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ORIGINAL CONTRIBUTION

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Effect of polymerization conditions on the molecular weight of polystyrene grafted onto silica in the radical graft polymerization initiated by azo or peroxyester groups introduced onto the surface

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Abstract The effect of polymerization conditions on the molecular weight of polystyrene grafted onto silica obtained from the radical graft polymerization initiated by azo and peroxyester groups introduced onto the surface was investigated. The molecular weight of polystyrene grafted onto silica obtained from the radical graft polymerization initiated by surface azo and peroxyester groups decreased with decreasing monomer concentration and polymerization temperature. The molecular weight of polystyrene was found to be controlled to some extent by the addition of a chain transfer agent. The molecular weight of grafted chain on silica surface obtained from the graft polymerization initiated by surface radicals formed by photodecomposition of azo groups was considerably smaller than that by thermal decomposition. The number of grafted polystyrene in photopolymerization, however, was much larger than that in thermal polymerization. These results are explained by the blocking of surface radicals formed on the silica surface by previously grafted polymer chain: when the decomposition of surface azo and peroxyester groups proceed instantaneously at the initial stage of the polymerization, the number of grafted polymer chains increased.

Key words Ultrafine silica – surface grafting – molecular weight – radical polymerization – chain transfer agent

Introduction

In a series of our papers, we have reported the grafting of various polymers onto ultrafine particle surfaces, such as carbon black, silica, and titanium oxide, by the polymerization of vinyl monomers initiated by initiating groups introduced onto these surfaces [1–3]. For instance, the radical polymerization of vinyl monomers was found to be initiated by azo [4], peroxide [5], and peroxyester groups [6] introduced onto silica surface to give polymer-grafted silica. In addition, the cationic polymerization of vinyl monomers and cationic ring-opening polymerization of cyclic monomers were initiated by acylium perchlorate [7] and benzylium perchlorate [8] groups introduced onto silica surface and the corresponding polymers were effectively grafted onto the surface. The anionic grafting of polyesters onto silica surface was also achieved by the anionic alternating copolymerization of epoxides with cyclic acid anhydrides initiated by potassium carboxylate groups introduced onto silica surface [9].

During the above graft polymerizations, polymer-grafted silica with a high percentage of grafting was readily obtained, because these polymers propagate from initiating groups on the surface. Little is known, however, about the effect of initiating groups and polymerization conditions on the molecular weight of polymer grafted onto the surface. In the proceeding paper, we reported that the molecular weight of polystyrene grafted onto the silica obtained from the radical graft polymerization initiated by peroxyester groups introduced onto the surface was much larger than that obtained from the cationic polymerization initiated by acylium perchlorate groups [10]. The number of grafted polystyrene obtained from the radical graft polymerization, however, was much less than that in the cationic polymerization.

In the present paper, the effects of polymerization conditions on the molecular weight of polystyrene grafted onto silica surface in the radical graft polymerization initiated by azo and peroxyester groups were investigated.

Experimental

Materials and reagents

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 after the heating at 200–250 °C in vacuo was determined by measuring volumetrically the amount of ethane evolved by the reaction with triethylaluminum [11]. The silica was washed with distilled water and dried in vacuo at 110 °C before use.

Styrene was washed with aqueous alkali, dried over barium oxide, and distilled twice under reduced pressure. Diethyl diallylmalonate (DEAM) obtained from Wako Pure Chemical Ind. Co., Ltd. was distilled before use. Tetrahydrofuran (THF) was refluxed over sodium and distilled. All other solvents and reagents were used after ordinary purification.

Introduction of azo groups onto silica surface

The introduction of azo groups onto silica surface was achieved by the reaction of isocyanate groups, which were introduced onto the surface by the treatment of tolylene-2,4-diisocyanate, with 4,4′-azobis(4-cyanopentanoic acid). The detailed procedures were described in the proceeding paper [4, 12].

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, which were introduced by the treatment with 4-trimethoxysilyl-1,2,5,6-tetrahydrophthalic anhydride, with α,α-dimethyl(4-isopropylbenzene) hydroperoxide. The procedures were described in detail in the preceding paper [6].

Graft polymerization

The radical graft polymerization of styrene initiated by azo and peroxyester groups introduced onto silica surface was carried out in a sealed tube with shaking [4–6].

