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POSTGRAFTING OF HYPERBRANCHED DENDRITIC POLYMER FROM TERMINAL AMINO GROUPS OF POLYMER CHAINS GRAFTED ONTO SILICA SURFACE

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Key Words: Dendritic Polymer, Ultrafine Silica, Surface Grafting, Postgrafting, Percentage of Grafting, Amino Group

ABSTRACT

This paper describes postgrafting of hyperbranched dendritic polyamidoamine initiated from terminal amino groups of polymer chains grafted onto ultrafine silica surface in order to modify the silica surface. Surface grafting of polymer having terminal amino groups as initiator sites was performed by a reaction of terminal diamine-type polyoxyethylene with epoxy groups previously introduced onto the surface by 3-glycidoxypropyltri-

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methoxysilane treatment. The postgrafting reaction of dendritic polyamidoamine from the terminal amino groups was achieved by repeating the Michael addition of methyl acrylate to amino groups followed by amidation of the resulting ester moieties with ethylenediamine or hexamethylenediamine. Both the amount of amino groups and the percentage of postgrafting of the resulting polyamidoamine increased with an increase in the number of generations: the amino group content increased from 0.40 mmol/g to 2.68 mmol/g, and the percentage of postgrafting reached 61.0% after the 12th generation by using ethylenediamine in amidation. These values, however, were considerably smaller than the theoretical values. This indicates that the postgrafted polyamidoamine was a hyperbranched polymer but not a precise dendrimer. Ethylenediamine as a reactant in amidation was more effective than hexamethylenediamine, and a low content of initial amino groups was also preferred to a large amount of them probably because of steric hindrance in the propagation of hyperbranched dendritic polyamidoamine. The average particle size of hyperbranched dendritic polyamido-amine-postgrafted silica measured by light scattering photometry increased with an increase in the number of generations of the resulting polyamidoamine.

INTRODUCTION

The dispersibility of ultrafine inorganic particles, such as silica, titanium oxide, and carbon black, in organic solvents or polymer matrices is known to be remarkably improved by surface grafting of polymers onto these particles [1-3]. The polymer chains grafted onto the surface are considered to interfere with the aggregation of particles and increase the affinity of the surface for solvents and polymer matrices.

We have already reported the surface grafting of various polymers onto these ultrafine particles by the polymerization of a variety of monomers initiated by initiating groups newly introduced onto these surfaces. For instance, the anionic, cationic, and radical grafting of various polymers onto these surfaces are initiated by potassium carboxylate [4, 5], acylium perchlorate [6, 7], and azo [8, 9], respectively. Furthermore, we pointed out that various polymers with well-defined molecular weight and structure also grafted onto these particles by the reaction of surface reactive groups introduced, such as acyl azide [10], acyl chloride [11], and acid anhydride [12] groups, with hydroxyl- or amino-capped polymers.

Recently, we reported postgrafting reactions of several polymers by using pendant azo [13], acylium perchlorate [14], and glycidyl [15] groups introduced to grafted polymer chains on the ultrafine particle surfaces. By these postgrafting reactions, branched polymer-grafted ultrafine particles with higher percentage of grafting were obtained, and the dispersibility and the wettability of the particles were able to be controlled.

'Dendrimer' which is representative of hyperbranched polymers has attracted considerable attention in the field of polymer chemistry due to its unique properties [16-19]. Dendrimers are constructed from identical monomeric building blocks carrying branching sites which are located in a spherical way around a core. The synthesis of dendrimers by the divergent method starts from an initial core with one or more functional groups. These are converted using monomers with protected reactive sites. The removal of the protecting groups and the repeated reaction with monomer units leads to an exponential increase of functional groups on the surface of the spherical molecule. Unlike most traditional polymers, we can take precise structural control over the molecular weight as well as chemical and physical properties of dendrimers.

In the preceding paper, we reported the grafting of dendritic polymer onto ultrafine silica particles by the divergent method started from amino groups introduced onto the surface [20]. Combining dendritic molecule with linear polymer having well-defined molecular weight and structure is expected to provide novel architecture and properties. In the present paper, therefore, we dealt with the postgrafting reaction of dendritic polyamidoamine by the divergent method started from terminal amino groups of linear polymer chains with well-defined molecular weight and structure previously grafted onto the silica surface (Figure 1). Furthermore, we investigated the relationship between the number of generations and particle size of dendritic polyamidoamine-postgrafted silica by light scattering photometry.

EXPERIMENTAL

Materials

Ultrafine silica used was Aerosil 200 obtained from Nippon Aerosil Company, Ltd., Japan. The specific surface area and particle size were 200 m2/g and 16 nm, respectively. The content of surface silanol groups was determined to be 1.37 mmol/g by volumetrically measuring the amount of ethane evolved by reaction with triethylaluminum [21, 22].

