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Surface grafting of polymers onto ultrafine silica: Cationic polymerization initiated by oxoaminium perchlorate groups introduced onto ultrafine silica surface

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Summary

The cationic polymerization initiated by oxoaminium perchlorate groups introduced onto ultrafine silica surface was investigated. The oxoaminium perchlorate groups were successfully introduced by treatment of nitroxyl radicals on silica surface with perchloric acid. The introduction of the nitroxyl radicals was achieved by reaction of 4–hydroxy–2,2,6,6–tetramethyl–piperidinyloxy radical with acid anhydride groups on the surface. The cationic polymerization of isobutyl vinyl ether, *N*–vinylcarbazole, 2,3–dihydrofuran, and γ–butyrolactone was initiated by oxoaminium perchlorate groups introduced onto the surface and the corresponding polymers were grafted onto the surface through the propagation of grafted polymer chain from the surface oxoaminium perchlorate groups.

Introduction

The modification of the powder surface by the grafting of polymers is known to be one of the effective procedures for the improvement of the adhesion of powder surface with matrix polymer in a high performance polymer–powder composite (1–3).

We have reported the grafting of various polymers onto ultrafine silica surface by the polymerization initiated by surface initiating groups such as azo (4), peroxyester (5), potassium carboxylate (6), and acylium perchlorate groups (7). In these polymerizations, polymer–grafted silicas with high percentage of grafting were readily obtained, because grafted polymer chain propagated from the surface initiating groups.

Recently, we have reported that oxoaminium salts, which can be prepared by the disproportionation reaction of stable nitroxyl radicals with perchloric acid, have an ability to initiate cationic polymerization of vinyl monomers (8). Although the polymerization of isobutyl vinyl ether (IBVE) can not proceed by oxoaminium salts having stronger nucleophilic counter anion such as Cl^- and NO_3^-, the polymerization was readily initiated with them

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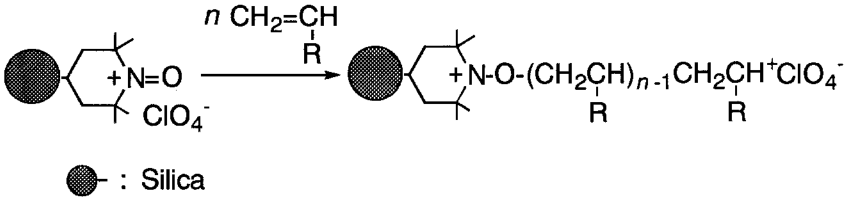
carrying weaker nucleophilic anion (ClO_4^- and SbF_6^-) to give poly(isobutyl vinyl ether) (PIBVE) in a good yield.

In the present paper, the introduction of oxoaminium perchlorate groups onto ultrafine silica surface and the cationic graft polymerization of several monomers initiated by the surface oxoaminium perchlorate groups are described (Eq. 1).



(1)

Experimental

Materials

Ultrafine silica used was Aerosil 200 (Nippon Aerosil Co., Japan). The BET specific surface area, particle size, and content of silanol group were 200 m^2/g, 16 nm, and 1.37 mmol/g, respectively. The content of silanol group was determined by measuring volumetrically the amount of ethane evolved by the reaction with triethylaluminum (9). The silica was washed with distilled water and dried *in vacuo* at 110°C before use.

4-Trimethoxysilyl-1,2,5,6-tetrahydrophthalic anhydride (TSPA) obtained from Nissan Chemical Ind. Ltd., Japan, was used without further purification. 4-Hydroxy-2,2,6,6-tetramethylpiperidinyloxy radical (4-Hydroxy TEMPO) obtained from Aldrich Chemical Co. was used without further purification. Perchloric acid (60% aqueous solution) and *N,N'*-dicyclohexylcarbodiimide (DCC) obtained from Kanto Chemical Co Ltd., Japan were also used without further purification.

Isobutyl vinyl ether (IBVE) and 2,3-dihydrofuran (DHF) were refluxed over sodium, and distilled before use. *N*-Vinylcarbazole (NVC) was recrystallized from *n*-hexane. γ-Butyrolactone (γ-BL) was dried over calcium hydride and distilled twice under reduced pressure.

