

Graft Polymerization of Triethoxyvinylsilane-Styrene and Triethoxyvinylsilane-Methyl Methacrylate Binary Monomers onto Various Silicates

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Synopsis

Triethoxyvinylsilane-styrene and triethoxyvinylsilane-methyl methacrylate binary monomers were polymerized by chemical initiation or by γ -ray irradiation in the presence of silica gel, fire brick, quartz wool, and glass beads. The amount and composition of the polymers grafted to silicates were analyzed by using pyrolysis gas chromatography. When triethoxyvinylsilane alone was subjected to the reaction with silicates, condensation occurred irrespective of the initiating means, and the extent of the reaction was almost proportional to the specific surface area of the silicate. When binary monomer mixture was applied, incorporation of styrene or methyl methacrylate into the grafted polymer was observed whenever a monomer mixture of high styrene or methyl methacrylate content was submitted to the reaction. On each silicate, the relationship between the composition of polymer grafted on it and that of monomer showed a similar pattern in spite of the great difference of the specific surface area. Almost no participation of styrene or methyl methacrylate was observed when the silicate preirradiated in air or under vacuum was heated with the binary monomer mixture. It was concluded that triethoxyvinylsilane reacts with silicates by condensation and that some of the pendent vinyl groups on the silicates are incorporated into the copolymer with styrene or methyl methacrylate.

INTRODUCTION

The grafting of organic polymer onto inorganic macromolecular materials is a fascinating problem not only in view of the widespread field of industrial application, but also because of the fundamental researches. Reactive organosilicon compounds as alkoxyvinylsilanes are regarded to possess the ability to react with silicates and also with vinyl monomers to form copolymers. The pretreatment of glass fibers with such reactive organosilicon compounds is a well-known sizing process to improve the strengths of the glass fiber-reinforced plastics. The formation of chemical bonding as Si—O—Si is generally recognized between the glass surface and such compounds, although other interpretations on the nature of reaction are still seen in the literature.¹ Besides glass fibers, many kinds of silicates were used for similar reactions.^{2,3} The reaction of copolymer composed of condensable vinylsilane and ordinary vinyl monomers with silicates could also be added to this category of study.⁴

On the other hand, the polymerization of the vinyl monomers adsorbed on silicic acid and others was well investigated to date mainly in the radiation-

chemical field, and the occurrence of ionic grafting along with that by radical mechanism has been discussed.^{5,6,7}

In several fields of investigation, one important problem seemed to be the difficulty of grafting organic polymer effectively enough for practical use on inorganic substances such as silicates. We have intended to graft copolymerize substantial amounts of organic polymers onto inorganic siloxane derivatives by the combination of silanol condensation and addition polymerization. As the reaction of active vinylsilane-vinyl compound binary monomers with silicates directly to form graft copolymer have hardly been studied yet, a few of the common vinyl monomers mixed with triethoxyvinylsilane were polymerized in the presence of silicates by such means as chemical initiation or γ -irradiation, and the polymers inseparable from the silicates were studied for the possible occurrence of grafting reaction between them.

EXPERIMENTAL

Materials

Five silicic compounds including silicic acid and some silicates which widely differed from each other in specific surface areas (called silicates for convenience in the following description) were chosen as the backbone materials: (a) silica gel, 30-60 mesh for gas chromatography (Nishio Kogyo Co. Ltd.); (b) crushed fire brick, 30-60 mesh for gas chromatography (C-22, Yanagimoto Seisakusho Co. Ltd.); (c) glass beads, 210-297 μ in diameter (GB 740K, Tokyo Shibaura Electric Co. Ltd.), washed with concentrated H_2SO_4 and water; (d) quartz wool, 2-4 μ thick (Grade Fine, Nippon Quartz Glass Co. Ltd.); (e) asbestos (Wako Pure Chemical Industries). The silicates, except the glass beads, were used without further purification.

Triethoxyvinylsilane (EVS) was purified by distillation under reduced pressure. Styrene (ST) and methyl methacrylate (MMA) were purified by the ordinary procedures.

