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Photochemical Reactions of High Polymers. XIII. Photografting of Methyl Methacrylate Onto the Polymers Bearing Thiosulfate Groups

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Synopsis

Polymers bearing pendent thiosulfate groups, that is, sodium poly(vinyl benzyl thiosulfate) (PVBB) and the sodium salt of poly(vinyl hydrothiosulfatoacetate)(PVAcB), were prepared. The photograft polymerization of methyl methacrylate onto these polymers was carried out. The relationships between irradiation time and conversion, degree of grafting, and grafting efficiency were investigated in the photograft polymerization. It was ascertained that the pendent thiosulfate groups acted as effective initiators for the graft polymerization. From the number of endgroups in the homopolymer formed along with the graft polymer, the mechanism of the graft polymerization was discussed and it was verified that the graft polymerization was initiated by the thiyl radical formed by scission of the sulfur–sulfur bond of the pendent thiosulfate group. An unusually high degree of grafting and extremely rapid polymerization rate observed in the graft polymerization suggested the dual functions of thiosulfate-bearing polymer as initiator and emulsifier. It was found that addition of $FeCl_2$ to this polymerization system increased the rate of polymerization and the degree of grafting but decreased the grafting efficiency. The effect of $FeCl_2$ was interpreted by assumption of a photo-redox reaction between thiosulfate group and Fe^{2+}.

INTRODUCTION

In previous papers[1-3] we have reported that organic thiosulfates (Bunte salts) are effective initiators for photopolymerization of vinyl monomers and that their functions as initiators result from the photolysis of the S—S bond.

In this paper, two kinds of polymers whose side chains are substituted partially with thiosulfate groups were prepared, and photopolymerizations of methyl methacrylate (MMA) were carried out in aqueous solutions of these polymers. As expected, the thiosulfate-bearing polymers caused rapid polymerization of MMA, and the corresponding graft polymers were formed along with homopolymer of MMA. Many examples of the graft polymerization utilizing functional groups on a backbone polymer as initiator are known. Present graft polymerizations belong to this category, but some unexpected phenomena, for example, high degree of grafting and high rate of polymerization, were observed. Although further studies are

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required to elucidate these phenomena, it seems quite probable that a unique nature of the backbone polymers bearing thiosulfate groups plays an important role. Furthermore, it was found that the photograft polymerization was affected remarkably by the addition of metal salts. The effects of $FeCl_2$ and $FeCl_3$ were investigated in detail. The former was discussed by assuming a redox reaction between thiosulfate group and Fe^{2+}. The latter, on the other hand, was interpreted from its well-known functions as initiator for photopolymerization and as terminator for radical polymerization.

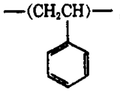
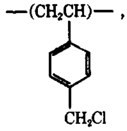
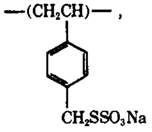
EXPERIMENTAL

Materials

Chloromethylated Polystyrene (ClMePS).[4] ClMePS-1 was synthesized by dissolving 11 g polystyrene ($\bar{P}_n = 180$) and 2.8 g molten zinc chloride in 50 ml chloromethyl ether and by stirring this solution at 30°C for 3 hr. The yield was 13 g. ClMePS-2 was synthesized using 10 g polystyrene ($\bar{P}_n = 180$), 2.6 g chloromethyl ether and 2.6 g molten zinc chloride in a similar manner as above. The reaction time was 2.5 hr.