Dichloromethane, benzene, toluene, tetrahydrofuran (THF), and ethyl ether were used after ordinary purification.

Introduction of Nitroxyl Radicals onto Silica Surface

The introduction of nitroxyl radicals onto silica surface was carried out by the reaction of 4-hydroxy TEMPO with silica surface carrying acid anhydride moieties using DCC as a catalyst.

The acid anhydride groups were introduced by the reaction of silanol groups on silica surface with TSPA in toluene. The procedures were described in detail in the previous paper (5,6).

The reaction of acid anhydride groups with 4-hydroxy TEMPO was carried out as follows. Into a 100 cm^3 flask containing 2.0 g of ultrafine silica having acid anhydride groups, 0.30 g of 4-hydroxy TEMPO, 0.30 g of DCC, and 30.0 cm^3 of toluene were added and the reaction mixture was stirred with a magnetic stirrer under nitrogen at 70°C. After the reaction for 8 h, the resulting silica was washed with methanol repeatedly and dried at 110°C *in vacuo.*

Introduction of Oxoaminium Perchlorate Groups onto Silica Surface

The introduction of oxoaminium perchlorate groups onto the silica surface was achieved by the treatment of surface nitroxyl radicals with perchloric acid (8). A typical example was as follows. Into a 100 cm^3 flask, 1.0 g of silica having nitroxyl radicals, 0.02 cm^3 of perchloric acid, and 20.0 cm^3 of ethyl ether were charged. The mixture was stirred with a magnetic stirrer for 1 h at 10°C. After the reaction, the mixture was filtered, washed with THF repeatedly, and dried at 110°C *in vacuo.* The silica having oxoaminium perchlorate groups was stored in a vacuum desiccator at room temperature.

Polymerization Procedures

Into a 100 cm^3 flask, 0.30 g of silica having oxoaminium perchlorate groups, 5.0 cm^3 of monomer, and 5.0 cm^3 of dichloromethane were charged under nitrogen. The mixture was stirred with a magnetic stirrer at 10°C. After the polymerization, the reaction mixture was poured into a large excess of methanol to precipitate polymer and silica. Then ungrafted monomer and solvent were pumped off at 40–60°C. In the case of NVC polymerization, 1.0 g of monomer and 5.0 cm^3 of benzene were used for the polymerization. After the polymerization, the reaction mixture was poured into a large excess of methanol and precipitate was filtered, dried *in vacuo*, and weighed.

The conversion was calculated by the following equation.

$$\text{Conversion (\%)} = \frac{\text{Obtained precipitate (g)} - \text{silica used (g)}}{\text{Silica used (g)}} \times 100$$

Percentage of Grafting and Grafting Efficiency

To separate the polymer–grafted silica from the ungrafted polymer, the product was dispersed in toluene and the dispersion was centrifuged at 1.0×10^4 rpm until the silica precipitated completely. The silica precipitated, *i.e.*, polymer–grafted silica, was allowed to extraction with toluene using a Soxhlet apparatus until no more polymer could be detected in the refluxing solvent. The percentage of grafting and grafting efficiency were calculated by the following equations. The quantity of grafted polymer was estimated from the weight of silica after the polymerization minus that before polymerization.

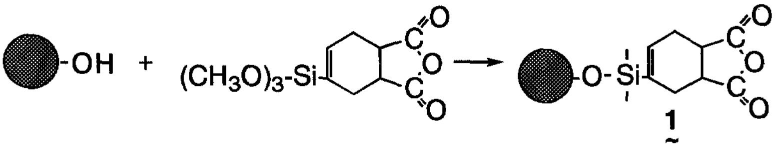
$$\text{Grafting (\%)} = \frac{\text{Polymer grafted (g)}}{\text{Silica charged (g)}} \times 100$$

$$\text{Grafting efficiency (\%)} = \frac{\text{Polymer grafted (g)}}{\text{Total polymer formed (g)}} \times 100$$