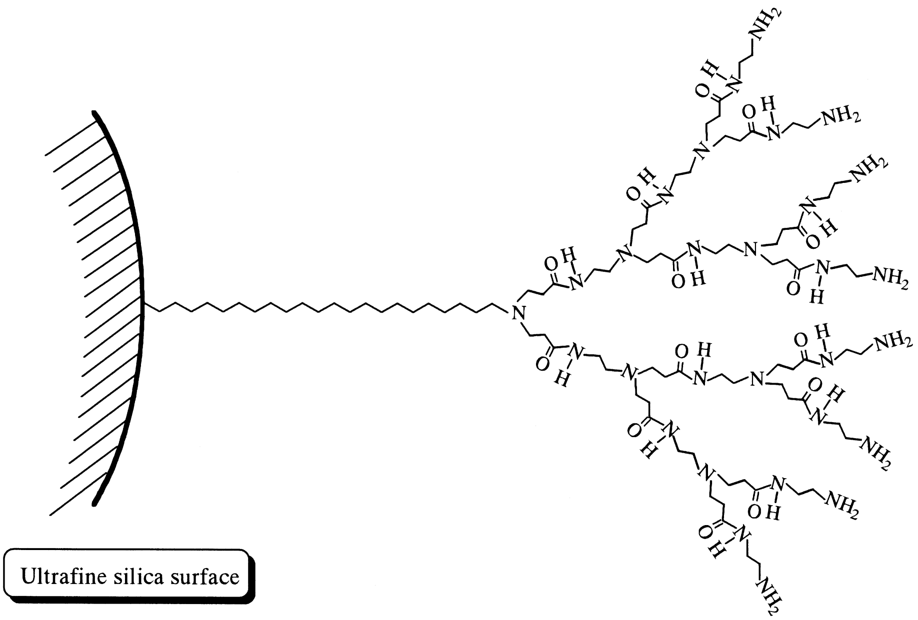


Figure 1. Sketching illustration of dendritic polyamidoamine-postgrafted silica.

Methyl acrylate (MA) obtained from Kanto Chemical Co., Inc., Japan was dried over sodium sulfate and distilled under reduced pressure before each usage. Ethylenediamine (EDA), hexamethylenediamine (HMDA), and methanol were obtained from Kanto Chemical Co., Inc. These were refluxed over sodium and distilled just before use.

3-Glycidoxypropyltrimethoxysilane (GPMS) (Kanto Chemical Co., Inc.) and 3-aminopropyltriethoxysilane (APES) (Kanto Chemical Co., Inc.) were used without further purification. Terminal diamine-type polyoxyethylene (POE) was kindly supplied by Sanyo Chemical Industries, Ltd., Japan. The number average molecular weight (Mn) was 1000 and 3000. They were dried *in vacuo* at 110°C for 48 hours before use.

Toluene and m-xylene obtained from Kanto Chemical Co., Inc. were washed with concentrated sulfuric acid, aqueous alkali and pure water, successively dried over calcium chloride, refluxed over sodium, and distilled before use. All other reagents were of the highest grade commercially available.

Grafting of POE Having Terminal Amino Groups onto Silica Surface

Introduction of Epoxy Groups onto Silica Surface by GPMS Treatment

The introduction of epoxy groups onto the silica surface was achieved by the treatment of surface silanol groups with GPMS. A typical example is as follows. Into a 300 mL flask, 5.0 g of silica and 150 mL of 5% toluene solution of GPMS were charged, and the mixture was refluxed for 8 hours under stirring with a magnetic stirrer. After the reaction, the mixture was centrifuged, and the precipitate was extracted with toluene for 24 hours using a Soxhlet apparatus. The resulting silica was dried *in vacuo* at room temperature and stored *in vacuo* at 110°C.

Grafting Reaction of POE with Epoxy Groups on Silica Surface

Grafting reaction of POE having terminal amino groups (NH2-(POE)) onto the silica surface, i.e., introduction of ‘initiator sites’ for propagation of dendrimer was achieved by the reaction of terminal amino groups with epoxy groups attached onto the surface. A typical example is as follows. Into a 300 mL flask, 5.0 g of silica having epoxy groups, 5.0 g of NH2-(POE), and 150 mL of m-xylene were charged, and the mixture was refluxed for 24 hours under stirring with a magnetic stirrer. After the reaction, the mixture was centrifuged, and the precipitate was extracted with m-xylene for 24 hours using a Soxhlet apparatus in order to remove ungrafted NH2-(POE). The resulting silica was dried and stored in vacuo at room temperature.

Postgrafting of Dendritic Polyamidoamine from Terminal Amino Groups of POE Grafted onto Silica Surface

Postgrafting reaction and propagation of dendritic polyamidoamine from the terminal amino groups of POE grafted onto the silica surface was achieved by repeating two processes: (1) Michael addition of MA to amino groups on the surface and (2) regeneration of terminal amino groups by amidation of resulting ester moieties of MA with EDA or HMDA. A typical example is as follows.