Polymerization Initiated by Benzoyl Peroxide (BPO)

The binary monomer mixture of EVS-ST or EVS-MMA, 2.0 to 2.5 ml, containing 0.005 g of BPO per 1 ml mixture, was poured on silicates, 0.3 to 0.5 g, in the glass tube. The glass tubes were sealed off at 10^{-4} mm Hg after thorough degassing with a freeze-thaw cycle, and the mixture was polymerized to the appropriate extent in a thermoregulated water bath. After the polymerization, the reacted silicates were washed with benzene⁷ and separated from the solution by glass filters. The silicates in the glass filters were dipped in benzene and thoroughly washed with benzene for a few days, and finally dried *in vacuo* to weigh the unextractable polymer (the organic substance unextractable by this procedure is called the unextractable polymer hereafter).

Polymerization by γ -Irradiation

Both in-source polymerization and postpolymerization were carried out to graft polymerize the binary monomers on silicates. In in-source polymerization, the ampoule was prepared the same way as above without the addition of BPO

and was irradiated with γ -rays from a ^{60}Co source at a dose rate of 2×10^4 or 2×10^5 R/hr at 25°C . In postpolymerization, binary monomers were added to the silicates which had been irradiated previously with γ -rays at a dose rate of 1×10^6 R/hr for 107 hr in air at 25°C and sealed under vacuum by the way already described, followed by heating for a given time in the thermoregulated water bath.

In a few cases, the silicates were sealed under 10^{-4} mm Hg into the glass ampoule equipped with a branch having a breakable seal. After irradiation, the other tube containing the monomer mixture was attached to the branch of the irradiated ampoule, and the monomer part was then sealed *in vacuo*. Then the monomer mixture was introduced to the irradiated silicates by breaking the seal between the monomer and the silicate.

Determination of Amount and Composition of Unextractable Polymer

The unextractable polymer supposedly reacted with or grafted onto the silicates should result in an overall increase in weight of the silicates; and actually a weight increase of 15% to 30% was observed for the silica gel subjected to reaction. In the cases of glass beads and fire brick, however, the increase in weight was too small to be measured. Regarding the reacted silica gel, carbon, and hydrogen analyses (by CHN-Corder, Model MT-2, Yanagimoto Seisakusho Co. Ltd.) afforded information on the amount and composition of the unextractable polymer to some extent, although a carbonized part was found to remain in the central domain of silica gel granules after baking of the EVS-containing silica gel for analysis. Nevertheless, this method was completely useless for obtaining information on other silicates owing to extremely low amount of unextractable polymer.

Therefore, the pyrolysis gas chromatography was adopted to determine the amount and composition of the unextractable polymer throughout the experiment. Pyrolysis of the reacted silicates was carried out in a hot tubular reactor, and the degradation products were analyzed with a Hitachi Model K-53 FID gas chromatograph combined with a Perkin-Elmer Printing Integrator 194B.⁸

Figure 1(a) and 1(b) show typical pyrolysis gas chromatograms of silicates containing polymers composed of ST or EVS. The most favorable pyrolysis temperature for both constituents was 650°C . Silicates which contained polymers composed of both ST and EVS developed peaks of both constituents some of which overlapped. Whereas the ST content can be calculated independently from the area of the peak ($t_R = 1.43$) as seen from Figure 1(c), some correction as to the contribution of polyST was inevitable for calculating EVS content from the peak of the lowest retention time ($t_R = 0.21$). The overlapping was more serious in the case of silicates onto which MMA-EVS was grafted, shown in Fig. 1(a')-1(c'), in spite of the change in optimum experimental conditions.

The extent of grafting was calculated to be 100 times the amount of unextractable polymer obtained from pyrolysis divided by the original weight of silicate, called $G\%$ for brevity.

Characterization of Reacted Silicates

Some of the reacted silica gel was stirred in concentrated hydrofluoric acid for 1 hr to separate the organic polymer from the silicate. After washing once,

