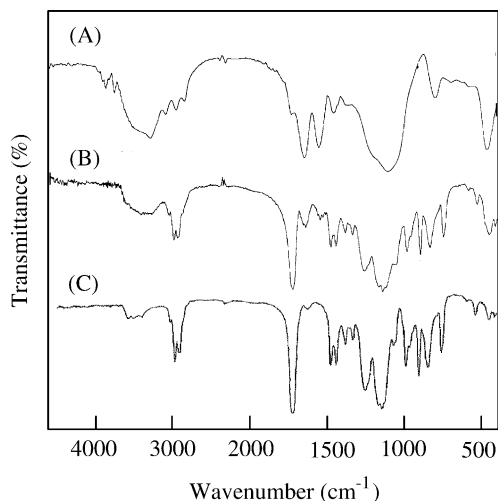


Fig. 4. FT-IR spectra of (A) hyperbranched PAMAM-grafted silica, (B) polyGMA-postgrafted silica, and (C) polyGMA.

system was prevented by use of hyperbranched PAMAM-grafted silica with higher percentage of grafting. This may be due to the fact that the bimolecular termination of growing polymer radicals from terminal groups of grafted hyperbranched PAMAM are suppressed, as the initiation site separates from the silica surface.

3.5. Graft polymerization of several vinyl monomers

The graft polymerization of several vinyl monomers initiated by Silica–PAMAM (RC-4)–COCCl₃ and Mo(CO)₆ system was examined. The results are shown in Table 3. This result clearly shows that the polymerizations of styrene and NVC are also successfully initiated by the above system and the corresponding polymers are effectively postgrafted onto PAMAM-grafted nano-sized silica surface.

The postgrafting of polystyrene also exceeded 200% after 400 min without the formation of gel. However, the

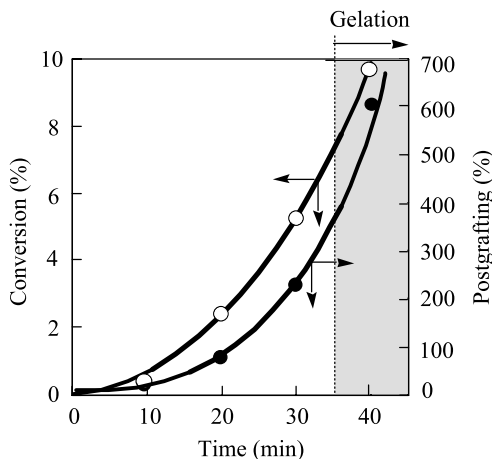


Fig. 5. Postpolymerization of MMA initiated by the system consisting of Silica–PAMAM–COCCl₃ and Mo(CO)₆. Silica–PAMAM–COCCl₃ (RC-4, grafting = 51.8%), 0.10 g; Mo(CO)₆, 0.01 g; MMA, 10.0 mL; 70 °C.

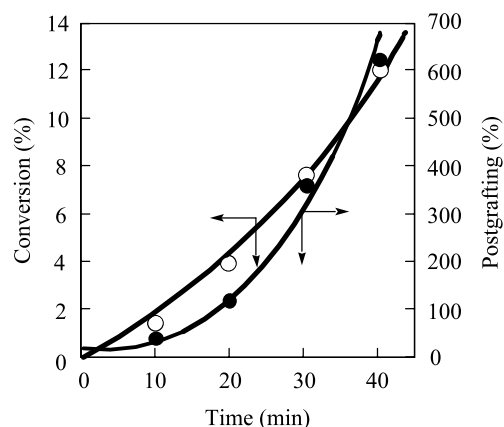


Fig. 6. Postpolymerization of MMA initiated by the system consisting of Silica–PAMAM–COCCl₃ and Mo(CO)₆. Silica–PAMAM–COCCl₃ (RC-6, grafting = 102.8%), 0.10 g; Mo(CO)₆, 0.01 g; GMA, 10.0 mL; 70 °C.

postgrafting and overall grafting of polyNVC were very small in spite of high conversion. This is due to the preferential formation of ungrafted polyNVC because Mo(CO)₆ have an ability to initiate the polymerization of NVC [26].

