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Grafting of Polyesters from Aluminum Hydroxide Surface : Anionic Ring-Opening Copolymerization of Epoxides with Cyclic Acid Anhydrides Initiated by Surface COOK Groups Introduced onto the Surface

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Abstract

The grafting of polyesters from aluminum hydroxide powder surface by use of potassium carboxylate (COOK) groups introduced onto the surface was investigated. Three types of aluminum hydroxide having COOK groups were prepared by neutralization of surface acid anhydride or carboxyl groups with potassium carbonate. The introduction of acid anhydride groups was carried out by the reaction of surface hydroxyl groups with 4-trimethoxysilyltetrahydrophthalic anhydride or trimellitic anhydride. Carboxyl groups were successfully introduced by the hydrolysis of surface acid chloride groups, which were introduced by the reaction with terephthaloyl dichloride, with water. It was found that the anionic ring-opening alternating copolymerization of epoxides with cyclic acid anhydrides was successfully initiated by COOK groups on these aluminum hydroxide powder surfaces. The corresponding polyester was grafted onto the surface as a result of the propagation of a polymer from COOK groups introduced on the surface. The percentage of grafting of the polyester from epichlorohydrin and phthalic anhydride was determined to be 14.0%. The polymerization rate increased with increasing COOK group content on the surface.

Key-words : *Aluminum hydroxide, Surface grafting, Polyester, Potassium carboxylate group, Anionic ring-opening alternating copolymerization*

1. Introduction

Recently, aluminum hydroxide powder has been widely used as a filler of various polymer materials. For instance, aluminum hydroxide is known to act as a flame retardant in polymers

and paper, because of its high exothermic property at above 200°C. In addition, unsaturated polyester filled with aluminum hydroxide has been used as an artificial marble.

In general, it is very difficult to disperse inorganic particles uniformly into a polymer matrix. Furthermore, the mechanical properties of inorganic powder-polymer composites are considered to depend not only on the mechanical properties of the polymer matrix, but also

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on the properties of interfacial regions between the powder surface and the matrix polymer.

By surface grafting of polymers onto inorganic particles, the dispersibility in solvents and compatibility with polymer matrices are remarkably improved^{1)–4)}. In a previous paper, we reported the graft polymerization of vinyl monomers onto aluminum hydroxide by the radical polymerization of vinyl monomers initiated by azo groups introduced onto the surface⁵⁾. On the other hand, we also reported the grafting of polyesters onto inorganic powder surface, such as carbon black^{6),7)} and silica⁸⁾, by the anionic ring-opening copolymerization of epoxides with cyclic acid anhydrides initiated by potassium carboxylate (COOK) groups introduced onto these surfaces.

In the present paper, the introduction of COOK groups onto the surface of aluminum hydroxide powder (**Eq. 1**) and the surface grafting of polyesters by the anionic ring-opening alternating copolymerization of epoxides with cyclic acid anhydrides initiated by COOK groups (**Eq. 2**) were investigated.

2. Experimental

2.1 Materials

Aluminum hydroxide powder was obtained from Sumitomo Chemical Co. Ltd., Japan under the designation C-301. It was washed with pure water and dried *in vacuo* at 100°C. The properties of the powder are shown in **Table 1**. The content of hydroxyl groups was determined

Table 1 Properties of aluminum hydroxide powder used

	BET surface area (m ² /g)	Particle size (μm)	OH group (mmol/g)
Al(OH) ₃ ^{a)}	6.0	1.0	0.71

^{a)} C-301 (Sumitomo Chemical Co., Ltd.)

by a volumetrical measurement of the amount of ethane evolved by the reaction with triethylaluminum^{9),10)}.

Epichlorohydrin (ECH) and styrene oxide (SO) were dried over calcium hydride and distilled before use. Phthalic anhydride (PAn), maleic anhydride (MAAn), and succinic anhydride (SAn) were purified by recrystallization and sublimation under reduced pressure.