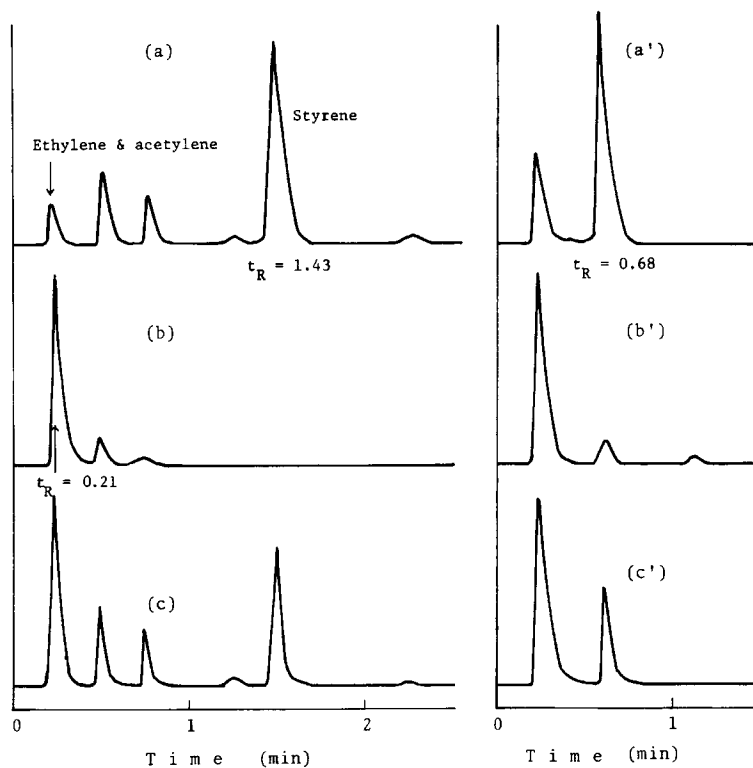


Fig. 1. Typical pyrolysis gas chromatograms of silicates containing various polymers: (a) silicates containing polyST, (b) those containing polyEVS, (c) those containing poly(EVS-ST), (a') those containing polyMMA, (b') those containing polyEVS, (c') those containing poly(EVS-MMA); (a)-(c) 15 sec pyrolysis at 650°C, column temperature, 150°C; (a')-(c') 15 sec pyrolysis at 550°C, column temperature, 120°C; column, Apiezon L, 2 m; detector, FID; carrier gas, He.

the treatment was repeated and the remaining moiety washed with water and methanol and dried in a desiccator.

Specific surface areas of silicates were measured by the ordinary B.E.T. method with nitrogen.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the reacted silicates were performed simultaneously by using a Rigaku Denki TGA-DTA apparatus at a temperature elevation of 5°C/min.

RESULTS

Reaction of Silicates with Triethoxyvinylsilane

While silica gel was treated with EVS in various ways, about 20% by extent of grafting of EVS seemed to react with silica gel independently of the presence of the substance which afforded free radicals, as seen in Table I. In the case of simultaneous irradiation, somewhat higher *G*% was observed. As prolonged evacuation of silica gel at 450°C or treatment with H₂SO₄ or NaOH prior to the operation did not bring about any significant improvement in the amount of

TABLE I
Reaction of Silicates with Triethoxyvinylsilane^a

Silicate	Reaction method	Temp., °C	Reaction time, hr	G% from wt. increase ^b	G% from pyro. GC	G% calcd. from sp. surface area	Remarks
Silica gel (481 m ² /g) ^c	heating	46	16	15.4	16.3	28.1	
Silica gel (481 m ² /g) ^c	heating	63	16	24.7	24.5	28.1	
Silica gel (481 m ² /g) ^c	heating	72	16	18.3	26.0	28.1	soaked in concd. H ₂ SO ₄ heated for 4 hr at 450° C in vacuo
Silica gel (481 m ² /g) ^c	heating with 0.5% BPO	63	16	19.5	13.0	28.1	
Silica gel (481 m ² /g) ^c	simult. irradi.	25	105	34.1	36.1	28.1	
Silica gel (preirrad.)	heating	72	17	20.7	22.4	28.1	2 × 10 ⁵ R/hr 10 ⁸ R preirrad. at 25° C in air
Fire brick (6.6 m ² /g) ^c	heating with 0.5% BPO	72	17	—	0.28	0.39	
Fire brick (6.6 m ² /g) ^c	simult. irradi.	25	105	—	0.78	0.39	
Fire brick (preirrad.)	heating	72	17	—	0.28	0.39	2 × 10 ⁵ R/hr 10 ⁸ R preirrad. at 25° C in air
Glass beads [(0.03 m ² /g)] ^c	heating with 0.5% BPO	72	17	—	0.02	(0.002)	
Glass beads (preirrad.)	heating	72	17	—	0.02	(0.002)	10 ⁸ R preirrad. at 25° C in air

^a Silicates, 0.5 g; EVS, 2.0 ml.

^b G% = 100 (P - P₀)/P₀.

^c Specific surface area.