The photopolymerization of styrene initiated by azo groups on silica surface was carried out in a photoreactor (Riko-Kagaku Sangyo Co. Ltd., Japan: Model UVL-100H) under nitrogen under stirring with a magnetic stirrer at 25 °C [12]. The reaction mixture in a pyrex flask was irradiated with a 100 W high-pressure mercury lamp.

After a prescribed polymerization time, the contents of the sealed tube and the photoreactor were poured into an excess of methanol to precipitate ungrafted polystyrene and polystyrene-grafted silica. The conversion was determined by

$$\text{conversion } (\%) = [(A - B)/C] \times 100 \ ,$$

where A is weight of product, B is weight of silica charged, and C is weight of monomer charged.

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. 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, grafting efficiency, and number of grafted polymer were calculated by

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

$$\text{grafting efficiency } (\%) = (A/C) \times 100$$

$$\text{number of grafted polymer (No./g)} = 6.02 \times 10^{23} \times (A/Mn) \ ,$$

where A is weight of grafted polymer, B is weight of silica charged, C is weight of total polymer formed, and Mn is number average molecular weight of grafted polymer.

Isolation of grafted polystyrene from the surface

The isolation of grafted polystyrene from the silica surface was achieved by the dissolution of silica by the treatment of polystyrene-grafted silica with aqueous alkali. A typical example is as follows [10]. 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 h. 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.

Results and discussion

Introduction of azo and peroxyester groups onto silica surface

The introduction of azo and peroxyester groups onto silica surface was achieved by the reaction as we reported (Fig. 1) [4, 6, 12]. The amount of azo and peroxyester groups introduced onto the surface was determined to be 0.08 mmol/g by elemental analysis and 0.11 mmol/g by iodometry, respectively. This indicates that about 6–8% of silanol groups are used for the introduction of these initiating groups. The silica having azo and peroxyester groups was abbreviated as Silica–Azo and Silica–POE, respectively.

Effect of polymerization time on the molecular weight

The effect of polymerization time on the molecular weight of polystyrene grafted onto silica surface in the radical graft polymerization initiated by Silica–Azo was investigated. Figure 2 shows the relationship between polymerization time and percentage of grafting or molecular weight of polystyrene grafted onto silica surface. As shown in Fig. 2, the percentage of polystyrene grafting increased with progress of the polymerization time, but no longer increased after 6 h. The increase of molecular weight of polystyrene with progress of the polymerization was small. The same tendency was observed in the polymerization initiated by Silica–POE.

Therefore, the molecular weight of polystyrene grafted onto the surface was compared with each other at the stage that the molecular weight and percentage of grafting reached to constant, i.e., after 9 h of polymerization.

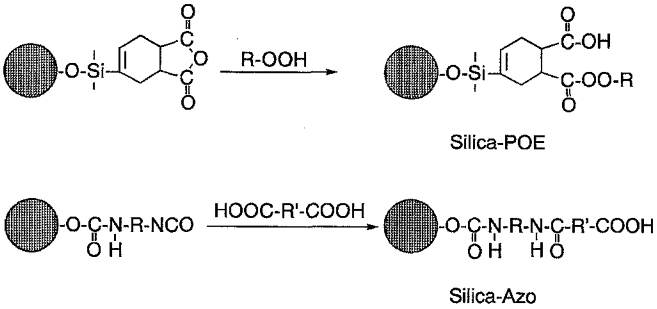

Fig. 1 Introduction of peroxyester and azo groups onto silica surface

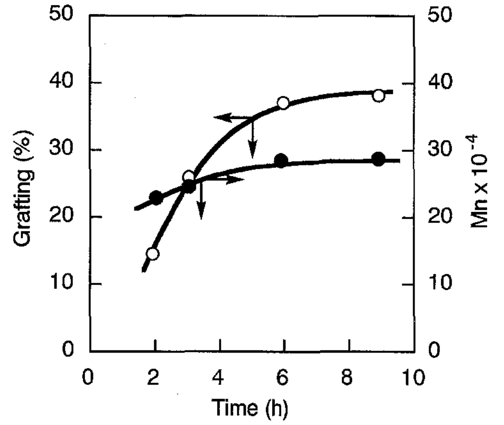

Fig. 2 Relationship between polymerization time and conversion and *Mn* of grafted polystyrene onto silica surface obtained from the polymerization initiated by Silica–Azo. Silica–Azo, 0.30 g; styrene 10.0 cm^3; 70 °C

Effect of monomer concentration on the molecular weight

The effect of styrene concentration on the molecular weight of polystyrene grafted onto silica obtained by the radical graft polymerization initiated by peroxyester groups on the surface was investigated. The results are shown in Table 1.