Sodium Poly(vinyl Benzyl Thiosulfate) (PVBB). To a solution of 4 g ClMePS-1 in 50 g DMSO was added 5 ml of an aqueous solution of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$, 5.6 g) at 50° — 60°C. After stirring for 2.5 hr at 75°–80°C, the solution was poured into acetone to precipitate the polymer. Sodium chloride and unreacted sodium thiosulfate in the polymer were removed by dialyzing against distilled water. Upon drying, the polymer (PVBB-1) became insoluble in water and in DMSO. Therefore, the dialyzed aqueous solution was used directly in the polymerization experiments. PVBB-2 was synthesized in a similar manner using 6 g ClMePS-2. 59 g DMSO, and 3 ml of an aqueous solution of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$, 3.5 g). The reaction time was 3 hr. PVBB-2 was insoluble in pure water but was soluble in a mixture of water and DMSO (volume ratio of 4:1). The composition of these polymers is shown in Table I.

TABLE I
Composition of PVBB and ClMePS

Polymers	Cl, %	S, %	 mole-%	 mole-%	 mole-%
ClMePS-1	16.4	—	37.9	62.1	—
PVBB-1	—	17.6	37.9	11.5	50.6
ClMePS-2	10.5	—	63.9	36.1	—
PVBB-2	—	10.6	63.9	12.1	24.0

Poly(vinyl Chloroacetate) (PVClAc).[5] PVClAc-1 was synthesized by heating 11 g poly(vinyl alcohol) ($\bar{P}_n = 500$), 20 g glacial acetic acid, and 60 g monochloroacetic acid on a steam bath with stirring for 4 hr, at which time a clear, homogeneous solution was obtained. The product was coagulated in water, washed with water, and dried under vacuum. The yield was 12 g. PVClAc-2 was synthesized in a similar manner as above, but the reaction time was 2.5 hr.

Sodium Salt of Poly(vinyl Hydrothiosulfatoacetate) (PVAcB). PVAcB-1 was synthesized by stirring a mixture of 4.2 g PVClAc-1, 17.5 g methyl cellosolve, and 3 ml of an aqueous solution of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$, 2.78 g) at 80°C for about 15 min according to the method of Izard et al.[5] The polymer was precipitated with acetone and then dialyzed against distilled water to remove sodium chloride and unreacted sodium thiosulfate. The yield was about 3 g. PVAcB-2 was synthesized using 20 g PVClAc-2, 85 g methyl cellosolve, and 13.3 ml of an aqueous solution of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$, 13 g). The composition of these polymers is shown in Table II.

Analysis of Polymers

The contents of chlorine and sulfur in the polymers were determined by the Carius method.

Photograft Polymerization

A mixture of 10 ml MMA and 10 ml of an aqueous solution of the polymer (PVAcB or PVBB) in a quartz flask was stirred under nitrogen atmosphere at 23 ± 1°C and irradiated with unfiltered UV light through the flask from a distance of 3 cm. The light source was a 100-W medium-pressure lamp (Toshiba SHL-100 UV). The mixture in the flask was in a state of emulsion before irradiation. With the initiation of polymerization, the solution became white, and soon polymer began to precipitate. After a given period, the polymer was completely precipitated by adding methanol and dried at 30°–40°C under reduced pressure. The polymer was extracted with acetone till no more polymer was extracted. Unextracted polymer, which was insoluble in DMF and in DMSO, was confirmed to be graft polymer from the infrared spectrum.

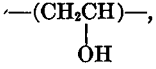
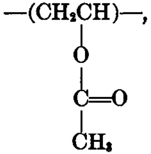
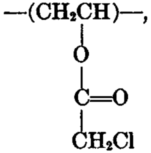
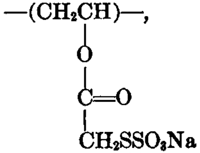
Conversion, degree of grafting, and grafting efficiency were calculated by the following equations:

$$\text{conversion } (\%) = \frac{\text{weight of polymerized MMA (g)}}{\text{weight of used MMA (g)}} \times 100$$

$$\text{degree of grafting } (\%) = \frac{\text{weight of grafted MMA (g)}}{\text{weight of backbone polymer (g)}} \times 100$$

$$\text{grafting efficiency } (\%) = \frac{\text{weight of grafted MMA (g)}}{\text{weight of polymerized MMA (g)}} \times 100$$