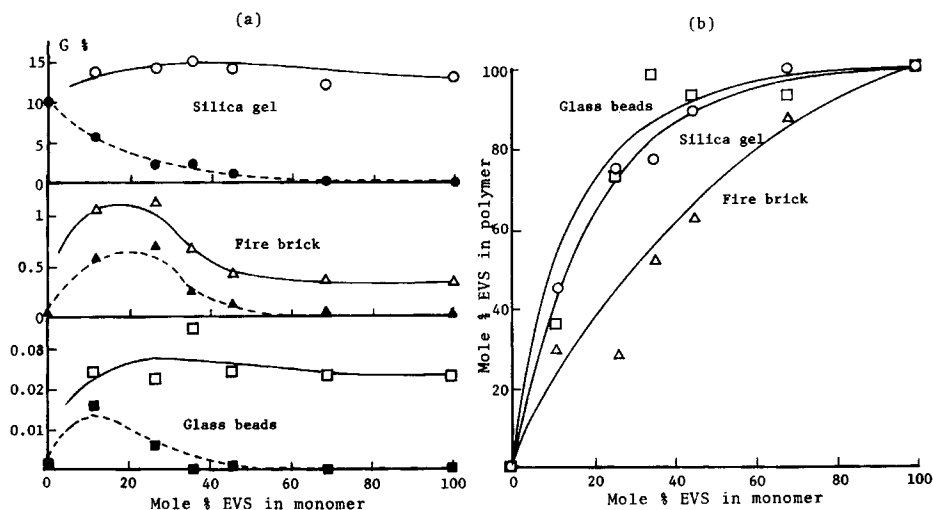


Fig. 2. Reaction of triethoxyvinylsilane-styrene binary monomers with silicates by the initiation of benzoyl peroxide (0.5%). Effect of monomer composition on (a) the amount of the unextractable polymer and on (b) the composition of the unextractable polymer: reaction time, 17 hr at 63°C for silica gel, 17 hr at 72°C for fire brick and glass beads; (a) (○ △ □) overall G%; (● ▲ ■) G% of ST monomeric unit in the unextractable polymer.

reacted EVS, the silicates were used in the subsequent experiments without further chemical or heat treatment.

Alternatively, the amount of unextractable polymer appeared to be proportional to the specific surface area of silicates. The calculated G% was shown in Table I, which is the required amount of EVS when the surface of silicate is assumed to be covered monomolecularly with EVS. The coincidence of the amount of unextractable polymer with the calculated one is fairly satisfactory, except for the case of glass beads. The specific surface area of the glass beads was too small to obtain a reliable value by the B.E.T. method.

The overall results show that the main reaction of EVS with silicates is the condensation with the silanol group on the surface of the silicates by releasing ethanol, with the vinyl group left unchanged on the surface. In the simultaneous irradiation method, part of the reacted EVS is possibly polymerized to grafted oligomer.⁹

Reaction of Silicates with EVS-ST or EVS-MMA Binary Monomers by Initiation of BPO

Figure 2(a) shows the overall amount of the unextractable polymer and the content of ST monomeric unit in the unextractable polymer as a function of monomer composition. Although the overall amount of the unextractable polymer was not significantly affected by monomer composition, the incorporation of ST in the unextractable polymer was limited to the case when monomer mixtures of high ST content were adopted.

In spite of the great difference in the amount of the unextractable polymer, the curves in Figure 2(b), indicating the relationship between the composition of the unextractable polymer and that of monomer, showed a similar pattern,