Michael Addition

Into a 100 mL flask that contained 0.50 g of NH2-(POE)-grafted silica, 20 mL of methanol and 0.20 mL of MA (1.3 equivalent to amino groups) were added. The flask was sealed under dry nitrogen, and the mixture was stirred (120 rpm) at 50°C. After 24 hours, the resulting silica was precipitated by centrifugation (1.5 × 104 rpm for 1 hour) and repeatedly washed with methanol to remove unreacted materials.

Regeneration of Terminal Amino Groups by Amidation

Into a 100 mL flask that contained the silica after Michael addition, 20 mL of methanol and 1.0 mL of EDA (large excesses to terminal ester moieties) were added. Subsequent procedures were similar to those of Michael addition.

The propagation for the second generation was carried out as follows. Into a 100 mL flask that contained the silica obtained after the above two processes, 20 mL of methanol and 0.40 mL of MA (twice the volume of the preceding reaction; 1.3 equivalent to theoretical amino groups) were added in Michael addition. Similarly, 20 mL of methanol and 2.0 mL of EDA (twice the volume of the preceding reaction; large excesses to terminal ester moieties) were added in amidation. These two reactions of Michael addition and amidation were repeated for the propagation of hyperbranched dendritic polyamidoamine from the terminal amino groups of POE grafted onto the silica surface.

Determination of Amino Group Content

The content of amino groups of the dendritic polyamidoamine-post-grafted silica was determined by consumption of HCl aqueous solution [20, 23]. Into a 100 mL flask, 0.10 g of polyamidoamine-postgrafted silica and 20 mL of 0.01 mol/L HCl aqueous solution were charged, and the mixture was stirred with a magnetic stirrer at room temperature for 2 hours. After the reaction, the mixture was filtrated, and the filtrate was back-titrated with aqueous solution of sodium hydroxide (0.01 mol/L) using phenolphthalein as an indicator. Then the amount of terminal amino groups per 1.0 g of pristine NH2-(POE)-grafted silica was calculated by the following equation:

Amino groups (mmol/g) = (HCl (mmol)/0.10) × {1 + (PG (%)/100)}, where HCl (mmol) is the number of moles of HCl consumed for the reaction with polyamidoamine-postgrafted silica, and PG (%) is the percentage of post-grafting value of polyamidoamine observed.

Determination of Percentage of Grafting

Percentage of grafting of POE having terminal amino groups onto the silica surface was determined by the following equation after Soxhlet extraction and drying in the grafting procedures:

$$\text{Grafting (\%)} = \frac{NH_2\text{-(POE) grafted (g)}}{\text{Silica charged (g)}} \times 100$$

The amount of NH_2-(POE) grafted onto the silica surface was determined by weight loss when NH_2-(POE)-grafted silica was heated at 500°C by use of a thermal analyzer (Shimadzu, Thermogravimetric Analyzer TGA-50).

In the case of the silica obtained from the postgrafting reaction of dendritic polyamidoamine, the polymer-grafted silica was dispersed in methanol, and the dispersion was allowed to centrifuge at 1.5×10^4 rpm. The silica precipitated was repeatedly washed by re-dispersing in methanol and centrifuging. The percentage of postgrafting and overall grafting were calculated by the following equations:

$$\text{Postgrafting (\%)} = \frac{\text{Polyamidoamine postgrafted (g)}}{NH_2\text{-(POE)-grafted silica charged (g)}} \times 100,$$

$$\text{Overall grafting (\%)} = \frac{\text{Total polymer grafted (g)}}{\text{Naked silica (g)}} \times 100.$$

The amount of polyamidoamine postgrafted and total polymer grafted onto the silica surface was determined by thermal analyzer as mentioned above.

Determination of Particle Size Distribution of Polyamidoamine-Postgrafted Silica

A prescribed amount of polyamidoamine-postgrafted silica was dispersed in 20 mL of methanol and was allowed to undergo supersonic wave at room temperature. After a definite time, particle size distribution and average particle size of dendritic polyamidoamine-postgrafted silica in methanol was measured by light scattering method using a Photal DLS 700 Light Scattering Spectrophotometer.

Infrared Analysis

The infrared spectra of polymer-grafted silicas were recorded on a Hitachi Infrared Spectrophotometer (Model 270-30) using KBr pellet.