4-Trimethoxysilyltetrahydrophthalic anhydride (TSPA) was obtained from Nissan Chemical Co. Ltd., Japan and used without further purification. Trimellitic anhydride chloride (TMAH-Cl), terephthaloyl dichloride (TP-Cl), 18-crown-6, and *N*-phenyl-β-naphthylamine (NPNA) were obtained from Aldrich Chemical Co. and used without further purification.

Toluene and tetrahydrofuran (THF) were refluxed over sodium and distilled twice. Other reagents and solvents were used after ordinary purification.

2.2 Preparation of Al(OH)₃(1)-COOK

Aluminum hydroxide having surface COOK groups, Al(OH)₃(1)-COOK, was prepared by neutralization of surface acid anhydride groups, which were introduced by the treatment with TSPA⁸⁾, with potassium carbonate.

A typical example was as follows. Into a flask that contained 5.0 g of aluminum hydroxide, 150 cm³ of 5.0% toluene solution of TSPA was added. The reaction mixture was refluxed in a stream of nitrogen for 8 h. After the treatment, aluminum hydroxide was extracted with THF for 24 h and dried *in vacuo*.

The neutralization of acid anhydride groups on the surface was carried out as follows. Into a flask that contained 5.0 g of aluminum hydroxide having acid anhydride groups, 50.0 cm³ of 0.1%

potassium carbonate aqueous solution was added. The suspension was stirred with a magnetic stirrer for 3 h at room temperature. After the reaction, the powder was filtered, washed with distilled water until the filtrate was neutral, and dried *in vacuo* at 80°C. The treated aluminum hydroxide was stored *in vacuo* at room temperature.

2.3 Preparation of Al(OH)₃(2)-COOK

Aluminum hydroxide having surface COOK groups, Al(OH)₃(2)-COOK, was prepared by neutralization of surface acid anhydride groups, which were introduced by treatment with TMAH-Cl, with potassium carbonate.

A typical example was as follows. Into a flask that contained 5.0 g of aluminum hydroxide, 50.0 cm³ of THF, and 4.0 cm³ of triethylamine, 6.30 g of TMAH-Cl was added. The reaction mixture was stirred with a magnetic stirrer at 50.0°C for 8 h. After the treatment, aluminum hydroxide was filtered, washed with THF and water, and dried *in vacuo*.

The neutralization of surface acid anhydride groups with potassium carbonate was carried out by the same methods as described above.

2.4 Preparation of Al(OH)₃(3)-COOK

Aluminum hydroxide having surface COOK groups, Al(OH)₃(3)-COOK, was prepared by neutralization of surface carboxyl groups, which were introduced by treatment with TP-Cl, with potassium carbonate.

A typical example was as follows. Into a flask that contained 5.0 g of aluminum hydroxide, 50.0 cm³ of THF, and 0.6 cm³ of triethylamine, 2.88 g of TP-Cl was added. The reaction mixture was stirred with a magnetic stirrer at 50.0°C for 8 h. After the treatment, aluminum hydroxide was filtered, washed with THF and water, and dried *in vacuo*.

The neutralization of surface carboxyl groups with potassium carbonate was carried out by the same methods as described above.

2.5 Determination of Carboxyl Group Content of Aluminum Hydroxide

The carboxyl group content of treated aluminum hydroxide powder was determined by the titration with aqueous alkali. A typical example was as follows. Into a flask that contained 0.30 g of aluminum hydroxide, 30.0 cm³ of 0.01 N NaOH aqueous solution was added. The mixture was stirred at room temperature for 30 min. Aluminum hydroxide was filtered and 5.0 cm³ of the filtrate was titrated with 0.01 N HCl aqueous solution.