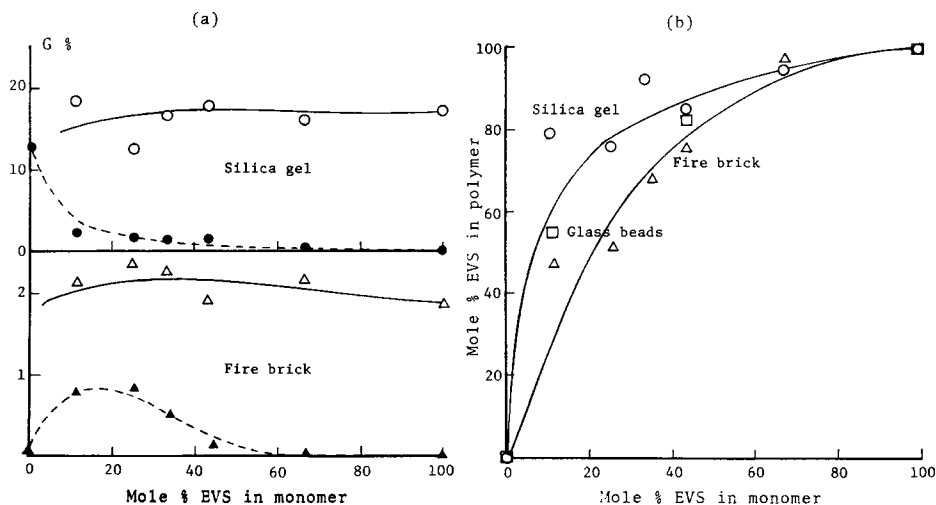


Fig. 3. Reaction of triethoxyvinylsilane-methyl methacrylate binary monomers with silicates by the initiation of benzoyl peroxide (0.5%). Effect of monomer composition on (a) the amount of the unextractable polymer and on (b) the composition of the unextractable polymer: reaction time, 17 hr at 36.5°C; (a) (○ △) overall G%; (● ▲) G% of MMA monomeric unit in the unextractable polymer.

and the EVS content in the unextractable polymer was always higher than that in the monomer mixture. The Fineman-Ross plot of the composition did not show a satisfactory linearity, but some data were roughly explained by $r_1(\text{ST}) = 0.06$ and $r_2(\text{EVS}) = 4.2$. However, considering the low polymerizability¹⁰ and copolymerizability of EVS [$r_1(\text{ST}) = 26$, $r_2(\text{EVS}) = 0$, or $r_1(\text{MMA}) = 37$, $r_2(\text{EVS}) = 0$, calculated from the reported Q and e values¹¹], the composition of polymer thus obtained from pyrolysis does not coincide with the copolymer composition, and instead the observed reactivity ratio was considered to be the results brought about by overlapping of the separately formed products. In other words, the bulk of EVS independently reacted with the silicate surface and coexisted with a minor amount of the grafted true copolymer. The fact that the by-product polymer recovered from the washing solution was composed mainly of ST supports the above considerations.

Figures 3(a) and 3(b) show the results of the EVS-MMA binary monomer system, corresponding to Figures 2(a) and 2(b). The results seem to be fairly similar to those of the EVS-ST system.

In the TGA and DTA curves of the reacted silica gel, only the endothermic peaks were observable, contrary to the results of Sidorovich et al.¹²

Reaction of Binary Monomers with Silicates Under γ -Ray Irradiation

Figures 4(a) and 4(b) and 5(a) and 5(b) show the amounts of the unextractable polymers and their compositions when the silicates have reacted with binary monomers by the simultaneous irradiation method. The overall feature observed more or less resembled the former cases, though the unextractable polymer was somewhat larger in quantity.

When pure monomer, ST or MMA, was used alone, only a minute amount of

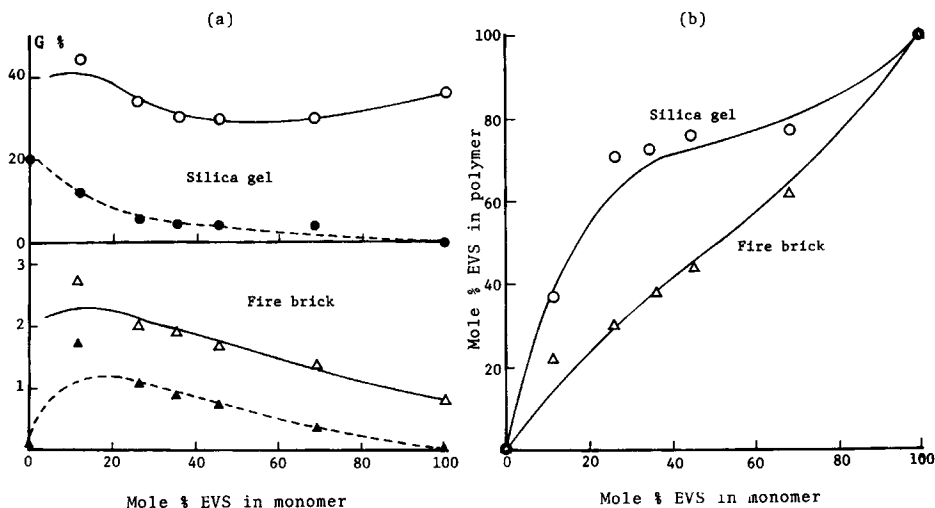


Fig. 4. Reaction of triethoxyvinylsilane-styrene binary monomers with silicates by γ -ray simultaneous irradiation method. Effect of monomer composition on (a) the amount of the unextractable polymer and on (b) the composition of the unextractable polymer: γ -ray irradiation, 105 hr at 2×10^5 R/hr, 25°C; (a) (O Δ) overall G%; (● \blacktriangle) G% of ST monomeric unit in the unextractable polymer.