TABLE II
Composition of PVAcB and PVClAc

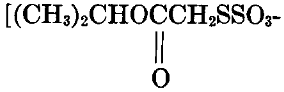
Polymers	Cl, %	S, %	Saponification value	 $-(CH_2\underset{\substack{\vert \\ OH}}{CH})-,$ mole-%	 $-(CH_2\underset{\substack{\vert \\ O \\ \vert \\ C{=}O \\ \vert \\ CH_3}}{CH})-,$ mole-%	 $-(CH_2\underset{\substack{\vert \\ O \\ \vert \\ C{=}O \\ \vert \\ CH_2Cl}}{CH})-,$ mole-%	 $-(CH_2\underset{\substack{\vert \\ O \\ \vert \\ C{=}O \\ \vert \\ CH_2SSO_3Na}}{CH})-,$ mole-%
PVClAc-1	12.6	—	50.4	20.9	47.8	31.3	—
PVAcB-1	—	13.6	—	20.9	47.8	7.9	23.5
PVClAc-2	16.1	—	45.3	29.5	31.1	39.4	—
PVAcB-2	—	6.3	—	29.5	31.1	29.9	9.5

Determination of Endgroups of Homopolymer

The number of endgroups (sulfonate group) was determined by the dye partition method described by Palit and co-workers[6] using chloroform as the polymer solvent and methylene blue in 10^{-2} *M* HCl as the dye. The optical density of the solvent phase after shaking with the dye was compared with a calibration curve obtained with sodium lauryl sulfate instead of the polymer. Number-average degree of polymerization ($\bar{P}_n$) of PMMA was calculated from the intrinsic viscosity $[\eta]$ by use of the following equation:

$$\log \bar{P}_n = 3.420 + 1.131 \log [\eta] \text{ (in benzene at } 30 \pm 0.1°\text{C)}^7$$

Photopolymerization Initiated with IAcB



Sodium isopropoxycarbonylmethylthiosulfate $[(CH_3)_2CHO\underset{\underset{O}{\|}}{C}CH_2SSO_3\text{-}Na\cdot H_2O]$ (IAcB) was prepared by the reaction of isopropyl chloroacetate with sodium thiosulfate. Elemental analysis: Found: C, 23.75%; H, 3.79%. Calcd: C, 23.62%; H, 4.36%. Photopolymerization of MMA in the presence of IAcB was carried out in a similar manner as the graft polymerization described above, except for the addition of sodium lauryl sulfate as emulsifying reagent.

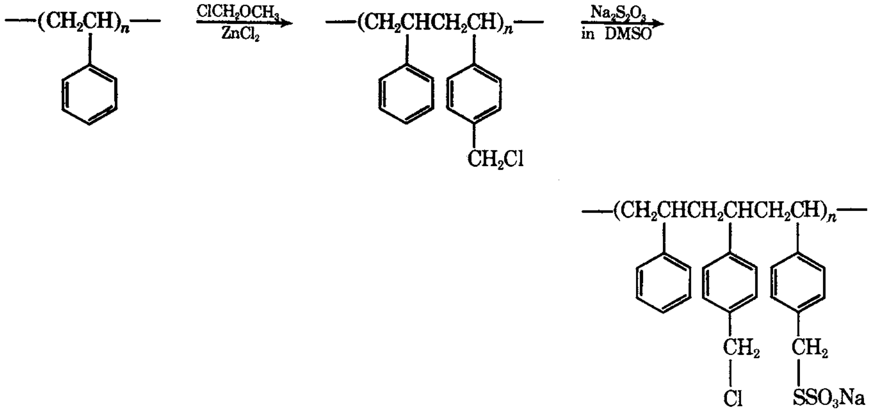
Photoreaction of IAcB with $FeCl_2$

IAcB, 1.7×10^{-2} mole/l. and $FeCl_2$, 1.68×10^{-4} mole/l., were dissolved in 5 ml water. The solution was sealed in a hard glass tube under nitrogen and irradiated with UV light from a distance of 6 cm. After a given period, concentrations of Fe^{2+} and Fe^{3+} in the solution were determined spectrometrically.[8] A Hitachi Model EPS-3T spectrophotometer was used for the measurement of UV absorption spectra.