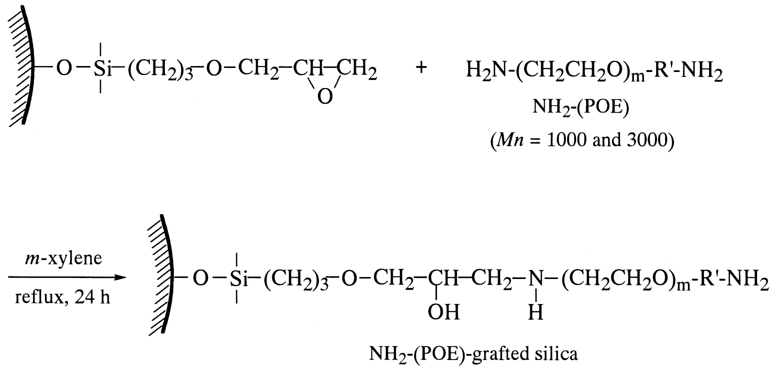
RESULTS AND DISCUSSION

Introduction of Amino Groups to Silica by Grafting of NH_2-(POE)

The introduction of terminal amino groups to silica, i.e., preparation of initiator sites for propagation of dendritic polyamidoamine was achieved by the grafting reaction of NH_2-(POE) with epoxy groups previously introduced onto silica surface (Scheme 1).

Figure 2 shows the IR spectra of untreated silica and NH_2-(POE) (Mn = 1000)-grafted silica. In the IR spectrum of NH_2-(POE)-grafted silica, new absorptions at 2990 cm^{-1} (methylene group) and 1640 cm^{-1} (amino group), which are characteristic of POE having terminal amino groups, were observed. This result reveals that terminal amino groups were introduced to the silica by the grafting of NH_2-(POE) onto the surface.

The amount of terminal amino groups introduced to silica, namely, the percentage of NH_2-(POE) grafting value could be controlled by a concentration of GPMS and NH_2-(POE) in the treatment of the silica. In this study, Mn of NH_2-(POE) used for the grafting reaction was of 1000 and 3000. As a result, silicas containing 0.40 mmol/g and 0.90 mmol/g (Mn = 1000), and 0.012 mmol/g (Mn = 3000) of terminal amino groups as initiator sites were prepared for the postgrafting reaction of polyamidoamine, and their percentages of NH_2-(POE) grafting were 9.8%, 23.2%, and 3.6%, respectively as shown in Table 1.



Scheme 1.

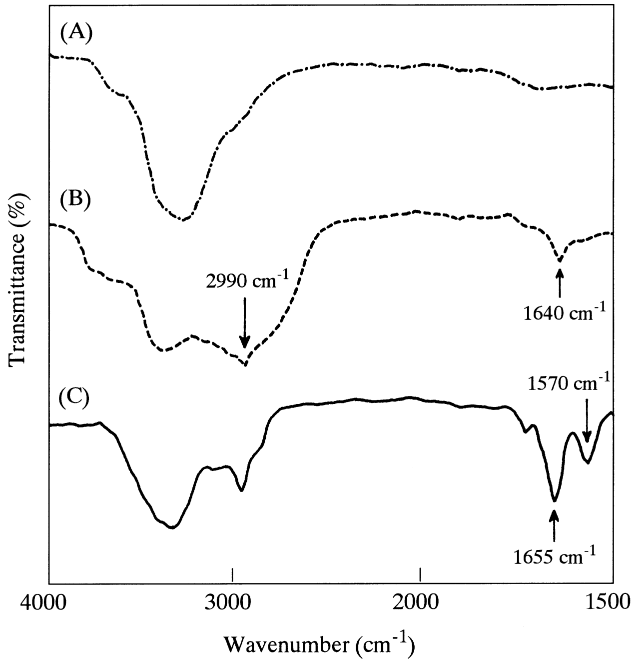


Figure 2. IR spectra of (A) untreated, (B) NH_2-(POE)-grafted, and (C) polyamidoamine (of 8th generation)-postgrafted silica. NH_2-(POE): *Mn* = 1000; grafting = 9.8%; terminal amino groups = 0.40 mmol/g. Polyamidoamine of 8th generation: postgrafting = 9.4%; overall grafting = 20.1%.