2.6 Polymerization Procedure

Into a flask, 0.30 g of aluminum hydroxide, 0.01 mol of epoxide, 0.01 mol of cyclic acid anhydride, 0.02 g of 18-crown-6, and 0.02 g of NPNA were charged. The reaction mixture was stirred with a magnetic stirrer under nitrogen at 120 °C. After a definite time, the content of the flask was poured into a large excess of methanol to precipitate the polymer-containing aluminum hydroxide. The conversion was determined by using the following equation :

$$\text{Conversion (\%)} = \frac{A}{B} \times 100$$

A = Precipitate (g) – Aluminum hydroxide used (g)

B = Epoxides and cyclic acid anhydrides used (g)

2.7 Percentage of Grafting

For the isolation of polyester-grafted aluminum hydroxide from the reaction product, the product was dispersed in THF and the dispersion was centrifuged at 5.0×10^3 rpm until aluminum hydroxide was precipitated completely. The precipitated aluminum hydroxide was dispersed in THF again and centrifuged. The procedures were repeated until no more polyester was detected in the supernatant solution. The percentage of grafting was determined by the following equation :

$$\text{Grafting (\%)} = \frac{\text{Polyester grafted (g)}}{\text{Aluminum hydroxide used (g)}} \times 100$$

3. Results and Discussion

3.1 Introduction of COOK Groups onto Aluminum Hydroxide Powder

In a previous paper, we reported that COOK groups were successfully introduced onto ultrafine silica surface by the neutralization of acid anhydride groups, which were introduced by treatment with TSPA, with potassium carbonate⁸⁾. In the present paper, the introduction of COOK groups onto aluminum hydroxide surface by neutralization of cyclic acid anhydride or carboxyl groups with potassium carbonate was examined.

The introduction of surface acid anhydride or carboxyl groups was carried out by three methods: reactions of surface hydroxyl groups with (1) TSPA, (2) TMAH-Cl, and (3) TP-Cl as shown in Eqs. 3, 4, and 5. Aluminum hydroxide having COOK groups prepared by the methods (1), (2), and (3) were abbreviated as $\text{Al}(\text{OH})_3(1)\text{-COOK}$, $\text{Al}(\text{OH})_3(2)\text{-COOK}$, and $\text{Al}(\text{OH})_3(3)\text{-COOK}$, respectively.

Table 2 Amount of COOK groups introduced onto the surface of aluminum hydroxide

$\text{Al}(\text{OH})_3$	COOK group (mmol/g)
$\text{Al}(\text{OH})_3(1)\text{-COOK}$	0.12
$\text{Al}(\text{OH})_3(2)\text{-COOK}$	0.20
$\text{Al}(\text{OH})_3(3)\text{-COOK}$	0.24

Table 2 shows the COOK group content of $\text{Al}(\text{OH})_3(1)\text{-COOK}$, $\text{Al}(\text{OH})_3(2)\text{-COOK}$, and $\text{Al}(\text{OH})_3(3)\text{-COOK}$. The COOK group content was determined from the carboxyl group content of aluminum hydroxide, because surface carboxyl groups quantitatively react with potassium carbonate.

As shown in Table 2, the introduction of COOK groups was successfully achieved by the reactions shown in Eqs. 3, 4, and 5. The COOK group content decreased in the following order; $\text{Al}(\text{OH})_3(3)\text{-COOK} > \text{Al}(\text{OH})_3(2)\text{-COOK} > \text{Al}(\text{OH})_3(1)\text{-COOK}$.

3.2 Copolymerization of ECH with PAn Initiated by $\text{Al}(\text{OH})_3(1)\text{-COOK}$

Alkali metal carboxylates such as sodium acetate are well known to have the ability to initiate the anionic ring-opening copolymerization of epoxides with cyclic acid anhydrides to give the corresponding polyesters¹¹⁾. We succeeded in grafting of polyesters onto carbon black^{6),7)} and ultrafine silica⁸⁾ by the anionic ring-opening copolymerization of epoxides with cyclic acid anhydrides initiated by alkali metal carboxylate groups introduced onto the surfaces.