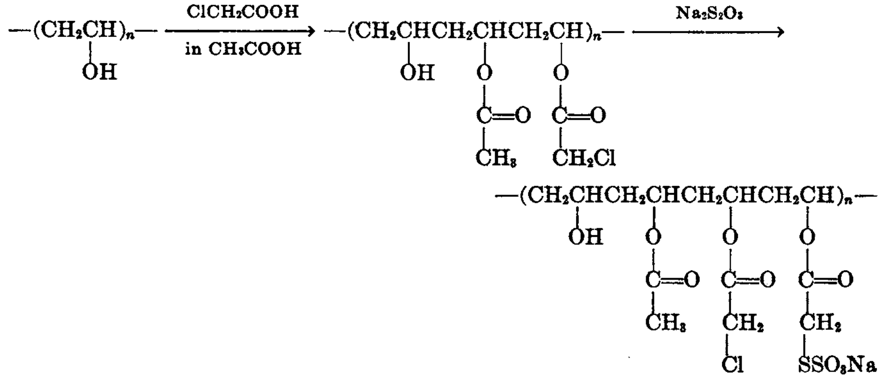
RESULTS AND DISCUSSION

Syntheses of Polymers Bearing Thiosulfate Groups

Synthesis of PVBB. PVBB has been synthesized by Oda et al.[9] by the reaction of chloromethylated polystyrene with soium thiosulfate in a mixture of water and dioxan as solvent. They have reported that crosslinks occur during the reaction and the resulting polymer becomes partially insoluble in water. In this study, however, water-soluble polymer was obtained by using DMSO containing a little amount of water as solvent. The route of the synthesis was as follows.



Synthesis of PVAcB. This polymer was prepared according to the method of Izard et al.[5] PVAcB in which unreacted sodium thiosulfate is incorporated as impurity has a tendency to become insoluble in water upon drying. This undesirable problem, however, could be solved by dialyzing the polymer against distilled water. The route of the synthesis was as follows:



Photograft Polymerization of MMA onto PVAcB or PVBB

The conversion–time curves of the polymerization are shown in Figure 1 (with PVBB) and in Figure 3 (with PVAcB). No polymerization was observed when ClMePS was used instead of PVBB under the same condition except for the use of DMSO as solvent. This shows that the thiosulfate groups in PVBB are effective initiators for the polymerization. The same was found to be true for PVAcB, that is, no polymerization occurred when PVClAc was used in place of PVAcB.

Previously, we reported that irradiation of Bunte salts with UV light led to homolytic scission of the S–S bond.[1] If the present polymerization is initiated by photolysis of the thiosulfate groups on the added polymer, graft polymer (PVBB-g-PMMA or PVAcB-g-PMMA) should be formed

