Polymer Bulletin 35, 399–406 (1995)

Polymer Bulletin

Surface grafting of polymers onto ultrafine silica: cationic polymerization initiated by benzylium perchlorate groups introduced onto ultrafine silica surface

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Received: 1 February 1995/Revised version: 26 May 1995/Accepted: 31 May 1995

Summary

The cationic graft polymerization initiated by benzylium perchlorate groups introduced onto ultrafine silica surface was investigated. The introduction of benzylium perchlorate groups onto the surface was achieved by the reaction of silver perchlorate with surface benzyl chloride groups, which were introduced by the treatment of silica with 4–(chloromethyl)phenyltrimethoxysilane. The cationic graft polymerization of styrene and cationic ring–opening polymerization of ε–caprolactone were found to be initiated by the surface benzylium perchlorate groups and the corresponding polymers were grafted onto the surface. The percentage of grafting onto silica surface decreased with increasing polymerization temperature, because chain transfer reaction of growing polymer cation is accelerated with increasing polymerization temperature.

Introduction

In a series of our papers, we have reported the surface grafting of polymers onto inorganic ultrafine particles, such as silica and carbon black (1–3). By the grafting of polymers onto the surfaces, the dispersibility of ultrafine particles in solvents and polymer matrices was remarkably improved: the polymer–grafted silica gave a stable colloidal dispersion in a good solvent of grafted polymer and the precipitation of particles was scarcely observed even after 1 month. This considered to be due to the fact that grafted chains on the surface interfere with the aggregation of particles and the affinity of particle surface to dispersing solvent was increased by the grafted chains.

For the effective grafting of polymers onto the particle surfaces, it is desirable to start the graft polymerization from surface initiating groups introduced onto these surfaces because grafted polymer chains propagate from the surface. We have reported the radical and anionic graft polymerization initiated by azo (4,5) and peroxyester groups (6,7) and potassium carboxylate groups (8,9) introduced onto ultrafine particle surface, respectively.

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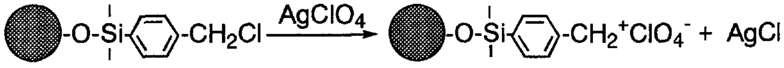
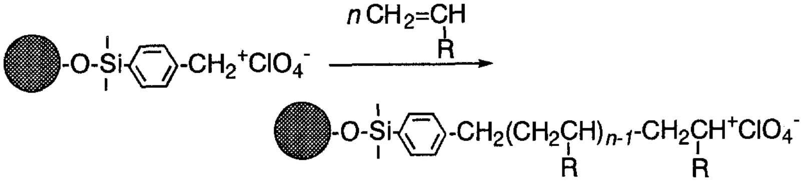
Furthermore, acylium perchlorate groups were introduced onto ultrafine silica and carbon black. These particles have the ability to initiate the cationic polymerization (10,11) of vinyl monomers and the cationic ring-opening polymerization (11,12) of cyclic ethers and lactones to give the corresponding polymer-grafted particles. More recently, we have reported that the cationic polymerization of vinyl monomers and the cationic ring-opening polymerization of cyclic monomers are initiated by oxoaminium perchlorate groups introduced onto silica surface and the corresponding polymers are grafted onto silica surface based on the propagation of polymers from the surface (13).

In the present paper, the introduction of benzylium perchlorate groups onto ultrafine silica (Eq. 1) and the cationic polymerization from the surface (Eq. 2) were investigated. Furthermore, the effect of temperature on the cationic graft polymerization will be also discussed.



(1)



(2)

Experimental

Materials and reagents

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 (14). The silica was washed with distilled water and dried *in vacuo* at 110°C before use.

4-(Chloromethyl)phenyltrimethoxysilane (CMTMS) obtained from Huls America Inc. was used without further purification. Guaranteed reagent-grade silver perchlorate (Kojima Chemical Co. Ltd., Japan) was dried *in vacuo* at 120°C before use.

Nitrobenzene was washed with dilute H_2SO_4, dried over calcium chloride, and distilled under reduced pressure just before use. Toluene was washed with concentrated H_2SO_4, refluxed over sodium, and distilled. Styrene was washed with aqueous alkali, dried over barium oxide, and distilled under reduced pressure just before use. ε-Caprolactone (CL) was dried over calcium hydride and distilled just before use.