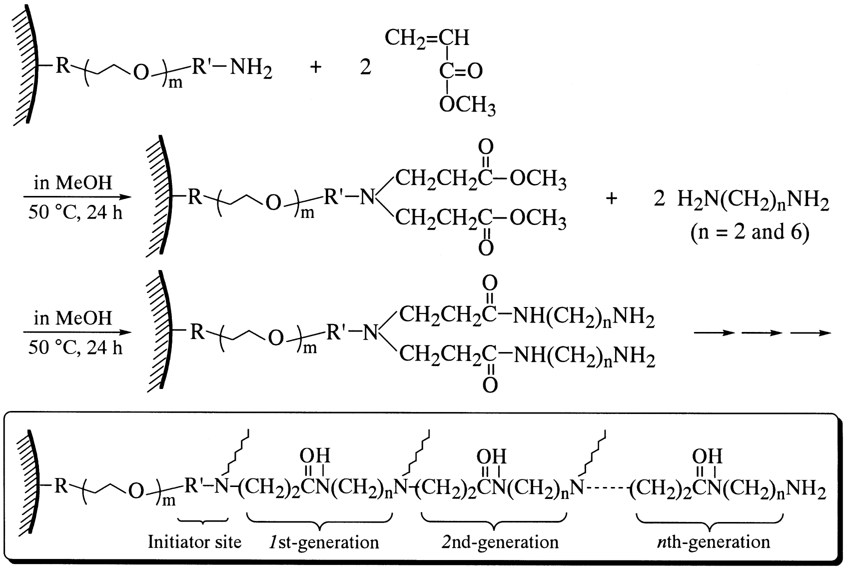
TABLE 1. The Amount of Terminal Amino Groups and the Percentage of Grafting of NH_2-(POE)

Mn of NH_2-(POE)	Terminal amino groups (mmol/g)	Grafting (%)
1000	0.40	9.8
1000	0.90	23.2
3000	0.012	3.6

Postgrafting of Dendritic Polyamidoamine from Terminal Amino Groups of POE Grafted onto Silica Surface

As mentioned above, it was reported that polyamidoamine dendrimer was synthesized by the divergent method, by repeating the following two processes [17]: (1) Michael addition of MA to amino groups of initiator sites and (2) regeneration of amino groups by amidation of resulting ester moieties with an alkylenediamine. Therefore, it is expected that the postgrafting of dendritic polyamidoamine is initiated from terminal amino groups of POE grafted onto silica surface as shown in Scheme 2. The treatment of NH_2-(POE)-grafted silica with MA and an alkylenediamine was repeated *n* times to obtain dendritic polyamidoamine (of *n*th generation)-postgrafted silica.

Table 2 shows the amino group content of silica after the postgrafting reaction of polyamidoamine by use of various silicas. In this system HMDA as an alkylenediamine was used for amidation. Untreated and GPMS-treated silicas had no ability to propagate polyamidoamine from the surface because they had no amino groups even after the 12th generation. On the contrary, when NH_2-(POE)-grafted silica having 0.40 mmol/g of terminal amino groups was used as initiator sites, the amount of amino groups of the silica increased with an increase in the number of generations. These results suggest that dendritic



Scheme 2.

TABLE 2. The Amount of Amino Groups of Silica after Postgrafting Reaction of Polyamidoamine by Using HMDA as an Alkylenediamine

Silica	Generation	Amino groups (mmol/g)	
		Observed	Theoretical [b]
Untreated	12th	0	0
GPMS-treated	12th	0	0
NH_2-(POE)-grafted [a]	4th	0.41	6.4
	6th	0.45	25.6
	8th	0.61	102.4
	10th	1.53	409.6
	12th	2.20	1638.4

a) NH_2-(POE) : *Mn* = 1000; grafting = 9.8%; terminal amino groups as initiator sites = 0.40 mmol/g.

b) Theoretical (mmol/g) = 0.40×2^n [n: number of generation].

polyamidoamine propagates from the terminal amino groups of POE grafted onto the silica surface. The amount of amino groups of every generation, however, was considerably smaller than that of each theoretical value. The theoretical value of amino group content was calculated from the amount of initial amino groups on the silica surface on the assumption that Michael addition and amidation proceeded completely.

Table 3 also shows the results of the amino group content of silica by using NH_2-(POE)-grafted silica having 0.90 mmol/g of terminal amino groups and HMDA as a reactant in amidation. The amount of amino groups of the resulting silica also increased with an increase in the number of generations, but it was much smaller than theoretical value of each generation similar to the case of the silica having 0.40 mmol/g of terminal amino groups.

These results indicate that the propagation of polyamidoamine dendrimer from the terminal amino groups of POE grafted onto the silica surface does not progress perfectly and therefore, the resulting polyamidoamine is hyperbranched dendritic but not precise dendrimer. We have only met with partial success in constructing coupled polymer of dendrimer with linear polymer. For this reason, we consider that both the reaction of Michael addition and ami-

TABLE 3. The Amount of Amino Groups of Polyamidoamine-Postgrafted Silica by Using HMDA as an Alkylenediamine[a)]

Generation	Amino groups (mmol/g)	
	Observed	Theoretical [b)]
4th	1.15	14.4
6th	1.48	57.6
8th	2.00	230.4
10th	2.95	921.6
12th	4.05	3686.4

a) NH_2-(POE) : *Mn* = 1000; grafting = 23.2%; terminal amino groups as initiator sites = 0.90 mmol/g.

b) Theoretical (mmol/g) = 0.90×2^n [n: number of generation].

dation do not proceed completely because of heterogeneous reaction system and steric hindrance of the grafted polymer chains.