the unextractable polymer was detected except for silica gel. Although more investigation is needed to determine whether pure polyST or polyMMA in silica gel was truly grafted or merely occluded, it was confirmed that the merely adsorbed polymer could be removed almost completely by the adopted method of washing in the cases of crushed fire brick and glass beads.

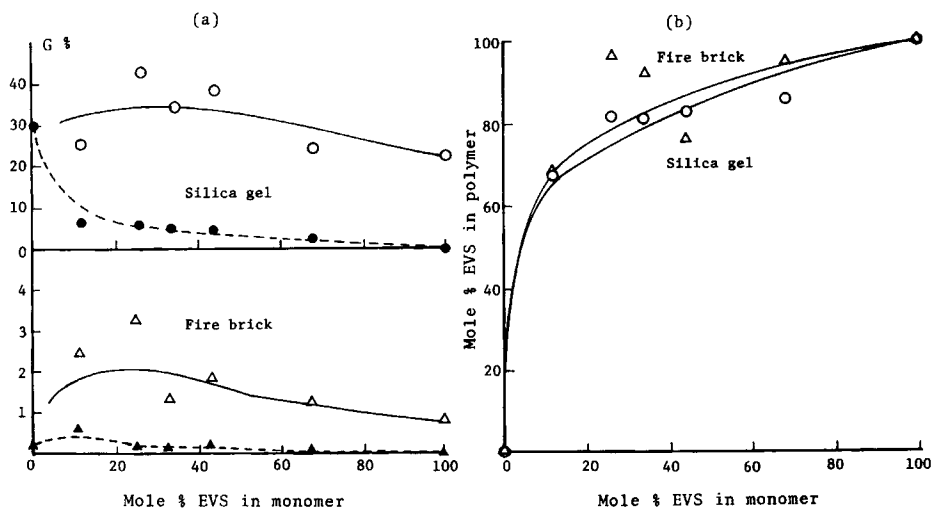


Fig. 5. Reaction of triethoxyvinylsilane-methyl methacrylate binary monomers with silicates by γ -ray simultaneous irradiation method. Effect of monomer composition on (a) the amount of the unextractable polymer and on (b) the composition of the unextractable polymer: γ -ray irradiation, 20 hr at 2×10^4 R/hr, 25°C; (a) (O Δ) overall G%; (● \blacktriangle) G% of MMA monomeric unit in the unextractable polymer.

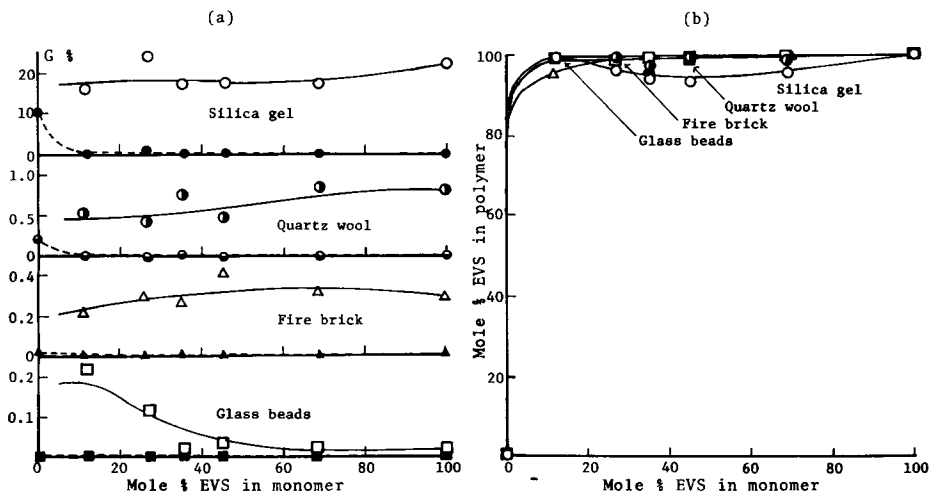


Fig. 6. Reaction of triethoxyvinylsilane-styrene binary monomers with the preirradiated silicates. Effect of monomer composition on (a) the amount of the unextractable polymer and on (b) the composition of the unextractable polymer: preirradiation, 107 hr at 1×10^6 R/hr, 25°C in air; grafting reaction, 17 hr at 72°C; (a) (○ ● △ □) overall G%; (● ● ▲ ■) G% of ST monomeric unit in the unextractable polymer.