Introduction of benzyl chloride groups onto silica surface

The introduction of benzyl chloride groups onto silica surface was achieved by the treatment of surface silanol groups with CMTMS. A typical example is as follows. Into a flask equipped with a reflux condenser, 5.0 g of silica and 100 cm^3 of 5.0% toluene solution of CMTMS were charged. The mixture was refluxed for 20 h under magnetic stirring in a stream of nitrogen. After the treatment, the resulting silica was extracted with absolute THF for 48 h using a Soxhlet extractor and dried *in vacuo* at 110°C.

Introduction of benzylium perchlorate groups onto silica surface

The introduction of benzylium perchlorate groups onto silica surface, *i.e.*, pretreatment, was carried out by the reaction of benzyl chloride groups with silver perchlorate in nitrobenzene. A typical example is as follows. Into a 100 cm^3 flask, 0.10 g of silica having benzyl chloride groups, 0.02 g of silver perchlorate, and 5.0 cm^3 of nitrobenzene were charged. The reaction mixture was stirred with a magnetic stirrer under dry nitrogen at 30.0°C for 48 h.

Graft polymerization

After the above pretreatment, 10.0 cm^3 of monomer was added to the mixture, and the polymerization was conducted with stirring at 30°C. After the polymerization, the content of the flask was poured into an excess of methanol to precipitate ungrafted polymer and polymer–grafted silica. The conversion was calculated by the following equation:

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

Percentage of grafting and grafting efficiency

To separate the polymer–grafted silica from the ungrafted polymer, the product was dispersed in THF and the dispersion was centrifuged at 1.0x10^4 rpm until the silica precipitated completely. The silica precipitated, *i.e.*, polymer–grafted silica, was allowed to extraction with THF 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.

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

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

Stability of polymer–grafted silica dispersion

The stability of polymer–grafted silica dispersion was estimated from the content of silica in the dispersion after standing. The detailed procedures were described in the previous paper (11).

Molecular weight of polymer

The molecular weight of polystyrene was determined by GPC using polystyrene standards. For GPC, a Hitachi 655A-11 Liquid Chromatograph was used.

Results and Discussion

Introduction of benzyl chloride groups onto ultrafine silica surface

The introduction of benzyl chloride groups was achieved by the treatment of silanol groups on the silica surface with silane coupling agent, CMTMS, in toluene. The amount of benzyl chloride groups introduced onto the surface was determined to be 0.60 mmol/g by elemental (chlorine) analysis. This indicates that about 45% of silanol groups are reacted with CMTMS. The silica having benzyl chloride groups was abbreviated as Silica-CH_2Cl.

Evidence for initiation of cationic polymerization

Dreyfuss and Kennedy reported that the cationic polymerization of THF is initiated by organic halides, such as poly(vinyl chloride) and benzyl chloride, in the presence of silver triflate (15). In the previous paper, we succeeded in the cationic graft polymerization initiated by benzylium perchlorate groups on carbon black surface which were introduced by the reaction of surface benzyl chloride groups with silver perchlorate (16). Therefore, the polymerization of styrene was carried out using Silica-CH_2Cl and silver perchlorate under several conditions.

The results are shown in Table 1. Styrene was not polymerized by silver perchlorate, untreated silica, or Silica-CH_2Cl alone (Runs 1,2, and 4). In addition, polymerization could not be detected even if untreated silica was pretreated with silver perchlorate (Run 3). On the contrary, the polymerization of styrene was initiated by Silica-CH_2Cl pretreated with silver perchlorate (Run 5) to give polystyrene-grafted silica. These results indicate that surface benzylium perchlorate groups formed *in situ* by the pretreatment of Silica-CH_2Cl

Table 1 Cationic graft polymerization of styrene initiated by benzylium perchlorate groups on silica surface

Run	Silica	$AgClO_4$ (g)	Conversion (%)	Grafting (%)
1	None	0.02	0	-
2	Untreated	-	0	0
3	Untreated	0.02	0	0
4	Silica-CH_2Cl	-	0	0
5	Silica-CH_2Cl	0.02	94.7	17.3

Pretreatment: Silica, 0.30 g; nitrobenzene, 5.0 cm^3; 30°C; 48 h.
Polymerization: Styrene, 10.0 cm^3; 10°C; 20 min.