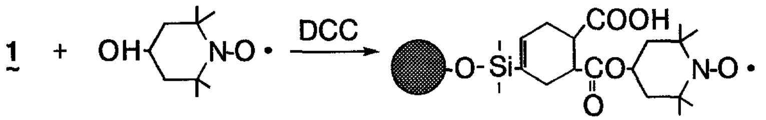
Results and Discussion

Introduction of Nitroxyl Radicals onto Silica Surface

The introduction of nitroxyl radicals onto silica surface was carried out by the reaction of 4-hydroxy TEMPO with silica having acid anhydride groups (Eq. 3), which were introduced by the treatment of silanol group with TSPA (Eq. 2), in the presence of DCC.



(2)



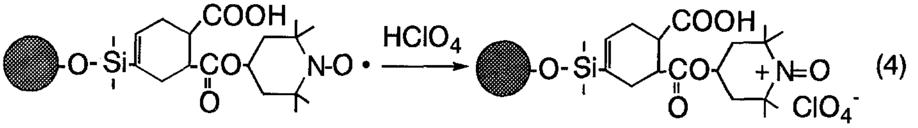
(3)

Figure 1 shows an ESR spectrum of the silica obtained from the above treatment. It is suggested that nitroxyl radicals were successfully introduced onto the silica surface. The amount of nitroxyl radicals introduced onto the surface was determined to be 0.20 mmol/g by elemental analysis. This indicates that only 20% of acid anhydride groups on the surface reacted with 4-hydroxy TEMPO, because the acid anhydride group content of silica surface was 0.96 mmol/g.

Introduction of Oxoaminium Perchlorate Groups onto Silica Surface

It is well known that nitroxyl radical, a stable radical, can be readily converted to oxoaminium salt by one electron oxidation and to hydroxyl amine by one electron reduction (10,11).

Figure 1 ESR spectrum of silica having nitroxyl radicals.


(4)

Therefore, the introduction of oxoaminium perchlorate groups was carried out by the disproportionation reaction of nitroxyl radicals with perchloric acid (Eq. 4). The amount of oxoaminium perchlorate groups was determined to be 0.18 mmol/g by elemental analysis. This indicates that the disproportionation reaction proceeds almost quantitatively.

Cationic Polymerization of IBVE Initiated by Oxoaminium Perchlorate Groups on Silica Surface

The polymerization of IBVE was carried out in the absence and in the presence of silica having nitroxyl radical and oxoaminium perchlorate groups. The results are shown in Table 1. As shown in Table 1, no polymerization of IBVE was initiated in the presence of silica having nitroxyl radical and untreated silica. On the contrary, the polymerization could be readily initiated by silica having oxoaminium perchlorate groups to graft PIBVE onto the surface.

To evaluate the effect of perchloric acid adsorbed on the silica surface during the introduction reaction of oxoaminium perchlorate groups, the initiating activity of perchloric acid-treated silica, which was prepared by the treatment of untreated silica with perchloric acid followed by washing with THF after the treatment, was compared with that of untreated silica. The result is also shown in Table 1. Table 1 clearly shows that perchloric acid-treated silica has no ability to initiate the polymerization of IBVE. Therefore, it is unnecessary to take into account the initiation by adsorbed perchloric acid on the silica surface during the introduction reaction.

Table 1 Cationic graft polymerization of IBVE in the presence of various treated silicas[a]

Functional group	Conversion (%)	Grafting (%)
None[b]	trace	-
Silanol[c]	trace	0
Nitroxyl radical	0	0
$HClO_4$-treated	trace	0
Oxoaminium salt	35.0	22.5

[a] Silica, 0.30 g; IBVE, 5.0 cm^3; CH_2Cl_2, 5.0 cm^3; 10°C; 24h.
[b] In the absence of silica. [c] Untreated silica.

Proof of Grafting onto Silica Surface

Figure 2 shows the time–conversion and time–grafting curves in the polymerization of IBVE initiated by oxoaminium perchlorate groups on silica surface. The conversion and percentage of grafted PIBVE increased with progress of the polymerization, but no longer increased after 15 h. This indicates that the surface oxoaminium perchlorate groups are blocked by grafted polymer chains.