It was found that the molecular weight of polystyrene grafted onto silica decreases with decreasing monomer concentration, especially the molecular weight of polystyrene remarkably decreases at monomer concentration less than 4.4 mol/dm^3. On the other hand, the number of grafted polymer chain on the surface was scarcely affected by monomer concentration.

This indicates that the percentage of peroxyester groups used for the starting of graft polymerization was not affected by monomer concentration. On the contrary, the decrease of molecular weight of grafted chain with decreasing monomer concentration was considered to depend on the decreasing polymerization rate: in general,

Table 1 Effect of styrene concentration on molecular weight of polystyrene grafted onto silica obtained from the polymerization initiated by Silica–POE in benzene[a]

Styrene (mol/dm^3)	Conversion (%)	Grafting (%)	$Mn \times 10^{-4}$	$Mw \times 10^{-4}$	$Gn^b \times 10^{-17}$
8.7	3.0	41.5	55.9	120.0	4.45
7.0	3.2	29.3	53.3	151.2	3.31
4.4	2.2	26.1	48.6	118.1	3.25
1.7	1.3	24.4	25.7	71.4	5.72

[a] Silica–POE, 0.30 g; total volume (benzene), 10.0 cm^3; 70 °C; 9 h.
[b] *Gn*; Number of grafted polymer chain.

Table 2 Effect of temperature on molecular weight of polystyrene grafted onto silica obtained from the polymerization initiated by Silica–Azo[a]

Temperature (°C)	Conversion (%)	Grafting (%)	$Mn \times 10^{-4}$	$Mw \times 10^{-4}$	$Gn^b \times 10^{-17}$
60	1.9	9.3	24.9	52.0	2.23
70	18.2	37.6	28.5	56.1	7.94
80	24.2	44.5	31.2	48.4	8.61

[a] Silica–Azo, 0.30 g; styrene, 10.0 cm^3; 9 h.
[b] *Gn*; Number of grafted polymer chain.

in the radical polymerization, degree of polymerization (kinetic chain length) is known to decrease with decreasing polymerization rate and monomer concentration [13].

Effect of polymerization temperature on the molecular weight

The effect of polymerization temperature on the molecular weight of polystyrene grafted onto silica obtained from the radical graft polymerization initiated by Silica–Azo was examined. The results are shown in Table 2.

It was found that the molecular weight of polystyrene grafted onto the surface gradually increased with increasing polymerization temperature. It is interesting to note that the number of grafted polymer chain drastically increased with increasing polymerization temperature.

The results are explained as follows: In the radical polymerization initiated by azo groups introduced onto the surface, the decomposition of surface azo groups proceeds gradually (non-instantaneous). Therefore, a radical formed on the surface at the initial stage of the polymerization can initiate the graft polymerization, but a radical formed on the surface at the middle and final stage of the polymerization cannot initiate the polymerization because the growing polymer radical from the surface and/or grafted polymer block the diffusion of monomer to the surface (Fig. 3). Accordingly, at higher polymerization temperature, the number of surface radicals formed by the decomposition of azo groups is considered to increase at initial stage of the polymerization. And then the number of grafted polymer chain at higher temperature is larger than that at lower polymerization temperature, as shown in Fig. 3.

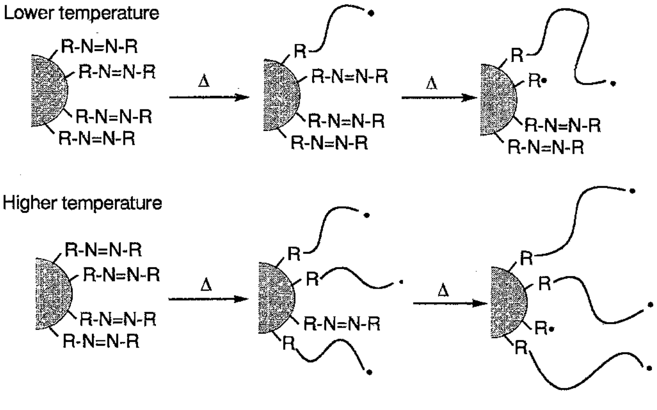

Fig. 3 Effect of temperature on the popagation of grafted chain from silica surface in the polymerization initiated by Silica–Azo

Table 3 shows the effect of temperature on the molecular weight of polystyrene grafted onto silica in the radical graft polymerization initiated by Silica–POE.

