Polymer Bulletin 31, 457–464 (1993)

Polymer Bulletin

Effect of initiating groups introduced onto ultrafine silica on the molecular weight polystyrene grafted onto the surface

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Summary

The effect of initiating groups introduced onto silica surface on the molecular weight of grafted polystyrene chain was investigated. By the treatment of polystyrene–grafted silica with aqueous solution of alkali, surface grafted polystyrene was isolated from the surface. The molecular weight of polystyrene grafted onto the silica obtained from the radical graft polymerization initiated by peroxyester groups introduced onto the surface was found to be much larger than that from the cationic polymerization initiated by acylium perchlorate groups. The number of grafted polystyrene in the radical polymerization, however, was much less than that in the cationic polymerization. Furthermore, the effect of molecular weight of grafted polystyrene on the dispersibility of silica in tetrahydrofuran was examined.

Introduction

In a series of our papers, we reported the graft polymerization of vinyl polymers initiated by initiating groups introduced onto ultrafine silica surface (1–5). For instance, peroxyester (1), peroxide (2), and azo groups (3) introduced onto silica surface initiate the radical polymerization of vinyl monomers and the vinyl polymer was effectively grafted onto the silica surface. In addition, acylium perchlorate groups are successfully introduced onto silica surface and the cationic polymerizations of vinyl monomers, cyclic ethers, lactones, and cyclic acetals are initiated by the acylium perchlorate groups to give the corresponding polymer–grafted silica (4).

During the above graft polymerization, polymer–grafted silica with a high percentage of grafting was obtained, because the polymer propagates from the surface radical or acylium cation. Even if almost equal amount of polymer was grafted onto silica in the radical and cationic polymerization, the molecular weight and number of grafted polymer chain on the surface was expected to be affected by the initiating groups on the surface.

In the present paper, the effects of initiating groups, such as peroxyester and acylium perchlorate, introduced onto silica surface (Eqs. 1 and 2) on the

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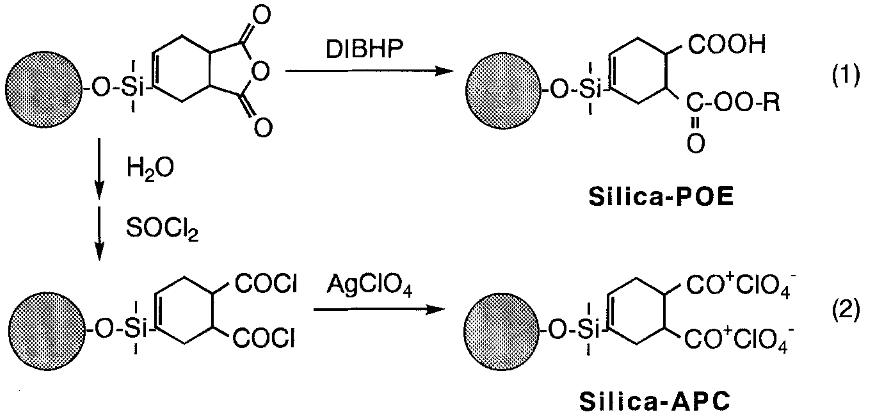


molecular weight and number of grafted polystyrene chain on the surface were investigated. Furthermore, the effect of molecular weight of grafted polystyrene on the stability of polystyrene-grafted silica dispersion in organic solvent was examined.

Experimental

Materials

Ultrafine silica used was Aerosil 200 (Nippon Aerosil Co., Japan). The BET specific surface area, particle size, and silanol group content were 200 m^2/g, 16 nm, and 1.37 mmol/g, respectively. Silanol group content was determined by measuring volumetrically the amount of ethane evolved by the reaction with triethylaluminum (6). The silica was washed with distilled water and dried *in vacuo* at 110°Cbefore use.

4-Trimethoxysilyl-1,2,5,6-tetrahydrophthalic anhydride (TSPA) obtained from Nissan Chemical Ind. Ltd., Japan, was used without further purification. α,α-Dimethyl(4-isopropylbenzyl) hydroperoxide (DIBHP) was obtained from Nippon Oil and Fats Co., Ltd., Japan, and used without further purification.

Styrene was washed with aqueous alkali, dried over barium oxide, and distilled twice under reduced pressure. Guaranteed reagent-grade silver perchlorate obtained from Kojima Chemical Co., Ltd., Japan, was dried *in vacuo* at 120°C before use. Tetrahydrofuran (THF) was refluxed over sodium and distilled. All other solvents and reagents were used after ordinary purification.