Figure 3 shows the relationship between polymerization time and grafting efficiency. As shown in Figure 3, the grafting efficiency was relatively high at the initial stage of the polymerization, but decreased with the progress of the polymerization.

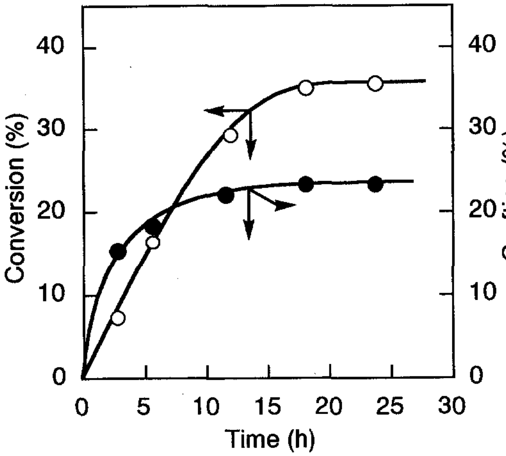


Figure 2 Cationic polymerization of IBVE initiated by silica having oxoaminium perchlorate groups. Polymerization conditions were given in Table 1.

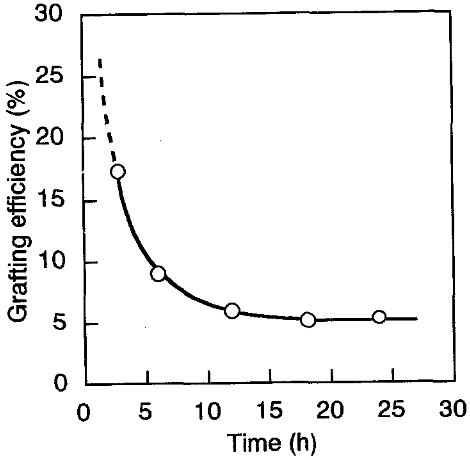


Figure 3 Relationship between polymerization time and grafting efficiency in the cationic graft polymerization shown in Figure 2.

Table 2 Cationic graft polymerization of some monomers initiated by oxoaminium perchlorate groups on silica[a]

Monomer	Time (h)	Conversion (%)	Grafting (%)
NVC	2	100	19.5
DHF	2	100	25.0
γ-BL	24	14.5	15.0

[a] Silica, 0.30 g; monomer, 5.0 cm^3; 10°C.

These results might indicate that although the polymerization started from surface oxoaminium perchlorate groups, ungrafted polymer was preferentially formed by chain transfer reaction of growing polymer cation with progress of the polymerization.

Based on the above results, it may be concluded that oxoaminium perchlorate groups introduced onto silica surface have an ability to initiate the cationic polymerization of IBVE to graft PIBVE onto silica surface through the propagation of the polymer chain from the surface.

Cationic Graft Polymerization of Several Monomers Initiated by Oxoaminium Perchlorate Groups on Silica Surface

The cationic graft polymerization of *N*-vinylcarbazole (NVC), 2,3-dihydrofuran (DHF), and γ-butyrolactone (γ-BL) initiated by oxoaminium perchlorate groups introduced onto silica surface was investigated. The results are shown in Table 2. It was found that the cationic polymerizations of NVC, DHF, and γ-BL could be successfully initiated by oxoaminium perchlorate groups on silica surface to give the corresponding polymer-grafted silica: the structure of polymers obtained from the graft polymerization was identified as the corresponding polymer by infrared spectra.

Conclusions

1. The introduction of oxoaminium perchlorate groups were successfully achieved by the reaction of perchloric acid with nitroxyl radicals on silica surface, which were introduced by the reaction of surface acid anhydride groups with 4-hydroxy TEMPO.
2. The oxoaminium perchlorate groups on silica surface have ability to initiate the cationic polymerization of IBVE, NVC, DHF, and γ-BL.
3. In the cationic polymerizations, the corresponding polymers were grafted onto the silica surface through the propagation of polymer chain from the surface oxoaminium perchlorate groups.

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