Differing from the graft polymerization initiated by Silica–Azo, in the polymerization of styrene initiated by Silica–POE, the molecular weight of polystyrene increased with increasing polymerization temperature, but decreased above 70 °C. This may be due to the fact that the activation energy in the decomposition of peroxyester groups is considerably lower than that of azo groups, because carbon blacks accelerate the decomposition of peroxide [14, 15]: the same tendency has been reported in the polymerization initiated by redox initiators [16, 17].

Table 3 Effect of temperature on molecular weight of polystyrene grafted onto silica obtained from the polymerization initiated by Silica–POE[a]

Temperature (°C)	Conversion (%)	Grafting (%)	$Mn \times 10^{-4}$	$Mw \times 10^{-4}$	$Gn^{b} \times 10^{-17}$
60	1.4	19.3	30.7	72.1	3.79
70	3.0	41.5	55.9	120.0	4.45
80	8.2	20.7	22.4	53.5	5.54

Silica–Azo, 0.30 g; styrene, 10.0 cm; 9 h.
Gn; Number of grafted polymer chain.

Table 4 Effect of chain transfer agent on the molecular weight of polystyrene grafted onto silica obtained from the polymerization initiated by Silica–POE

DEAM[b] (cm^3)	Conversion (%)	Grafting (%)	$Mn \times 10^{-4}$	$Mw \times 10^{-4}$	$Gn^{c} \times 10^{-17}$ (No./g)
0.0	3.0	41.5	55.9	120.0	4.45
2.0	4.1	30.1	43.7	91.0	4.15
5.0	1.3	27.6	37.9	70.4	4.39

[a] Silica–POE, 0.30 g; styrene, 10.0 cm^3; 70 °C; 9 h.
[b] Diethyl diallylmalonate.
[c] *Gn*; Number of grafted polymer chain.

On the other hand, the number of grafted polystyrene tends to increase with increasing polymerization temperature. This indicates that the number of propagating chains from the surface increase with increasing polymerization temperature.

Effect of chain transfer agent on the molecular weight

The effect of chain transfer agent on the molecular weight of polystyrene grafted onto silica obtained from the radical graft polymerization initiated by Silica–POE was examined. In the experiment, diethyl diallylmalonate was used as a chain transfer agent. The results are shown in Table 4.

The molecular weight of grafted polystyrene onto silica surface decreased with increasing amount of the chain transfer agent, but the number of grafted chains was scarcely affected by the addition of the chain transfer agent. This indicates that in the presence of chain transfer agent, the propagating radicals are terminated during the initial stage of the polymerization as shown in Fig. 4.

In conclusion, by use of chain transfer agent, the molecular weight of grafted polystyrene can be controlled to some extent without decrease in the number of grafted chains.

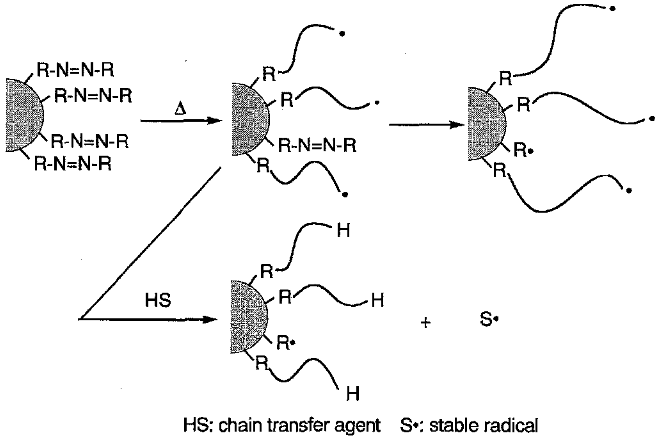

Fig. 4 Effect of chain transfer agent on the molecular weight of grafted chain on the surface

Effect of photopolymerization on the molecular weight

In the preceding paper, we have reported that the percentage of grafting and grafting efficiency onto silica in the graft polymerization initiated by photodecomposition of azo groups (photopolymerization) introduced onto the surface are much larger than those initiated by thermal decomposition (thermal polymerization) [12]. Therefore, the effect of photopolymerization on the molecular weight of polystyrene grafted onto silica was investigated. The results are shown in Table 5.

