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Norio Tsubokawa^a; Kazuyo Seno^a

^a Department of Material Science and Technology, Faculty of Engineering Niigata University, Niigata, Japan

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RADICAL GRAFT POLYMERIZATION OF VINYL MONOMERS ONTO BARIUM SULFATE INITIATED BY AZO GROUPS INTRODUCED ONTO THE SURFACE

NORIO TSUBOKAWA* and KAZUYO SENO

Department of Material Science and Technology
Faculty of Engineering
Niigata University
8050, Ikarashi 2-nocho, Niigata 950-21, Japan

ABSTRACT

To modify the surface of barium sulfate, the radical graft polymerization of vinyl monomers initiated by azo groups introduced onto the surface was investigated. The introduction of azo groups onto the surface was achieved by the direct condensation of carboxyl group of 4,4'-azobis(4-cyanopentanoic acid) with 12-hydroxystearate groups on modified barium sulfate using *N,N'*-dicyclohexylcarbodiimide as a condensing agent. It was found that the radical polymerizations of methyl methacrylate (MMA), styrene, and *N*-vinylcarbazole were initiated by the azo groups introduced onto the surface, and the corresponding polymers were grafted onto the surface based on the propagation of grafted polymer from the surface: the percentage of PMMA grafting onto the surface reached 25.3% at 70°C after 1.5 hours and the grafting efficiency was 21.4%. The polymerization rate (R_p) of styrene initiated by the surface azo groups was given by

$$R_p = k[\text{styrene}][\text{BaSO}_4\text{-Azo}]$$

where k is a constant, [styrene] is the styrene concentration, and [BaSO₄-Azo] is the concentration of barium sulfate having azo groups. The result suggests that in such an initiating system the unimolecular termination of growing polymer radicals from the surface proceeds preferentially at the initial stage of the polymerization.

EXPERIMENTAL

Materials and Reagents

Guaranteed reagent grade barium chloride and sodium sulfate obtained from Kanto Chemical Ind. Co., Ltd., Japan, were used without further purification. 4,4'-Azobis(4-cyanopentanoic acid) (ACPA) obtained from Wako Pure Chemical Co., Ltd., Japan, was recrystallized from methanol. *N,N'*-Dicyclohexylcarbodiimide obtained from Aldrich Chemical Co. was dried in vacuo before use.

Sodium 12-hydroxystearate was prepared by the neutralization of 12-hydroxystearate acid with sodium hydroxide in methanol at 85°C.

Methyl methacrylate (MMA) was washed with 10% aqueous solution of sodium hydrogen sulfite, 5% aqueous solution of sodium hydroxide, and 20% aqueous solution of sodium chloride. Then it was dried over sodium sulfate and distilled twice before use. Styrene was washed with a 10% aqueous solution of sodium hydroxide followed by water, dried over barium oxide, and distilled twice under reduced pressure. *N*-Vinylcarbazole (NVC) was recrystallized from *n*-hexane and dried in vacuo at room temperature.

Preparation of Barium Sulfate Modified by 12-Hydroxystearate Groups

Barium sulfate modified by 12-hydroxystearate groups ($\text{BaSO}_4\text{-HS}$) was prepared by the reaction of barium chloride with sodium sulfate containing a small amount of sodium 12-hydroxystearate according to the method of Kotani et al. [14]. The detailed procedures are described in a previous paper [13].

Introduction of Azo Groups onto Barium Sulfate Surface

The introduction of azo groups onto barium sulfate was achieved by the direct condensation of the carboxyl group of ACPA with the alcoholic hydroxyl groups on $\text{BaSO}_4\text{-HS}$ using DCC as a condensing agent. A typical example was as follows. Into a flask, 3.0 g $\text{BaSO}_4\text{-HS}$, 30 mmol ACPA, 30 mmol DCC, and 150 cm³ THF were charged. The reaction mixture was stirred with a magnetic stirrer at 30.0°C for 24 hours. After the reaction, the barium sulfate was collected by filtration and then dispersed in methanol. The dispersion was centrifuged at 1.2×10^4 , and the supernatant solution was removed. The precipitated barium sulfate was dispersed again in THF and the dispersion was centrifuged. The procedures were repeated until no more DCC and ACPA could be detected in the supernatant solution. The resulting barium sulfate was dried in vacuo at room temperature and stored in a refrigerator. The barium sulfate having azo groups is abbreviated as $\text{BaSO}_4\text{-Azo}$.

Graft Polymerization

Into a glass ampule, 0.50 g of $\text{BaSO}_4\text{-Azo}$ and 10.0 cm³ of vinyl monomer were charged. Then the ampule was cooled, thawed three times with nitrogen, and sealed under high vacuum. The sealed ampule was heated at a definite time with shaking. After the reaction, the content of the ampule was poured into an excess of methanol to precipitate the polymer containing barium sulfate. The precipitate was filtered and dried in vacuo at 60°C. The conversion was determined by

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

where A is weight of precipitate, B is weight of barium sulfate charged, and C is weight of monomer charged.