Introduction of Acid Anhydride Groups onto Silica Surface

The introduction of acid anhydride groups onto silica surface was achieved by the reaction of silanol groups on silica with TSPA. The procedures were described in detail in the preceding paper (1,4,5). The amount of acid anhydride groups introduced onto the surface was determined by elemental analysis.

Introduction of Peroxyester Groups onto Silica Surface

The introduction of peroxyester groups onto silica surface was carried out by the reaction of surface acid anhydride groups with DIBHP. The procedures were described in detail in the preceding paper (1). The resulting silica was stored *in vacuo* in a refrigerator. The amount of peroxyester groups introduced onto the surface was determined by titration (iodometry) according to the method of literatures (7,8).

Introduction of Acylium Perchlorate Groups onto Silica Surface

The introduction of acylium perchlorate groups onto silica surface was achieved by the reaction of acyl chloride groups on the surface with silver perchlorate in nitrobenzene at room temperature. The introduction of acyl chloride groups was carried out by the treatment of surface carboxyl groups with thionyl chloride. The detailed procedures were described in the preceding paper (4). The amount of acylium perchlorate groups on silica surface was determined by titration (4,9).

Graft Polymerization

The radical graft polymerization of styrene initiated by peroxyester groups introduced onto silica surface was carried out in a sealed tube with shaking. The cationic graft polymerization initiated by acylium perchlorate groups on the surface was conducted in a flask under dry nitrogen. The reaction mixture was stirred with a magnetic stirrer.

After a prescribed polymerization time, the contents of the sealed tube and the flask were poured into an excess of methanol to precipitate ungrafted polystyrene and polystyrene–grafted silica.

Percentage of Grafting

To separate the polystyrene–grafted silica from the ungrafted polystyrene, the product was dispersed in THF and the dispersion was centrifuged at 1.0×10^4 rpm until the silica precipitated completely. Ungrafted polystyrene was obtained from the supernatant solution. On the other hand, the silica precipitated, *i.e.*, polystyrene–grafted silica was extracted with THF using a Soxhlet apparatus until no more polystyrene cloud be detected in the refluxing solvent. The percentage of grafting was calculated as follows.

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

Isolation of Grafted Polystyrene from the Surface

To isolate grafted polystyrene from the surface, the polystyrene–grafted silica was treated with aqueous alkali. A typical example is as follows. Into a flask 1.0 g of polystyrene–grafted silica and 100 cm^3 of 12% NaOH aqueous solution was charged and the reaction mixture was stirred at 110°C for 8 hours. The aqueous solution was extracted with benzene twice. The benzene phase was washed with water and dried over sodium sulfate. By the evaporation of benzene, polystyrene was obtained and purified by reprecipitation.

Determination of Molecular Weight

The molecular weight of polystyrene was estimated by GPC using polystyrene standards: for GPC, a Hitachi 655A–11 Liquid Chromatograph was used.

Dispersibility of Polystyrene–Grafted Silica

Polystyrene–grafted silica dispersion in THF was estimated from the content of silica in the dispersion as shown in the following equation. Detailed procedures were described in the previous paper (3,4).

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

where A=silica in dispersed phase (g), and B=silica used (g).

Results and Discussion

Radical and Cationic Grafting of Polystyrene onto Silica Surface

To initiate the radical and cationic graft polymerization of styrene from silica surface, the introduction of peroxyester (Eq. 1) and acylium perchlorate groups (Eq. 2) onto the surface was examined. Table 1 shows that peroxyester groups are able to introduce onto silica surface by the reaction of surface acid anhydride groups with diisopropylbenzene hydroperoxide (1). Acylium perchlorate groups onto silica surface was found to be achieved by the reaction of acyl chloride groups with silver perchlorate (4).

The polymerization of styrene was carried out in the presence of silica having peroxyester (Silica–POE) and acylium perchlorate (Silica–APC) groups. The results are also shown in Table 1. The polymerization of styrene was found to be initiated by Silica–POE and Silica–APC.

These results indicate that the radical and cationic graft polymerizations

Table 1 Graft polymerization of styrene initiated by initiating groups on the silica surface

Silica	Initiating group content (mmol/g)	Conversion (%)	Grafting (%)
Silica-POE[a]	0.11	5.0	41.5
Silica-APC[b]	0.35	47.5	64.5

[a] Silica-POE, 0.30 g; styrene, 10.0 ml; 70℃; 12 h.