As mentioned above, the percentage of grafting and grafting efficiency in the photopolymerization is much larger than those in the thermal polymerization. On the other hand the molecular weight of polystyrene grafted onto silica in photopolymerization at 25 °C is smaller than that in thermal polymerization at 70 °C, but the number of grafted polymer onto silica in the photopolymerization is much larger than that in the thermal polymerization.

Table 5 Molecular weight and number of polystyrene grafted onto silica surface obtained from thermal and photopolymerization initiated by Silica–Azo[a]

Initiation	Conversion (%)	Grafting (%)	$Mn \times 10^{-4}$	$Mw \times 10^{-4}$	$\mathrm{Gn}^{b} \times 10^{-17}$
Thermal[b]	18.2	37.6	28.5	56.1	7.94
Photo[c]	10.6	111.2	13.1	41.9	16.25

[a] Silica–Azo, 0.30 g; styrene, 10.0 cm^3.
[b] 70 °C; 9 h.
[c] 25 °C; 4 h.

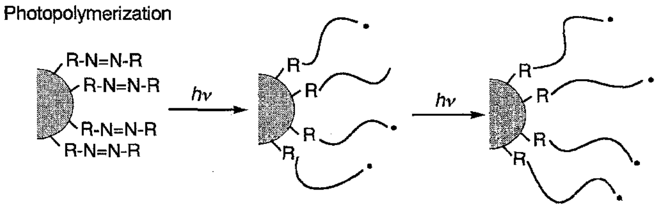

Fig. 5 Propagation of grafted chain from silica surface in the photopolymerization initiated by Silica–Azo

These results indicates that the decomposition of surface azo groups in the photopolymerization proceeds more instantaneously than that in the thermal polymerization. Therefore, in the photopolymerization, more surface radicals than thermal polymerization initiates the polymerization without blocking effect by previously grafted polymer, and the polystyrene can propagate instantaneously as shown in Fig. 5.

Based on the above results, it is concluded that the effective grafting onto silica surface can be achieved in the photopolymerization.

Conclusions

1) The molecular weight of polystyrene grafted onto silica obtained from the radical graft polymerization initiated by surface azo and peroxyester groups decreased with decreasing monomer concentration and polymerization temperature.

2) By the addition of a chain transfer agent, the molecular weight of polystyrene grafted onto the surface was controlled to some extent.

3) The number of grafted chain on silica surface obtained from the radical graft polymerization initiated by surface radicals formed by photodecomposition of azo groups was considerably larger than that by thermal decomposition.

References

1. Tsubokawa N, Endo T (1998) Tanso No. 140:322
2. Tsubokawa N (1990) Hyoumen 28:286
3. Tsubokawa N (1992) Prog Polym Sci 17:417
4. Tsubokawa N, Kogure A, Maruyama K, Sone Y, Shimomura M (1990) Polym J 22:827
5. Tsubokawa N, Ishida H (1992) J Polym Sci Part A Polym Chem 30:2241
6. Tsubokawa N, Ishida H (1992) Polym J 24:809
7. Tsubokawa N, Kogure A (1993) Polym J 25:83
8. Tsubokawa N, Saitoh K (1995) Polym Bull 35:399
9. Tsubokawa N, Kogure A (1991) J Polym Sci Part A Polym Chem 29:697
10. Tsubokawa N, Ishida H, Hashimoto K (1993) Polym Bull 31:457
11. Sato M, Kanbayashi Y, Kobayashi K, Shima Y (1976) J Catalysis 1:342
12. Tsubokawa N, Shirai Y, Tsuchida H, Handa S (1994) J Polym Sci Part A Polym Chem 32:2327
13. Odian G (1991) Principles of Polymerization, John Wiley, New York, p 241
14. Ohkita K, Kasahara H, Iida M, Watanabe Y, Suzuki S (1962) Nippon Gomu Kyokaishi 35:22
15. Ohkita K, Uchiyama M, Shimomura M (1979) Kobunshi Ronbunshu 36:465
16. Kawakami H, Mori N, Washimi M (1961) Kobunshi Kagaku 20:408
17. Talamini G, Vidotto G (1961) Makromol Chem 50:129