Percentage of Grafting and Grafting Efficiency

In order to isolate polymer-grafted barium sulfate, the product was dispersed in THF and the dispersion was centrifuged at 1.2×10^4 rpm until the barium sulfate precipitated completely. The supernatant solution was removed. The precipitated barium sulfate was dispersed in THF again and the dispersion was centrifuged. The procedures were repeated until no more polymer could be detected in the supernatant solution. The percentage of grafting and grafting efficiency in the above polymerization conditions were calculated by

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

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

where A is weight of grafted polymer, B is weight of barium sulfate charged, and C is weight of total polymer formed. The weight of grafted polymer was determined by weight increment after the graft polymerization.

Determination of Polymerization Rate

The polymerization was conducted in several flasks, and the polymerization in each flask was terminated at a different time before the conversion reached 10%. The rate of polymerization was estimated from the slope of the time-conversion curve.

Instruments for XPS Analysis

A Kratos X-ray Photoelectron Spectrometer, Model XSAM-800, was used for the surface analysis of modified barium sulfate.

RESULTS AND DISCUSSION

Introduction of Azo Groups onto Barium Sulfate Surface

It has been reported by Kohtani et al. that barium sulfate modified by 12-hydroxystearate groups, i.e., $\text{BaSO}_4\text{-HS}$, is readily prepared by the reaction of barium chloride with sodium sulfate containing a small amount of sodium 12-hydroxystearate [14]. In a previous paper we reported that the redox graft polymerization of acrylamide (AAM) is initiated by a system consisting of ceric ion and $\text{BaSO}_4\text{-HS}$ [13].

It is expected that azo groups can be introduced onto the barium sulfate surface by the direct condensation of surface 12-hydroxystearate groups with the carboxyl group of ACPA as shown in Eq. 1. Therefore, the introduction of azo groups by the reaction of $\text{BaSO}_4\text{-HS}$ with ACPA using DCC as a condensing agent was examined.

TABLE 1. Analysis of BaSO₄-HS and BaSO₄-Azo by XPS

	BaSO ₄ -HS, %	BaSO ₄ -Azo, %
C _{1s}	1.0	43.4
O _{1s}	73.2	31.6
N _{1s}	0	10.5
S _{2p}	8.3	7.8
Ba _{3d}	17.5	6.7

Table 1 shows the results of surface analysis of BaSO₄-HS and barium sulfate obtained from the above reaction, i.e., BaSO₄-Azo, by XPS. From the results, the presence of nitrogen on the surface of BaSO₄-Azo was confirmed.

The amount of azo groups introduced onto the surface was determined by elemental (nitrogen) analysis to be 0.06 mmol/g. The difference in average particle size between BaSO₄-HS and BaSO₄-Azo was minute: 0.3 μm by SEM. This indicates that the average particle size of barium sulfate was not affected by the introduction of azo groups.

Initiating Activity of BaSO₄-Azo for the Polymerization of MMA

The polymerization of MMA was carried out in the presence of BaSO₄-Azo at 70°C, and the initiating activity of azo groups on the surface was examined. The results, shown in Table 2, are that the thermal polymerization of MMA proceeded even in the absence of initiator, although the rate of polymerization was negligibly small. Unmodified barium sulfate has no ability to initiate polymerization; conversion was equal to that of thermal polymerization. On the contrary, in the presence of BaSO₄-Azo the polymerization of MMA was initiated and gave polyMMA-grafted barium sulfate.

As shown in Table 2, ACPA-adsorbed barium sulfate failed to initiate polymerization. This suggests that ACPA adsorbed on barium sulfate surface during the introduction reaction of azo groups is removed almost completely by washing with THF.

TABLE 2. Polymerization of MMA Initiated by Azo Groups Introduced onto BaSO₄ Surface^a

BaSO ₄	Conversion, %	Grafting, %
None	0.2	—
Unmodified BaSO ₄	0.2	2.4
ACPA-adsorbed	0.8	4.3
BaSO ₄ -Azo	15.2	25.3

^aBaSO₄, 0.50 g; MMA, 10.0 cm³; 70°C; 1.5 hours.

Based on the above results, it is concluded that $\text{BaSO}_4\text{-Azo}$ has the ability to initiate the radical polymerization of MMA.

Proof of Grafting onto Barium Sulfate

Figure 1 shows the time vs conversion curve and the time vs percentage of grafting curve for the polymerization of MMA initiated by $\text{BaSO}_4\text{-Azo}$. Conversion was found to linearly increase, and the percentage of PMMA grafting onto the surface immediately increased at the initial stage of the polymerization but not after 1.5 hours.