Table 4 shows the percentage of polyamidoamine grafting to silica surface when NH_2-(POE)-grafted silicas having 0.40 mmol/g and 0.90 mmol/g of terminal amino groups were used as initiator sites. The percentages of postgrafting and overall grafting to silica surface increased with an increase in the number of generations as expected from the results of the amino group content. The IR spectra of the silica after the postgrafting reaction of 8th generation initiated from 0.40 mmol/g of terminal amino groups was also shown in Figure 2. Absorptions at 1570 cm^{-1} and 1655 cm^{-1}, which are characteristic of amide group were newly observed.

From the above results, it is concluded that hyperbranched polyamidoamine was postgrafted from terminal amino groups of POE grafted onto the silica surface by repeating treatment with MA and HMDA.

Effect of Alkylenediamine for Amidation on the Postgrafting Reaction

Table 5 shows the percentage of polyamidoamine grafting to silica surface obtained by using NH_2-(POE)-grafted silica having 0.40 mmol/g of terminal amino groups and EDA as an alkylenediamine in amidation. In comparison

TABLE 4. Percentage of Polyamidoamine Grafting to Silica by Using HMDA as an Alkylenediamine

Terminal amino groups (mmol/g)	Generation	Postgrafting (%)	Overall grafting (%)
0.40 a)	4th	1.3	11.2
	6th	3.8	14.0
	8th	9.4	20.1
	10th	27.3	39.8
	12th	36.8	50.2
0.90 b)	4th	6.8	31.6
	6th	19.7	47.5
	8th	37.9	69.9
	10th	61.9	99.5
	12th	77.5	118.7

Grafting of NH_2-(POE) (*Mn* = 1000) : a) = 9.8%; b) = 23.2%.

TABLE 5. Percentage of Polyamidoamine Grafting to Silica by Using EDA as an Alkylenediamine

Generation	Postgrafting (%)	Overall grafting (%)
4th	4.9	15.2
6th	11.7	22.7
8th	24.1	36.3
10th	43.0	57.7
12th	61.0	77.0

NH_2-(POE) : *Mn* = 1000; grafting = 9.8%; terminal amino groups as initiator sites = 0.40 mmol/g.

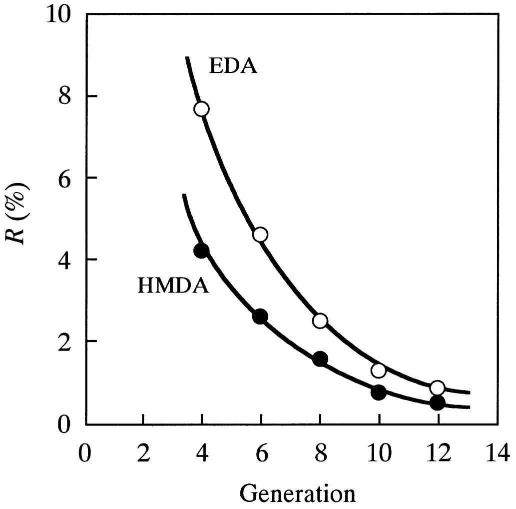


Figure 3. Effect of alkylenediamine on the postgrafting of polyamidoamine to NH_2-(POE)-grafted silica. *R* (%) = (Postgrafting observed/Theoretical postgrafting) × 100. Theoretical postgrafting = A × 10^{-3} × MW × 100 [A: terminal amino group content as initiator sites (mmol/g). MW: molecular weight of precise polyamidoamine dendrimer at each generation]. NH_2-(POE): *Mn* = 1000; grafting = 9.8%; terminal amino groups as initiator sites = 0.40 mmol/g.

with the results of HMDA shown in Table 4, the percentage of postgrafting in EDA system was higher than that in HMDA system at the same generation.

Figure 3 shows the effect of alkylenediamine (EDA and HMDA) on the postgrafting of polyamidoamine. In this Figure, R is the proportion of grafting value obtained from the experiment to theoretical grafting value. The theoretical grafting value at each generation was calculated from the content of amino groups used as initiator sites (0.40 mmol/g) and the molecular weight of grafted polyamidoamine supposing that precise polyamidoamine dendrimer was synthesized. R decreased with an increase in the number of generations in both EDA and HMDA systems. Furthermore, R for EDA was higher than that for HMDA.

These indicate that EDA is more effective than HMDA for the propagation of dendritic polyamidoamine. Because C-C chain length of EDA is shorter than that of HMDA, EDA may be favorable for contribution to lowering of steric hindrance in the propagation of dendritic polyamidoamine initiated from terminal amino groups introduced by the grafting of NH_2-(POE) (Mn = 1000).