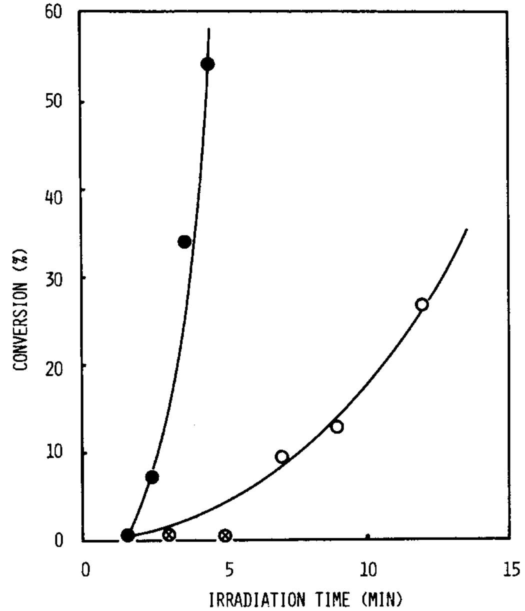


Fig. 1. Photograft polymerization of MMA onto PVBB. Relationship between irradiation time and conversion: —●— PVBB-1(0.4304g) (as thiosulfate groups 5.90 $\times 10^{-2}$ (mole/l)); —○— PVBB-2 (0.3913g) (as thiosulfate groups 3.22 $\times$ 10^{-2} (mole/l.)); —⊕— ClMePS-1 (0.2872g) (as chloromethyl groups 1.63 $\times$ 10^{-1} (mole/l.).

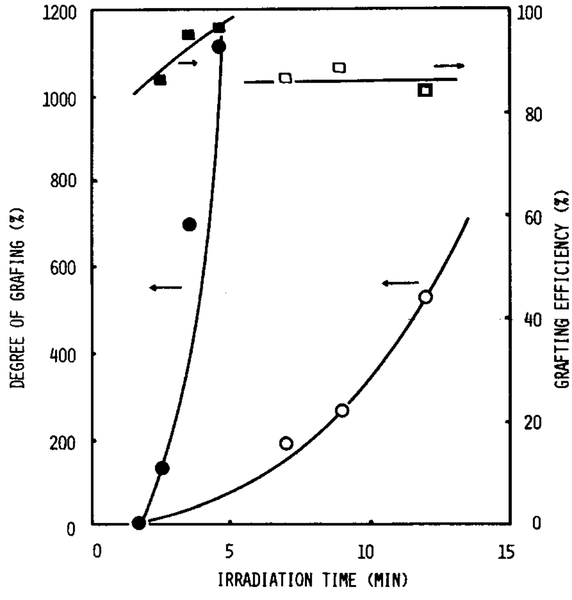


Fig. 2. Relationship between irradiation time and degree of grafting or grafting efficiency (cf. Fig. 1): —●—, —■—, PVBB-1; —○—. —□—, PVBB-2.

TABLE III
Number of Sulfonate Endgroups in Homopolymer Formed in Photograft Polymerization in the Presence of PVAcB or PVBB

			Homopolymer			
Backbone polymer	Polymerization time, min	Total conversion, %	Conversion, %	Number-average degree of polymerization ($\bar{P}_n$)	Number of sulfonate endgroups per polymer chain	Average number of sulfonate endgroups per polymer chain
PVBB-2	9	12.5	1.43	5080	1.06	1.25
	12	26.4	4.14	5500	1.43	
PVAcB-2	30	12.1	5.53	9930	1.81	1.61
	48	27.0	10.38	10120	1.41	

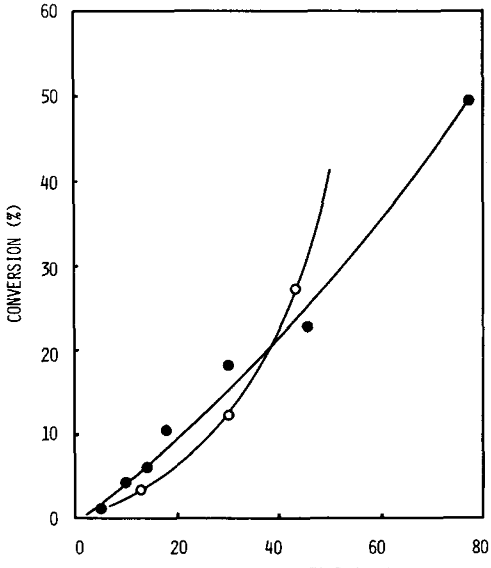


Fig. 3. Photograft polymerization of MMA onto PVAcB. Relationship between irradiation time and conversion: —●— PVAcB-1 (0.3292g) (as thiosulfate groups 3.46 × 10^{-2} (mole/l.)); —○— PVAcB-2 (1.0359g) (as thiosulfate groups 5.09 × 10^{-2} (mole/l)).

along with homopolymer of MMA. This was verified experimentally; extraction of the resulting polymer with acetone gave the graft polymer and PMMA. The degree of grafting and grafting efficiency in this polymerization are shown in Figures 2, 4, and 5.

