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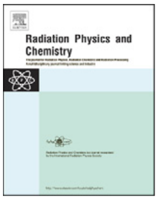

Radiation-induced graft polymerization of amphiphilic monomers with different polymerization characteristics onto hydrophobic polysilane

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ABSTRACT

The structures of poly(methyl-*n*-propylsilane) (PMPrS) amphiphilically modified through γ-ray-induced graft polymerization were investigated with ^{1}H NMR measurement. By the use of methyl methacrylate (MMA) or diethyl fumarate (DEF) as monomers for the graft polymerization, grafting yield rose with increasing total absorption dose and monomer concentrations, but decreased with increasing dose rate. This result means that grafting yield of modified PMPrS can be controlled by changing irradiation conditions. However, the number of PMMA or PDEF graft chains per PMPrS chain was estimated to be less than 1.0 by analysis of ^{1}H NMR spectra, and this value was lower than that we had expected. To improve graft density, maleic anhydride (MAH), which is known as a non-homopolymerizable monomer in radical polymerization, was used as a monomer for grafting. As a result, high density grafting (one MAH unit for 4.2 silicon atoms) was attained. It demonstrates that the structure of γ-ray-modified polysilane strongly depends on the polymerization characteristics of grafted monomers.

1. Introduction

Polysilane has attracted much attention because it has unique properties arising from delocalized electrons along the silicon backbone (Miller and Michl, 1989; West, 1986, 1992). If polysilane is applied to fabricate ordered materials in the nanometer scale, further unique properties can be developed. The utilization of self-assemblies is considered as powerful methods for preparing ordered structures. Since it is widely known that amphiphilic block or graft copolymers can form self-assemblies such as micelles and oriented Langmuir monolayers (Alexandridis and Lindman, 2000; Riess, 2003; Webber et al., 1996), amphiphilic polysilane copolymers are also expected to serve as ordered materials.

For the synthesis of polysilane copolymers with hydrophilic or amphiphilic chains, we can consider the following two approaches: the modification of presynthesized hydrophobic polysilane and the direct polymerization of monomeric silanes with hydrophilic or amphiphilic groups. In the latter case, however, the Wurtz-type coupling reaction, which is commonly used for the synthesis of polysilane, cannot be applied because sodium metal used in the reaction violently attacks reactive functional groups (Miller and Michl, 1989; West, 1986). Thus, this method is limited in its use. In contrast, the former method is free from such a limitation. Therefore we studied the modification of presynthesized polysilane to obtain polysilane-based amphiphilic graft copolymers by utilizing γ-ray-induced graft polymerization.

In the present study, we investigated the structures of amphiphilic graft polysilane modified under various irradiation conditions to establish optimized irradiation. As a hydrophobic base polymer for the graft polymerization, poly(methyl-*n*-propylsilane) (PMPrS) was employed. For grafted molecules, three types of monomers bearing hydrophilic groups were used: methyl methacrylate (MMA), diethyl fumarate (DEF) and maleic anhydride (MAH). MMA and DEF are homopolymerizable monomers having different propagation rate constants, while MAH is known as a non-homopolymerizable monomer in radical polymerization (Hodge et al., 1985, 1990). It can be expected that the structure and property of modified PMPrS differ according to the polymerization characteristics of these grafted monomers. In each experiment performed with the grafting monomers, we tried to control grafting yield, which is defined as monomer units of grafted chains per silicon atom of PMPrS, by changing irradiation conditions such as total absorption dose, dose rate and the concentrations of grafting monomers.

2. Experimental

2.1. Monomers

Methyl-*n*-propyldichlorosilane (Shin-Etsu Chemical, Co.), methyl methacrylate (MMA) (Nakalai Tesque, Inc.) and diethyl fumarate (DEF) (Nakalai Tesque, Inc.) were used after purification

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Table 1
Number average molecular weight (M_n) and polydispersity index (PDI) of PMPrS.

	$M_n \times 10^{-4}$	PDI
PMPrS1	1.3	2.4
PMPrS2	1.2	3.8
PMPrS3	1.1	3.8

by reduced-pressure distillation. Maleic anhydride was employed after purification by re-crystallization with toluene.

2.2. *Synthesis of PMPrS*

PMPrS was synthesized via the Wurtz-type coupling reaction of methyl-*n*-propyldichlorosilane. Crude PMPrS was purified by re-precipitation from a toluene solution into methanol, and then pure PMPrS was obtained by freeze-drying from a benzene solution. The number average molecular weight of PMPrS used in the following experiments is listed in Table 1. PMPrS1, PMPrS2 and PMPrS3 were employed for grafting poly(methyl methacrylate) (PMMA), poly(diethyl fumarate) (PDEF) and MAH, respectively.

2.3. *Radiation-modification of PMPrS*

PMMA-grafted PMPrS (PMPrS-*g*-PMMA), PDEF-grafted PMPrS (PMPrS-*g*-PDEF) and MAH-grafted PMPrS (PMPrS-*g*-MAH) were synthesized as follows: PMPrS and each monomer were co-dissolved in toluene. The toluene solution was degassed and sealed in a glass tube, and then irradiated with ^{60}Co-γ-rays at room temperature.