[b] Silica-APC, 0.30 g; styrene, 10.0 ml; 40℃; 10 h.

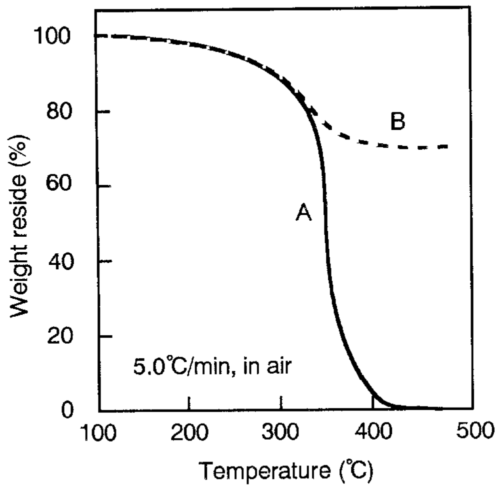


Figure 1. Thermogravimetric curves of (A) grafted polystyrene isolated and (B) polystyrene-grafted silica.

are successfully initiated by surface initiating groups to give polystyrene-grafted silica based on the propagation of polymer radical or cation from the surface.

Isolation of Polystyrene Grafted onto Silica Surface

To isolate the surface-grafted polystyrene from silica particle, the polystyrene-grafted silicas were treated with aqueous solution of alkali and liberated polystyrene was extracted with benzene.

The infrared spectra of polystyrene-grafted silica exhibited absorptions at 1605, 1498, 1454 cm^{-1}, which are characteristic of polystyrene, and at 1040 cm^{-1}, which characteristic of -Si-O-Si- bonds. On the contrary, the absorptions at 1040 cm^{-1} in the infrared spectra of isolated polystyrene was found to be completely disappeared. In addition, the infrared spectra was in agreement with those of authentic polystyrene.

Furthermore, thermogravimetric curves of polystyrene-grafted silica and isolated polystyrene were shown in Figure 1. It was found that differing from polystyrene-grafted silica, isolated polystyrene decomposed completely at 410°C.

Based on the above results, polystyrene grafted onto silica surface was able to isolate from the surface by the treatment of alkali solution.

Effect of Initiating Groups on the Molecular Weight of Grafted Polystyrene

Table 2 shows the molecular weight of polystyrene grafted onto silica obtained from the radical and cationic polymerization initiated by peroxyester and acylium perchlorate groups, respectively. The number and mass average molecular weight was determined by GPC using polystyrene standards.

It is interesting to note that the molecular weight of polystyrene grafted

Table 2 Molecular weight of polystyrene grafted onto silica surface

Grafting	Initiating group	$\overline{\mathrm{Mn}} \times 10^{-4}$	$\overline{\mathrm{Mw}} \times 10^{-4}$	$\overline{\mathrm{Mw}}/\overline{\mathrm{Mn}}$
Radical	POE	55.9	120.0	2.1
Cationic	APC	0.27	0.43	1.6

Table 3 The number of grafted polystyrene chain and initiating groups used for the grafting

Initiating group	Content (μmol/g)	Grafted polystyrene (μmol/g)	Grafted polystyrene (μmol/m^2)	f [a] (%)
POE	110	0.74	0.004	0.7
APC	350	238.8	1.189	68.2

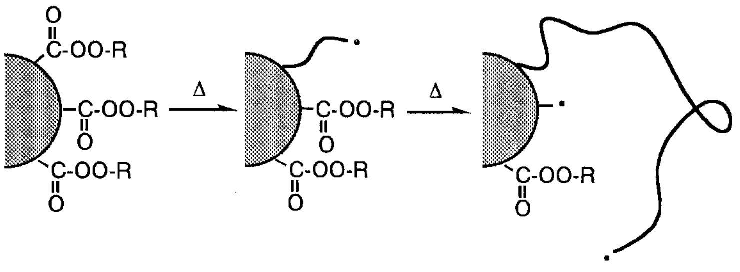
$$^{a}\ f = \frac{\text{initiating groups used for the grafting}}{\text{initiating groups on the surface}} \times 100$$

onto silica obtained from the radical polymerization was much larger than that from the cationic polymerization.