Effect of Terminal Amino Group Content as Initiator Sites on the Postgrafting Reaction

The effect of terminal amino group content on the postgrafting of polyamidoamine was examined. Figure 4 shows the results obtained by using HMDA as an alkylenediamine. *R* for NH_2-(POE)-grafted silica having 0.40 mmol/g of terminal amino groups was higher than that having 0.90 mmol/g of terminal amino groups. This indicates that for the propagation of dendritic polyamidoamine from terminal amino groups introduced by the grafting of NH_2-(POE), low density of initial amino groups is more effective than high density of them because of steric hindrance in the propagating reaction of dendritic polyamidoamine. A similar tendency was observed in the grafting reaction initiated from surface amino groups attached by the treatment of the silica with silane coupling agent, 3-aminopropyltriethoxysilane [20].

The amino group content and the percentage of polyamidoamine grafting value by using NH_2-(POE) (Mn = 3000)-grafted silica having 0.012 mmol/g of terminal amino groups were shown in Tables 6 and 7, respectively. Every amount of amino groups of the resulting silica was also smaller than theoretical value of each generation, but the degree of decrease against the theoretical value

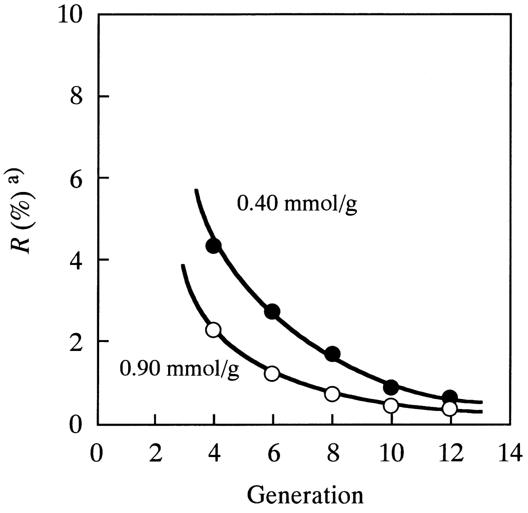


Figure 4. Effect of terminal amino group content on the postgrafting of polyamidoamine to NH_2-(POE)-grafted silica. HMDA was used as an alkylenediamine. NH_2-(POE): Mn = 1000; grafting = 9.8% (0.40 mmol/g) and 23.2% (0.90 mmol/g). a) Description of *R* is given in Figure 3.

TABLE 6. The Amount of Amino Groups of Polyamidoamine-Postgrafted Silica[a)]

Diamine	Generation	Amino groups (mmol/g)	
		Observed	Theoretical [b)]
EDA	4th	0.12	0.192
	8th	0.58	3.072
	12th	3.22	49.152
HMDA	4th	0.046	0.192
	8th	0.452	3.072
	12th	0.597	49.152

a) NH_2-(POE) : *Mn* = 3000; grafting = 3.6%; terminal amino groups as initiator sites = 0.012 mmol/g.

b) Theoretical (mmol/g) = 0.012×2^n [n: number of generation].

TABLE 7. Percentage of Polyamidoamine Grafting to Silica Initiator Sites = 0.012 mmol/g

Diamine	Generation	Postgrafting (%)	Overall grafting (%)
EDA	4th	2.4	9.8
	8th	11.9	20.0
	12th	49.2	63.8
HMDA	4th	1.5	8.8
	8th	13.5	21.7
	12th	17.3	25.7

NH_2-(POE) : *Mn* = 3000; grafting = 3.6%; terminal amino groups as initiator sites = 0.012 mmol/g.

was lower than that observed in NH_2-(POE) (Mn = 1000)-grafted silicas having 0.40 mmol/g and 0.90 mmol/g of terminal amino groups. Therefore, the highest value of R (from the minimum of 2% to the maximum of 28%) was obtained in this reaction system even if Mn of NH_2-(POE) did not agree with the results in 0.40 mmol/g and 0.90 mmol/g of terminal amino group system.

Furthermore, EDA was found to be more effective than HMDA as a reactant suitable for propagation of dendritic polyamidoamine as well as the results in NH_2-(POE) (Mn = 1000)-grafted silica having 0.40 mmol/g of terminal amino groups.

Effect of Space between Terminal Amino Groups and Silica Surface on the Grafting of Polyamidoamine

Figure 5 shows the effect of space between terminal amino groups as initiator sites and the silica surface on the grafting of dendritic polyamidoamine by using silicas having 0.40 mmol/g of amino groups in MA/EDA system. The silica having short spacer was prepared by the treatment of the silica with APES in