In the case of PMPrS-*g*-PMMA, the toluene solution after γ-irradiation was poured into methanol to precipitate a product. To remove PMMA homopolymer contained in the crude product, the precipitate was purified by fractional precipitation with acetone/methanol. Acetone is a good solvent for PMMA but a poor solvent for PMPrS, and methanol is a poor solvent for both PMMA and PMPrS. When a small amount of a toluene solution of the crude product was dropped into a large amount of acetone, PMPrS-*g*-PMMA formed emulsions. By adding methanol into the acetone solution containing the emulsions of the product, four regimes were found according to the methanol amount. In the first regime, no changes were recognized in spite of methanol addition. In the second regime, however, further methanol addition caused the solution more opaque and the amount of centrifuged precipitates was increased. In the third regime, the amount of precipitates was constant independent of the methanol amount, but in the fourth regime, precipitates obtained were again increased with increasing methanol amount. PMPrS-*g*-PMMA was successfully recovered in the second regime. After the fractional precipitation, PMPrS-*g*-PMMA was freeze-dried with benzene.

The purity of PMPrS-*g*-PMMA obtained was verified by iodine-staining thin-layer chromatography (TLC) with a silica plate and an eluent of a tetrahydrofuran (THF)/toluene (4/6, v/v) mixture. The eluent could separate PMPrS-*g*-PMMA and PMMA homopolymer completely. In the TLC experiment with purified PMPrS-*g*-PMMA, we could not recognize the spot of PMMA homopolymer. This fact indicates that the amount of PMMA contained was under the detection limit in the purified product. The detection limit of PMMA was determined in another TLC experiment, and finally the content of PMMA homopolymer in PMPrS-*g*-PMMA was found to be less than 1.0 wt%.

In the case of PMPrS-*g*-PDEF, solvent toluene was removed by evaporation from the reaction solution after irradiation, and then crude PMPrS-*g*-PDEF was freeze-dried from a benzene solution. Next, PMPrS-*g*-PDEF was precipitated from a THF solution into water, and recovered again by freeze-drying after unreacted DEF monomers contained in the precipitate were removed by filtration. This re-precipitation procedure was repeated 3–5 times. Some products containing PDEF homopolymer above 1.0 wt% were further purified by fractional precipitation with THF/hexane. THF is a good solvent for both PMPrS and PDEF, while hexane is a good solvent only for PMPrS but not for PDEF. When hexane is added to the THF solution of the product, PMPrS-*g*-PDEF forms emulsions and PDEF homopolymer precipitates. Accordingly, PDEF homopolymer could be removed by centrifugation after successive addition of hexane. Finally, the product was freeze-dried twice from a benzene solution and then vacuum-dried for 40 h to remove water completely.

The purity of PMPrS-*g*-PDEF was verified by TLC with a methanol eluent and a sulfuric acid stain in the same manner as described above. The content of PDEF homopolymer was also found to be less than 1.0 wt%.

In the case of PMPrS-*g*-MAH, solvent toluene was removed by evaporation from the reaction solution after irradiation. Pure PMPrS-*g*-MAH was isolated from the crude product by solvent extraction with hexane and then obtained by freeze-drying from a benzene solution. The content of unreacted MAH was checked to be less than 0.5 wt% by GPC with a UV detector.

2.4. *Spectroscopy*

^{1}H NMR spectra were recorded on a JEOL EX 400 spectrometer at 25 or 55 °C in deuterated chloroform solutions.

2.5. *Evaluation of grafting yield*

Grafting yield, which we define as the number of monomer unit per silicone atom of PMPrS, was calculated from the intensity ratio of ^{1}H NMR signals. In reference to the integrated signal intensity for a methyl proton of PMPrS ($SiCH_3$, δ 0.25 ppm), the intensity ratios of a methyl proton of PMMA ($COOCH_3$, δ 3.7 ppm) for PMPrS-*g*-PMMA, a methylene proton of PDEF ($COOCH_2CH_3$, δ 4.2 ppm) for PMPrS-*g*-PDEF and a methine proton of MAH (CHCH, δ 2.0–5.0 ppm) for PMPrS-*g*-MAH were calculated to evaluate their grafting yields.

3. Results and discussion

3.1. *Irradiation effect on PMPrS*

The molecular weight of PMPrS modified with grafted chains should become larger than that of PMPrS irradiated without monomers. Therefore, we examined the change of molecular weight of PMPrS when PMPrS was irradiated by γ-rays with and without MMA monomers in toluene. Fig. 1 shows the variation of molecular weight depending on dose. When PMPrS alone is irradiated with γ-rays, its molecular weight decreases with an increase of dose. This result indicates that PMPrS is degraded by γ-rays. When PMPrS is irradiated together with MMA, on the other hand, the decrease of the molecular weight is smaller. One reason is that MMA monomers shows protection effect on PMPrS degradation by absorbing γ-rays and consuming radicals. Moreover, PMMA grafting on PMPrS is also responsible for this smaller molecular weight decrease. The result obtained here suggests that γ-irradiation successfully causes the graft polymerization of MMA onto PMPrS in spite of degradation of PMPrS.