The number of sulfonate groups per polymer chain in the homopolymer formed was determined by the dye-partition method.[6] The results are shown in Table III. Although a little difference exists between the values obtained in the presence of PVBB (1.25) and in the presence of PVAcB (1.61), both of them are in fairly good agreement with the theoretical value

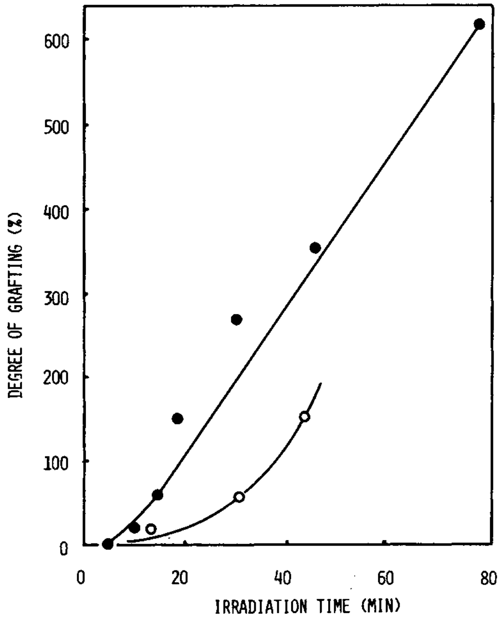


Fig. 4. Relationship between irradiation time and degree of grafting (cf. Fig. 3): —●— PVAcB-1, —○— PVAcB-2.

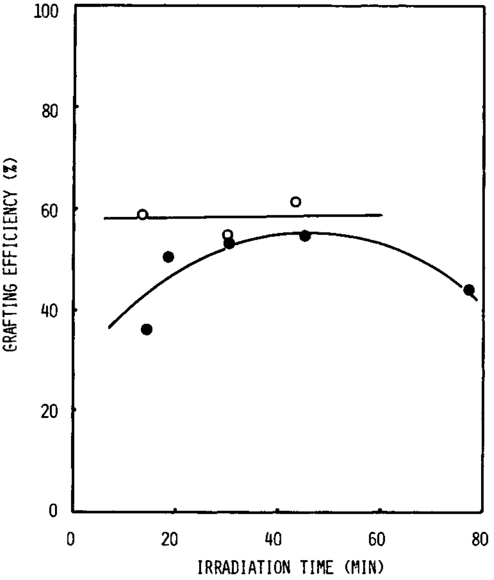


Fig. 5. Relationship between irradiation time and grafting efficiency (cf. Fig. 3): —●— PVAcB-1, —○— PVAcB-2.

(1.32) calculated on the assumption that termination of PMMA radicals occurs by combination and disproportionation in a ratio of 32:68.

Extremely rapid polymerization and unusually high grafting efficiency were observed in the polymerization using PVBB. In the case of PVAcB, rate of polymerization and grafting efficiency seemed to be reasonable. Even in this case, however, the rate at an initial stage was almost independent of the concentration of thiosulfate groups. Although no conclusive evidence is obtained, it appears to be sure that unusual property of the backbone polymer plays an important role. The thiosulfate-bearing polymer is a kind of polysoap and hence expected to act not only as initiator but also as emulsifier. The rapid polymerization of MMA and the unusually high grafting efficiency in the presence of PVBB might result from the function of PVBB as emulsifier. Differences in the effects of PVBB and PVAcB on polymerization rate, grafting efficiency and degree of grafting also might be ascribed partly to the difference in their functions as emulsifier.