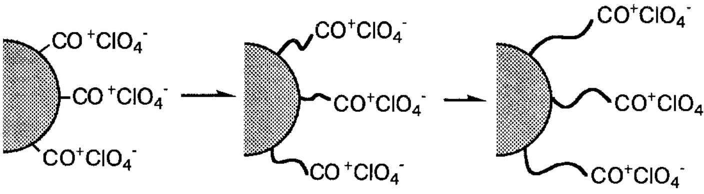
The number of polystyrene chain grafted onto silica surface was calculated from the number average molecular weight and the results are shown in Table 3. As shown in Table 3, the number of polymer chain grafted in the radical polymerization was much smaller than that in cationic polymerization.

Furthermore, the percentage of initiating groups used for grafting of polystyrene to that introduced onto the silica surface, *i.e.*, initiating efficiency (*f*), was also calculated and the results are shown in Table 3. It became apparent that in the radical graft polymerization, the peroxyester groups used for the grafting was only 0.7%, but in the cationic graft polymerization, the acylium perchlorate groups used for the grafting was about 70%.

These results are explained as follows: In the radical polymerization initiated by peroxyester groups introduced onto the silica surface, the decomposition of peroxyester groups is considered to proceed gradually (non–instantaneous). Therefore, a radical formed on the surface at the initial stage of the polymerization can initiated the graft polymerization, but a radical formed on the surface at the middle and final stage of the polymerization, can not initiate the polymerization because the growing polymer radical from the surface and/or grafted polymer block the diffusion of monomer to the surface (Eq. 3). Since the growing polymer chains from the surface were fixed on the silica and the motion of the molecule was restricted, the termination of growing polymer



(3)



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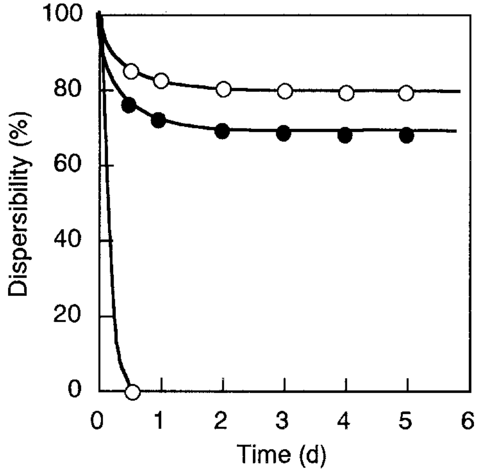

Figure 2. Effect of molecular weight of grafted polystyrene on the dispersibility of silica in THF.
(○), untreated.
(●), polystyrene–grafted ($\overline{Mn}$= 55.9×10^4).
(◐), polystyrene–grafted ($\overline{Mn}$= 0.27×10^4)

radicals from the surface was considered to be retarded. This is reason why high molecular weight of polystyrene was grafted onto silica surface.

On the other hand, in the cationic polymerization initiated by acylium perchlorate groups introduced onto the silica surface, most of acylium perchlorate groups initiate the cationic polymerization of styrene and grafted chains can propagate instantaneously (Eq. 4). Therefore, the initiating efficiency in the cationic polymerization was very high, but the molecular weight of grafted polymer is very small because of chain transfer reaction of growing polymer cation.

Based on the above results, the molecular weight and the number of grafted polymer on the surface was remarkably affected by the initiating groups introduced onto the surface.

Effect of Molecular Weight of Grafted Polystyrene on the Dispersibility

The dispersibility of silica in organic solvent is known to be remarkably improved by the grafting of polymers onto the surface because the grafted polymer chain on the surface interfere with the aggregation of silica particles (10). Therefore, the effect of molecular weight and the number of grafted polystyrene on the silica surface was investigated.

Figure 2 shows the dispersibility of polystyrene-grafted silica obtained from the radical and cationic graft polymerization shown in Table 1. Ungrafted silica in THF precipitated within 1 day. On the contrary, polystyrene-grafted silica give a stable colloidal dispersion in THF. The dispersibility of silica having larger number of shorter grafted chain (lower molecular weight) tends to be more stable than that having smaller number of longer grafted chain (higher molecular weight).

Conclusions

1. By the treatment of polystyrene-grafted silica with aqueous solution of alkali, the surface grafted polystyrene was readily isolated from the surface.
2. The molecular weight of polystyrene grafted onto silica obtained from the radical graft polymerization was found to be much larger than that from the cationic graft polymerization. The number of grafted polystyrene in the radical polymerization, however, was much less than that in the cationic polymerization.
3. The dispersibility of polystyrene-grafted silica was considered to be affected not only by the length (molecular weight) but also by the number of grafted chain.

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Accepted July 29, 1993 S