The surface azo groups produce both surface radicals and fragment radicals, i.e., 4-cyanopentanoic acid radicals, by their decomposition. The former initiate graft polymerization from the surface, but the latter produce ungrafted polymer.

The grafting efficiency in the above polymerization conditions (the proportion of grafted polymer to total polymer formed), decreased with the progress of polymerization: the grafting efficiency after 0.5 and 1.5 hours was 21.4 and 8.9%, respectively.

This indicates that although the polymerization of MMA is started from surface radicals, the formation of ungrafted polymer preferentially proceeds because surface radicals are readily blocked by grafted polymer chains.

Graft Polymerization of Several Monomers

The radical graft polymerization of styrene and *N*-vinylcarbazole in the presence of $\text{BaSO}_4\text{-Azo}$ was examined. The results are shown in Table 3. It was found that the radical polymerization of these vinyl monomers is also successfully initiated by $\text{BaSO}_4\text{-Azo}$ to give the corresponding polymer-grafted barium sulfate.

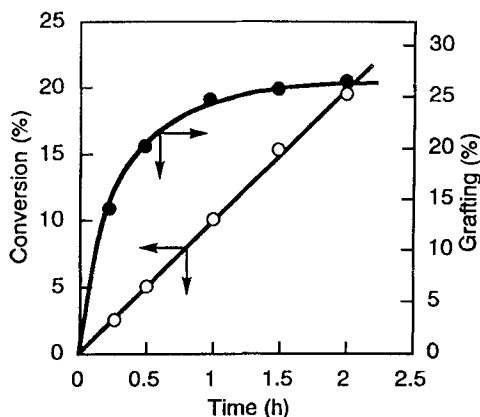


FIG. 1. Graft polymerization of MMA initiated by azo groups introduced onto BaSO_4 . $\text{BaSO}_4\text{-Azo}$, 0.50 g; MMA, 10.0 cm^3 ; 70°C.

TABLE 3. Graft Polymerization of Vinyl Monomers Initiated by BaSO₄-Azo

Monomer	Temperature, °C	Time, h	Conversion, %	Grafting, %
MMA ^a	70	1.5	15.2	25.3
Styrene ^a	80	2.5	17.9	10.3
NVC ^b	70	3.0	37.4	15.1

^aBaSO₄, 0.50 g; monomer, 10.0 cm³.

^bBaSO₄, 0.50 g; NVC, 0.30 g; benzene, 10.0 cm³.

Effects of Monomer and BaSO₄-Azo Concentration on the Polymerization Rate

Radical graft polymerization initiated by azo groups introduced onto the surface has been reported [4, 5, 15], but no kinetic study of such radical graft polymerization in a heterogeneous system has been reported. Therefore, the dependence of the polymerization rate of MMA and styrene initiated by BaSO₄-Azo on the monomer and initiator concentration was investigated.

Figure 2 shows the effect of monomer concentration on the polymerization rate (R_p) of styrene initiated by BaSO₄-Azo. It was found that the rate of polymerization increased with increasing styrene concentration. The plot of $\log R_p$ vs $\log[\text{Styrene}]$ is linear with a slope of 1, indicating first order with respect to monomer concentration.

Figure 3 shows the effect of BaSO₄-Azo concentration ($[\text{BaSO}_4\text{-Azo}]$) on the polymerization rate of styrene. The polymerization rate increased with increasing BaSO₄-Azo concentration. The plot of $\log R_p$ vs $\log [\text{BaSO}_4\text{-Azo}]$ is also linear with a slope of 1, indicating first order with respect to BaSO₄-Azo concentration.

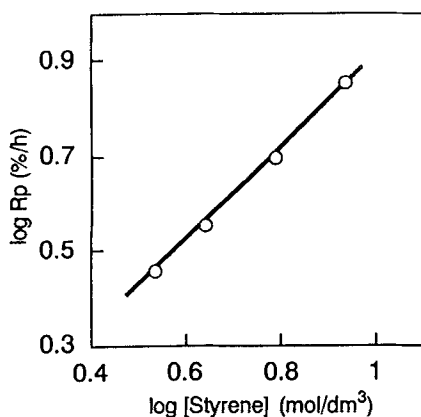


FIG. 2. Relationship between polymerization rate (R_p) and styrene concentration ($[\text{Styrene}]$). BaSO₄-Azo, 0.50 g; total volume (in benzene), 10.0 cm³; 70°C.

[7] and by the redox initiating system consisting of alcoholic hydroxyl groups and ceric ion [13].

CONCLUSIONS

1. Azo groups were introduced onto barium sulfate by direct condensation of hydroxyl groups on barium sulfate modified with 12-hydroxystearate groups with ACPA using DCC as a condensing agent.
2. The radical graft polymerization of vinyl monomers was initiated by surface radicals formed by the thermal decomposition of azo groups to give the corresponding polymer-grafted barium sulfate.

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