3.6. Wettability and dispersibility of vinyl polymer-postgrafted PAMAM-grafted silica

Fig. 7 shows the results of penetrating rate of water through a column packed with (A) untreated, (B) hyperbranched PAMAM-grafted, (C) PMMA-postgrafted, and (D) polystyrene-postgrafted silica. These results clearly show that hyperbranched PAMAM-grafted silica surface shows extremely hydrophobic nature, but PMMA-postgrafted and polystyrene-postgrafted silica shows extremely hydrophilic nature. This suggests that PAMAM grafted onto the silica surface was covered by postgrafted PMMA and polystyrene as shown in Fig. 2.

In addition, hyperbranched PAMAM-grafted silica gave a stable colloidal dispersion in methanol, but by postgrafting of PMMA, the dispersibility in methanol was completely

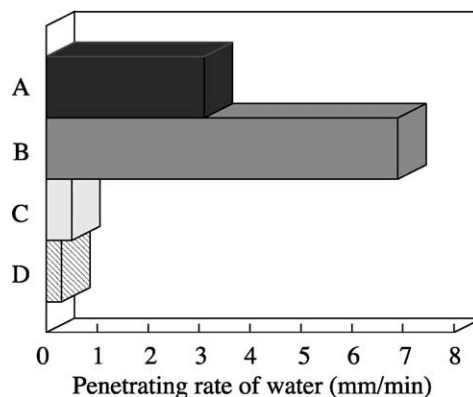


Fig. 7. Penetrating rate of water through the column packed with (A) untreated, (B) hyperbranched PAMAM-grafted, (C) PMMA-postgrafted, and (D) polystyrene-postgrafted silica.

Table 3
Polymerization of vinyl monomers initiated by the system consisting of Silica–PAMAM(RC-4)–COCCl₃/Mo(CO)₆

Vinyl monomer	Time (min)	Conversion (%)	Postgrafting (%)	Overall grafting (%)
Methyl methacrylate	30	5.5	230.0	400
Styrene	400	12.0	245.2	424
N-Vinylcarbazole	30	8.6	4.8	59.0
Glycidyl methacrylate	15	14.7	352.2	586

Silica–PAMAM(RC-4)–COCCl₃(51.8%), 0.10 g; Mo(CO)₆, 0.01 g; Vinyl monomer, 10.0 mL; 70 °C.

lost. However, these vinyl polymer-postgrafted silicas gave a stable colloidal dispersion in good solvent of PMMA, such as toluene and THF.

The results indicate that postgrafted vinyl polymer as hydrophobic shell on the nano-sized silica surface act as important roll on the dispersibility of the silica in solvent.

4. Conclusions

1. Trichloroacetyl groups were introduced onto hyper-branched PAMAM-grafted nano-sized silica surface by the reaction of trichloroacetyl isocyanate with terminal amino groups of PAMAM-grafted chains on the surface.
2. The system consisting of Silica–PAMAM–COCCl₃ and Mo(CO)₆ has an ability to initiate the radical polymerization of vinyl monomers and the corresponding vinyl polymer was successfully postgrafted to grafted PAMAM chain on the nano-sized silica to give polymer-grafted nano-sized silica with hydrophilic core and hydrophobic shell.
3. The percentage of vinyl polymer-postgrafting was extremely high and exceeded 400%, because of propagation of postgrafted chain from the surface radicals.
4. The formation of gel was observed in the postgrafting system with progress of the polymerization. The formation of gel tends to decrease by use of hyperbranched PAMAM-grafted silica with higher percentage of grafting.
5. Vinyl polymer-postgrafted nano-sized silica with hydrophilic core and hydrophobic shell gave a stable dispersion in organic solvent for grafted chains.
6. The polymer-grafted nano-sized silica with hyper-branched PAMAM core and functional shell, such as biocompatible and antibacterial properties, with higher percentage of grafting has the potential to be used as novel functional nano-composites.

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