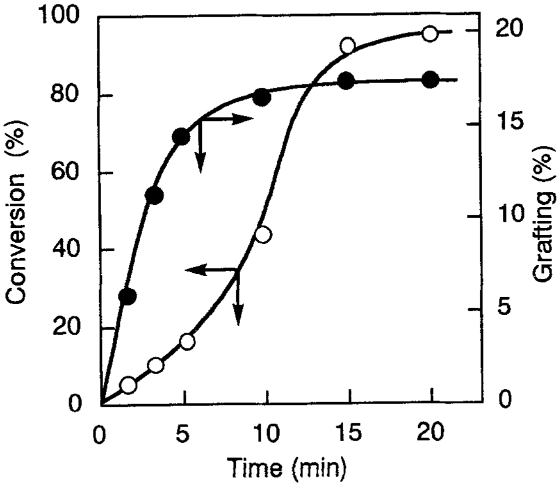


Figure 1 Cationic polymerization of styrene initiated by benzylium perchlorate groups on silica surface. Polymerization conditions are given in Table 1.

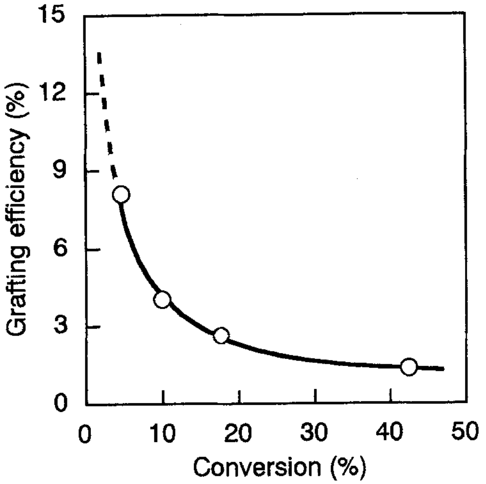


Figure 2 Relationship between conversion and grafting efficiency in the cationic graft polymerization shown in Figure 1.

with silver perchlorate initiate the polymerization and that grafted polystyrene chains propagate from silica surface as shown in (Eqs. 1 and 2).

Figure 1 shows the relationship between reaction time and conversion and percentage of grafting in the polymerization of styrene initiated by benzylium perchlorate groups on silica surface. The conversion of styrene increased with progress of the polymerization and reached about 90% after 15 h. The percentage of grafting immediately increased at the initial stage of the polymerization as a result of propagation of polystyrene from the surface, but no longer increased after 10 h.

On the other hand, Figure 2 shows the relationship between conversion and grafting efficiency. Grafting efficiency at initial stage of the polymerization was relatively high, but immediately decreased with progress of the polymerization.

These results suggest that the initiation of cationic polymerization from

Table 2 Effect of temperature on the cationic polymerization of styrene initiated by benzylium perchlorate groups on silica surface[a]

Temperature (°C)	Conversion (%)	Grafting (%)	Grafting efficiency[b] (%)	$\overline{M}n \times 10^{-3}$
0	10.1	23.4	7.8	2.0
10	94.7	17.3	4.2	1.4
30	81.0	7.5	2.5	1.0

[a] Pretreatment: Silica, 0.30 g; nitrobenzene, 5.0 cm^3; 30°C; 48 h. Polymerization: Styrene, 10.0 cm^3; 10°C; 20 min.
[b] At 10% conversion.

surface acylium perchlorate groups are gradually inhibited by neighboring grafted polymer chains and the formation of ungrafted polymer by chain transfer reaction of growing cation preferentially proceeded at the middle and last stage of the polymerization. In the polymerization, a mild induction period was observed. The reason why the polymerization is retarded at the initial stage is now under investigation.

Effect of temperature on the polymerization

The chain transfer reaction of propagating cation is known to be accelerated at higher temperature. Therefore, the effect of temperature on the cationic graft polymerization initiated by benzylium perchlorate groups on silica was investigated. The results are shown in Table 2. The percentage of polystyrene grafting, grafting efficiency, and molecular weight of ungrafted polymer decreased with increasing polymerization temperature. The same tendency was reported in the cationic graft polymerization initiated by acylium perchlorate groups introduced onto ultrafine powder surface such as carbon black and silica (10–12).

These results clearly show that rate of the chain transfer reaction of growing polymer cation from the surface increases with increasing polymerization temperature.

Cationic ring-opening polymerization of CL

The cationic ring-opening polymerization of CL initiated by benzylium perchlorate groups introduced onto the silica surface was examined. The results are shown in Figure 3. The cationic ring-opening polymerization of CL was found to be initiated by benzylium perchlorate groups introduced onto the silica surface and polyCL was grafted onto the surface thorough the propagation of grafted chains from the surface.