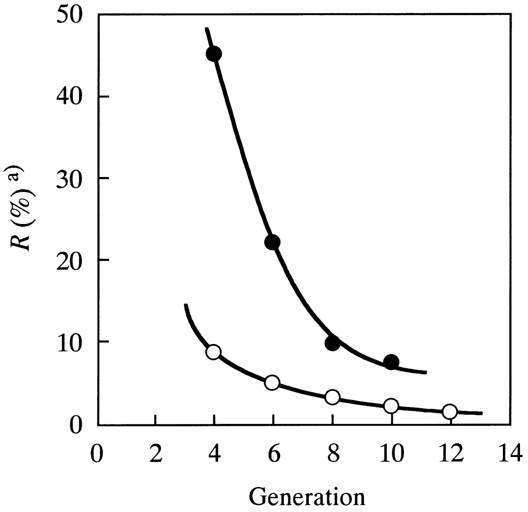


Figure 5. Effect of space between terminal amino groups as initiator sites and the silica surface on the grafting of polyamidoamine. EDA was used as an alkylenediamine. (●), APES-treated silica; surface amino groups as initiator sites = 0.40 mmol/g; (○), NH_2-(POE) (*Mn* = 1000)-grafted silica; terminal amino groups as initiator sites = 0.40 mmol/g. a) Description of *R* is given in Figure 3.

a manner similar to the GPMS treatment, and NH_2-(POE) (Mn = 1000)-grafted silica was used as silica having long spacer.

In contrast to our expectation, R for the silica having short spacer was larger than that having long spacer. This implies that the postgrafting reaction of dendritic polyamidoamine was interfered with POE chains grafted onto the silica surface. We estimate that the propagating reaction of dendritic polyamidoamine has a certain relationship between amino group content as initiator sites and space from the silica surface to the amino groups. The difference of solubility into the reaction system between APES-treated and NH_2-(POE)-grafted silicas also may influence the value of R. The optimum amount of terminal amino groups as initiator sites and the effect of Mn of NH_2-(POE) for the propagation of dendritic polyamidoamine are now under detailed investigation.

Particle Size Distribution of Dendritic Polyamidoamine-Postgrafted Silica

Particle size distribution of dendritic polyamidoamine-postgrafted silica by light scattering photometry was compared with that of untreated silica in methanol. The particle size of untreated silica was distributed from about 80 nm to 220 nm because of aggregation. On the other hand, dendritic polyamidoamine-postgrafted silica at 8th generation obtained by MA/EDA system shifted its particle size distribution to the range of about 160 nm to 660 nm.

Moreover, Figure 6 shows the relationship between the number of generations and average particle size of dendritic polyamidoamine-postgrafted silica. It became apparent that the average particle size increased with an increase in the number of generations.

These results also indicate that dendritic polyamidoamine was propagated from terminal amino groups of POE grafted onto the silica surface.

CONCLUSION

The postgrafting reaction of hyperbranched dendritic polyamidoamine was achieved from the terminal amino groups of POE grafted onto the silica surface by repeating two processes: (1) Michael addition of MA to amino groups on the surface and (2) regeneration of terminal amino groups by amidation of resulting ester moieties of MA with EDA or HMDA.

The percentage of postgrafting of polyamidoamine increased with an increase in the number of generations but was much smaller than the theoretical

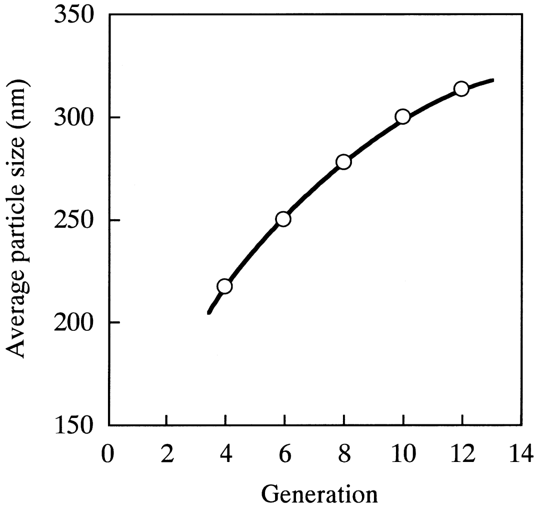


Figure 6. Relationship between the number of generations and average particle size of polyamidoamine-postgrafted silica in MeOH. EDA and NH_2-(POE) (*Mn* = 1000)-grafted silica having 0.40 mmol/g of terminal amino groups were used as an alkylenediamine and initiator sites, respectively.

value. This reveals that the resulting postgrafted polyamidoamine is hyperbranched dendritic polymer but not accurate dendrimer. The reason for this may be that both the reaction of Michael addition and amidation proceed incompletely because of heterogeneous reaction system and steric hindrance of the grafted polymer chains.

For the propagation of dendritic polyamidoamine from terminal amino groups of NH_2-(POE)-grafted silica, low density of initial amino groups was more effective than high density of them. EDA was found to be more suitable than HMDA as an alkylenediamine in amidation.

The average particle size of dendritic polyamidoamine-postgrafted silica measured by light scattering method increased with an increase in the number of generations.

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