The unusual behavior of a compound having dual functions as initiator and as emulsifier seems very interesting to us.

Effects of Metal Salts on Photograft Polymerization onto PVAcB

In the course of study on the photograft polymerization onto PVAcB-1, it was found that some metal salts increased the rate of polymerization, as shown in Table IV. Ce(IV) is known to be an effective initiator for the photo- and thermal-graft polymerizations onto cellulose and poly(vinyl alcohol).[10a] The present effect of Ce(IV) on the photograft polymerization onto PVAcB-1, which contains an appreciable amount of poly(vinyl alcohol) residue, may be due to the well-known function of Ce(IV). In this study, effects of $FeCl_2$ and $FeCl_3$ were investigated in detail. Figure 6 shows that $FeCl_3$ results in a slight increase of the polymerization rate, while $FeCl_2$ increases it remarkably. Furthermore, as seen in Figure 7, $FeCl_3$ reduces the degree of grafting, whereas $FeCl_2$ enhances it. These re-

TABLE IV
Influence of Additives on Photograft Polymerization[a]

Run no.	Additive	Polymerization time, min	Conversion, %	Degree of grafting, %	Grafting efficiency, %
1	$FeCl_2 4H_2O$	16	7.72	131.7	23.5
2	$FeCl_3 6H_2O$	30	4.42	8.5	2.6
3	$Ce(NO_3)_3 6H_2O$	30	0	0	—
4	$Ce(NO_3)_4 2(NH_4NO_3)$	16	12.45	540	59.5
5	$MnSO_4$	30	4.76	155.2	44.7
6	$AgNO_3$	30	0.71	33.9	65.3

[a] PVAcB-1, 0.1283 g; MMA, 10 ml; H_2O, 10 ml; temperature, 23 ± 1°C; additive, 2.75×10^{-2} mole/l.

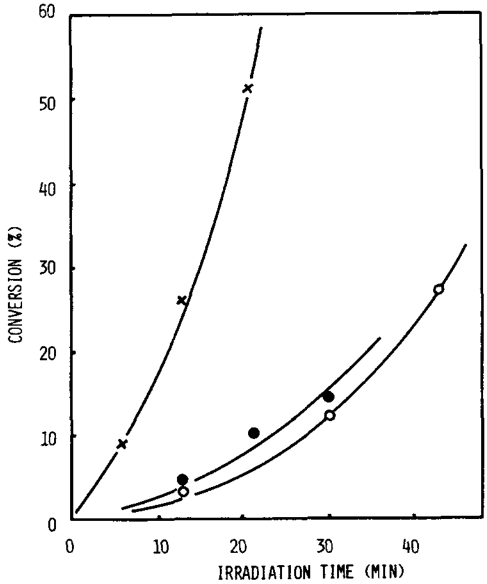


Fig. 6. Effects of Fe^{2+} and Fe^{3+} on conversion: —○— PVAcB-2 (1.0359g) (as thiosulfate groups 5.09 × 10^{-2} (mole/l)); —×— Addition of $FeCl_2 4H_2O$(0.0964g) (2.42 × 10^{-2} (mole/l)); —●— Addition of $FeCl_3 6H_2O$(0.1310g) (2.43 × 10^{-2} (mole/l)). In this experiment, a hard glass flask was used as the reaction vessel to control the rate of polymerization.