Characterization of polystyrene-grafted silica

Figure 4 shows IR spectra of Silica-CH_2Cl, polystyrene-grafted, and

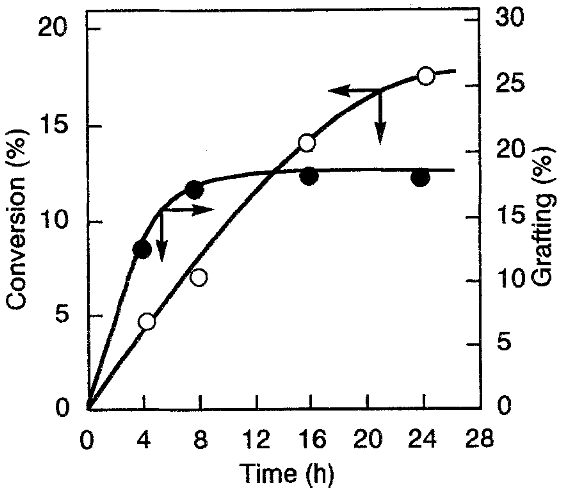


Figure 3 Cationic ring-opening polymerization of CL initiated by benzylium perchlorate groups on silica surface. Pretreatment: Silica-CH_2Cl, 0.30 g; $AgClO_4$, 0.02 g; nitrobenzene, 5.0 cm^3; 30°C; 48 h. Polymerization: CL, 10.0 cm^3; 10.0 °C

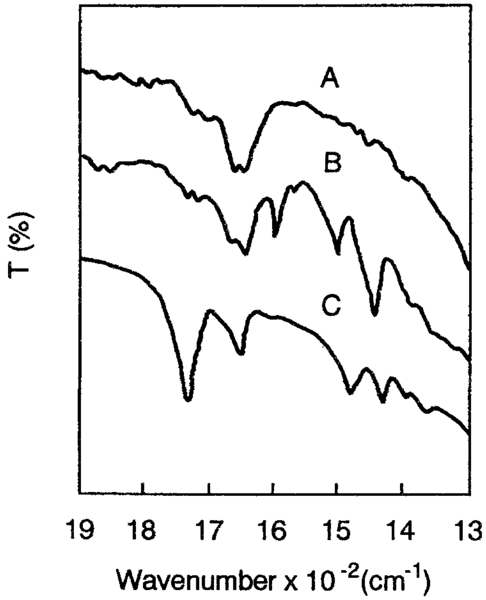


Figure 4 Infrared spectra of (A) Silica-CH_2Cl, (B) polystyrene-grafted silica, and (C) polyCL-grafted silica.

polyCL-grafted silica. Polystyrene-grafted silica shows the absorptions at 1602, 1499, and 1450 cm^{-1}, which are characteristic of polystyrene. On the other hand, IR spectra of polyCL-grafted silica exhibited absorptions characteristic of polyCL. These results also show that the polystyrene and polyCL were grafted onto the silica surface.

In general, by the grafting of polymers onto ultrafine particles, the dispersibility of the particles was remarkably improved. The stability of polystyrene-grafted and polyCL-grafted silica dispersion in THF was compared with that of untreated silica dispersion. The results are shown in Figure 5.

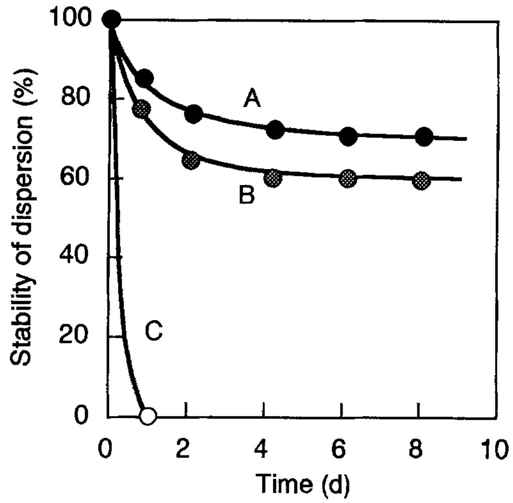


Figure 5 Stability of dispersion of (A) polystyrene-grafted, (B) polyCL-grafted, and (C) untreated silica in THF at room temperature。

Untreated silica precipitated immediately, polymer-grafted silica gave stable colloidal dispersions in THF. This may be due to the fact that grafted polymer chains on the surface interfere with the aggregation of silica particles and that the affinity of silica surface to THF is increased.

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