Therefore, the anionic ring-opening copolymerization of ECH with PAn was also carried out in the presence of $\text{Al}(\text{OH})_3(1)\text{-COOK}$ under several conditions. The results are shown in **Table 3**. In the polymerization, 18-crown-6 and NPNA were added to accelerate the copolymerization and to inhibit thermal polymerization, respectively.

As is seen in Table 3, the copolymerization of ECH with PAn could not be detected in the absence or in the presence of untreated aluminum hydroxide. In addition, neither ECH nor PAn alone was polymerized by $\text{Al}(\text{OH})_3(1)\text{-COOK}$.

Table 3 Copolymerization of ECH with PAn initiated by COOK groups introduced onto aluminum hydroxide powder surface

Al(OH) ₃	ECH (mol)	PAn (mol)	Conversion (%)	Grafting (%)
None	0.01	0.01	0	—
Untreated	0.01	0.01	0	—
Al(OH) ₃ (1)-COOK	0.01	—	0	—
Al(OH) ₃ (1)-COOK	—	0.01	0	—
Al(OH) ₃ (1)-COOK	0.01	0.01	15.1	14.0

Al(OH)₃, 0.30 g; 18-crown-6, 0.02 g; NPNA, 0.02 g; 120°C; 2 h.

COOK. On the contrary, when equimolecular amounts of ECH and PAn were heated at 120°C in the presence of Al(OH)₃(1)-COOK, the copolymerization was found to be initiated to give the corresponding polyester-grafted aluminum hydroxide: The polymer formed was identified as the expected polyester by IR and ¹H-NMR spectra: IR (KBr): 1722 (vs; C=O), 1660 and 1581 (m; *o*-phenylene), 1120 (s; C-O-C), and 1070 cm⁻¹ (s; C-O-C); ¹H-NMR (CDCl₃): δ = 3.62–3.99 (2H, -CH₂Cl), 4.41–4.75 (2H, -CH₂O-), 5.33–5.70 (1H, >CH-), and 7.32–7.85 ppm (4H, *o*-phenylene).

3.3 Initiating Activity of Al(OH)₃(2)-COOK and Al(OH)₃(3)-COOK

The initiating activity of Al(OH)₃(2)-COOK and Al(OH)₃(3)-COOK for the copolymerization of SO with PAn was compared with that of Al(OH)₃(1)-COOK. The results are shown in Table 4.

It was found that Al(OH)₃(2)-COOK and Al(OH)₃(3)-COOK also have the ability to initiate the copolymerization of SO with PAn to give the corresponding polyester-grafted aluminum hydroxide. The initiating activity was found to

Table 4 Copolymerization of SO with PAn initiated by aluminum hydroxide having COOK groups

Al(OH) ₃	Conversion (%)	Grafting (%)
Al(OH) ₃ (1)-COOK	50.1	3.0
Al(OH) ₃ (2)-COOK	60.1	3.8
Al(OH) ₃ (3)-COOK	76.8	8.1

Al(OH)₃, 0.30 g; SO=PAn=0.01 mol; 18-crown-6, 0.02 g; NPNA, 0.02 g; 120°C; 2 h.

tend to increase with increasing COOK group content.

The percentage of grafting of polyester onto aluminum hydroxide was considerably small even at high conversion. This is due to the fact that the Al-O-Si- and Al-O-CO- bonds, with which carboxyl groups are supported on the surface, undergo hydrolysis during the polymerization at high temperature, 120°C.

3.4 Proof of Polyester Grafting onto Aluminum Hydroxide

Figure 1 shows the time-conversion curves of the anionic ring-opening copolymerization of SO with PAn at 120°C in the presence of Al(OH)₃(1)-COOK, Al(OH)₃(2)-COOK, and Al(OH)₃(3)-COOK. As mentioned above, the rate of the polymerization of SO with PAn was found to increase with increasing COOK group content.