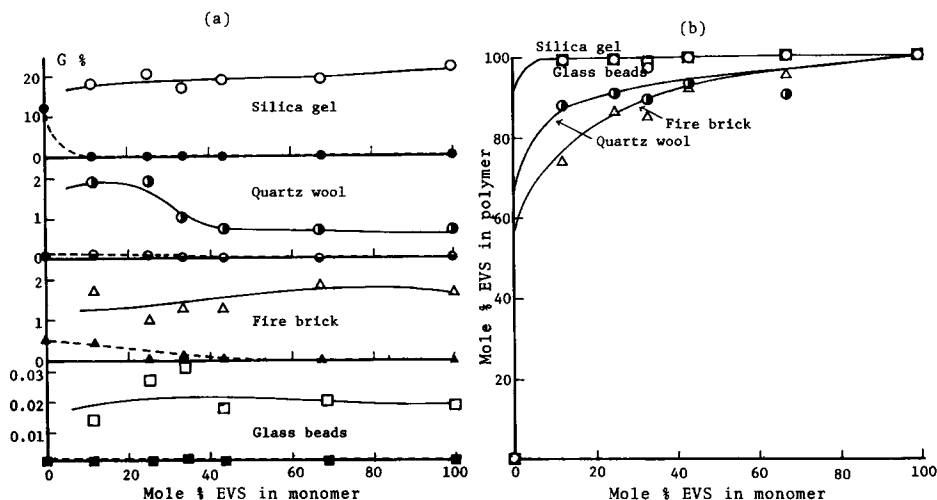


Fig. 7. Reaction of triethoxyvinylsilane-methyl methacrylate binary monomers with the preirradiated silicates. Effect of monomer composition on (a) the amount of the unextractable polymer and on (b) the composition of the unextractable polymer: preirradiation, 107 hr at 1×10^6 R/hr, 25°C in air; grafting reaction, 2 hr at 72°C; (a) (○ ● △ □) overall G%; (● ● ▲ ■) G% of MMA monomeric unit in the unextractable polymer.

Reaction of Binary Monomers with Preirradiated Silicates

The possibility was expected for the preirradiated silicates to initiate the copolymerization, inasmuch as the polymerization of MMA by the trapped electron on the aluminosilicate⁵ and the existence of SiO radical in the irradiated silicates had been reported.^{7,13} Figures 6(a) and 6(b) and 7(a) and 7(b) show the results when the silicates preirradiated by γ -rays in air were heated with binary mono-

TABLE II
Reaction of Triethoxyvinylsilane–Styrene and Triethoxyvinylsilane–Methyl Methacrylate Binary Monomers with Silicates Preirradiated Under Vacuum^a

Silicate	Comonomer of EVS	EVS in monomer mixture, mole %	Overall G% from pyro. GC	EVS in unextractable polymer, mole %
Silica gel	ST	12.0	19.0	100.0
Asbestos	ST	12.0	3.66	96.9
Fire brick	ST	12.0	0.24	78.0
Quartz wool	ST	12.0	1.03	90.3
Glass beads	ST	12.0	0.0064	100.0
Silica gel	MMA	11.3	28.2	87.6

^a Preirradiation, 100 hr at 1×10^6 R/hr, 25° C under vacuum; grafting reaction, 17 hr at 72° C.

mers. Table II shows some of the results for the silicates preirradiated under vacuum. The contribution of monomer composition on the amount of the unextractable polymer was rather obscure. The most remarkable feature was that the existence of ST or MMA monomeric unit was hardly if at all observed in the unextractable polymer in the whole range of composition of binary monomers, except for the case when pure ST or MMA was applied, no matter whether the irradiation had been carried out in air or under vacuum. As the preirradiated silicates were thought to have no ability to initiate copolymerization in this reaction condition, the condensation reaction of EVS was regarded as predominant on these preirradiated silicates.

DISCUSSION

It is very difficult to determine whether true grafting was achieved on the silicates. However, as far as experimental observation is concerned, many facts seem to support, though indirectly, the occurrence of true grafting of the concerned copolymer which constitutes part of the unextractable substance on the surface of silicates.

Table III shows the change of the specific surface area before and after the reaction and the change in solubility of the reacted silica gel in hydrofluoric acid. It can be seen that the silica gel which contained only EVS as organic component, including those prepared by preirradiation and heating, retained fairly large specific surface areas and dissolved completely in hydrofluoric acid. On the other hand, when the silica gel contained ST or MMA besides EVS as a constituent of unextractable polymer, the polymer buried the cavities of silica gel completely, and the insoluble silica gel was left behind after treatment with hydrofluoric acid. The remaining silica gel, retaining a glassy form on microscopic observation, did not dissolve in toluene in spite of high ST or MMA monomeric units. When polyST was solely included in silica gel, the reacted silica gel completely dissolved in hydrofluoric acid, leaving polyST as a bulky cluster of granules which freely dissolved in toluene.

When silica gel which had reacted with EVS previously was heated with ST or MMA containing BPO or irradiated in the presence of ST or MMA, the resulting silica gel was found to contain ST or MMA monomeric unit, and the

TABLE III
Specific Surface Area and Solubility of Reacted Silica Gel

Sample	Reaction method	Overall G%	G% of ST or MMA unit	S_s , m ² /g	Insoluble fraction in HF, % ^a	Solubility in toluene of HF-insolu- ble fraction	Remarks
Silica gel (SG)	—	—	—	481	0.0	—	
SG-EVS	Simult. irradi.	23.8	—	187	0.0	—	
SG-EVS-(ST)	Preirrad and heating	15.6	0.0	278	0.0	—	
SG-ST	Heating with BPO	10.1	10.1	±0	10.9	Soluble	b
SG-EVS-ST	Simult. irradi.	30.0	4.4	±0	10.8	Insoluble	c
SG-EVS-(MMA)	Preirrad and heating	20.8	0.1	194	0.0	—	
SG-EVS-MMA	Simult. irradi.	34.1	3.8	±0	9.0	Insoluble	c

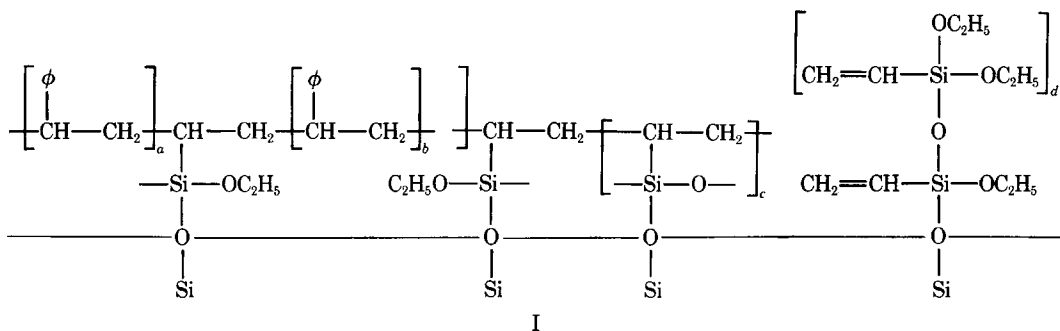
^a Stirred for 1 hr in concentrated HF followed by washing with water. Then stirred another 2 hr in HF and washed with water and methanol and dried in desiccator.

^b Insoluble part of HF treatment was a cluster of powder-like polymer.

^c Insoluble part of HF treatment was a glassy substance which resembled the original silica gel.

composition of the unextractable polymer resembled that of the reacted silica gel directly prepared from the binary monomers.

In conclusion, the unextractable polymers in silicates can be regarded as the grafted polymers. The mode of the possible reaction in this system can be explained as follows; (1) the hydrolysis followed by condensation took place between EVS and the silanol group on the surface of the silicates in the presence or possibly in the absence of adsorbed water, and part of EVS may be addition-polymerized with γ -irradiation⁹ or condensation-polymerized mutually to oligomers; (2) copolymerization was initiated by BPO or γ -rays, and some of the pendent vinyl groups on the surface of silicates were incorporated in the grafted copolymer (I):



and (3) the radicals, if any, on the preirradiated silicates were not active for inducing copolymerization.

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