Figure 2 shows the relationship between polymerization time and percentage of grafting of polyester onto aluminum hydroxide obtained from the polymerization shown in Figure 1. It

Fig. 1 Anionic copolymerization of SO with PAn initiated by Al(OH)₃(1)-COOK, Al(OH)₃(2)-COOK, and Al(OH)₃(3)-COOK. Al(OH)₃-COOK, 0.30 g; SO=PAn=0.01 mol; 18-crown-6, 0.02 g; NPNA, 0.02 g; 120°C.

Fig. 2 Percentage of polyester grafting onto $\text{Al}(\text{OH})_3$ surface obtained from the polymerization of SO with PAn. Polymerization conditions are given in Figure 1.

was found that the percentage of grafting of polyester increased with increasing conversion. The percentage of polyester grafting onto aluminum hydroxide increased with increasing COOK group content.

No proportional relationship between COOK content and the polymerization rate and percentage of grafting, however, was observed. This may be due to the difference in easiness of hydrolysis of ester bond with which COOK group is supported.

Figure 3 shows IR spectra of untreated and poly(SO-*alt*-PAn)-grafted aluminum hydroxide. Infrared spectra of the polyester-grafted aluminum hydroxide show new absorptions at 1734 cm^{-1} , which is characteristic of the carbonyl of ester bond, and at 1669 and 1580 cm^{-1} , which are characteristic of the phenyl group.

Based on the above results, it is concluded that the anionic ring-opening copolymerization of SO with PAn is initiated by COOK groups on the surface and the corresponding polyester, i.e., poly(SO-*alt*-PAn) is grafted onto aluminum hydroxide as a result of the propagation of the

Fig. 3 Infrared spectra of (A) untreated $\text{Al}(\text{OH})_3$ and (B) poly(SO-*alt*-PAn)-grafted $\text{Al}(\text{OH})_3$.

polyester from surface COOK groups.

3.5 Grafting of Polyester from Several Epoxides with Cyclic Acid Anhydrides

The grafting of polyesters onto aluminum hydroxide by the anionic copolymerization of several epoxides with cyclic acid anhydrides initiated by COOK groups introduced onto the surface was examined. The results are summarized in **Table 5**. As shown in Table 5, it is apparent that COOK groups introduced onto aluminum hydroxide have an ability to initiate the anionic ring-opening copolymerization of epoxides with cyclic acid anhydrides to give the corresponding polymer-grafted aluminum hydroxide. In the copolymerization of ECH with MAn, the gel containing aluminum hydrox-

Table 5 Grafting of polyesters onto aluminum hydroxide by the copolymerization of several epoxides with cyclic acid anhydrides^{a)}

Epoxide	Anhydride	Time (h)	Conversion (%)	Grafting (%)
SO	PAn	2	76.8	8.1
SO	MAn	4	32.0	8.3
SO	SAn	7	30.6	7.1
ECH	MAn	6	30.4	78.2 ^{b)}

^{a)} $\text{Al}(\text{OH})_3(3)$ - COOK, 0.30 g; Epoxide = Anhydride = 0.01 mol; 18-crown-6, 0.02 g; NPNA, 0.02 g; 120°C .

^{b)} Gelation

ide was obtained. This may be due to the fact that unsaturated polyester formed was thermally cross-linked because of a high polymerization temperature.

All of the polymers obtained from the copolymerizations shown in Table 5 were identified as the corresponding alternating polyesters by IR and $^1\text{H-NMR}$ spectra.

4. Conclusions

1. Potassium carboxylate groups were successfully introduced onto aluminum hydroxide powder surface.

2. The anionic ring-opening copolymerization of epoxides with cyclic acid anhydrides was successfully initiated by the surface COOK groups.

3. During the copolymerization, the corresponding polymer, i.e., polyester, was effectively grafted onto the aluminum hydroxide surface as a result of the propagation of the polymer from

the surface COOK groups.

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