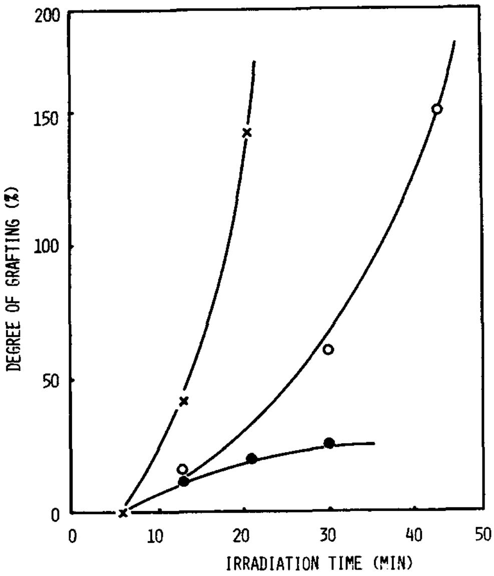


Fig. 7. Effects of Fe^{2+} and Fe^{3+} on degree of grafting (cf. Fig. 6).

TABLE V
Number of Sulfonate Endgroups in Homopolymer Formed in Photograft Polymerization in the Presence of PVAcB-2–Fe^{2+}(Fe^{3+})

			Homopolymer			
Additive	Polymerization time, min	Total conversion, %	Conversion, %	Number-average degree of polymerization ($\bar{P}_n$)	Number of sulfonate endgroups per polymer chain	Average number of sulfonate endgroups per polymer chain
Fe^{2+}	6	8.80	8.80	5700	0.68	0.57
	13	26.07	21.50	6160	0.46	
Fe^{3+}	21	10.02	7.81	1844	0.14	0.21
	30	14.29	11.49	2535	0.27	

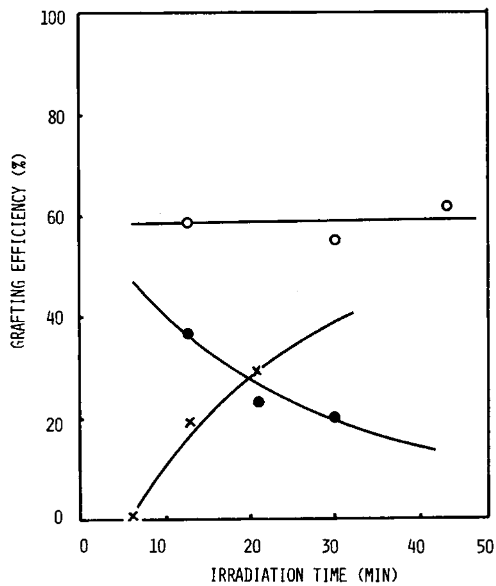


Fig. 8. Effects of Fe^{2+} and Fe^{3+} on grafting efficiency (cf. Fig. 6).

sults suggest that $FeCl_3$ accelerates the formation of homopolymer and reduces that of graftpolymer with a slight increase in the total conversion. In fact, Figure 8 shows the grafting efficiency in the presence of $FeCl_3$ is lower than that in the absence. The grafting efficiency in the presence of $FeCl_2$ which increases both the polymerization rate and the degree of grafting is also lower than that of the control. This means that $FeCl_2$ accelerates the formations of both homopolymer and graft polymer, but the former more effectively. The number of endgroups (sulfonate groups) per polymer chain in the homopolymer was determined to be 0.57 (in the presence

TABLE VI
Photopolymerization of MMA[a]

Run no.	Initiator system			Conversion, %
1	—	—	NaLS	0
2	IAcB	—	NaLS	1.0
3	IAcB	Fe^{2+}	NaLS	4.17
4	—	Fe^{2+}	NaLS	0.79
5	—	Fe^{2+}	—	0
6	IAcB	Fe^{3+}	NaLS	3.38
7	—	Fe^{3+}	NaLS	1.47

[a] MMA, 4.68 mole/l.; IAcB, 4.72 × 10^{-2} mole/l.; $FeCl_2 \cdot 4H_2O$, 2.42 × 10^{-2} mole/l.; $FeCl_3 \cdot 6H_2O$, 2.42 × 10^{-2} mole/l.; sodium lauryl sulfate (NaLS), 1.48 × 10^{-2} mole/l.; solvent was water; 23 ± 1°C; 50 min.

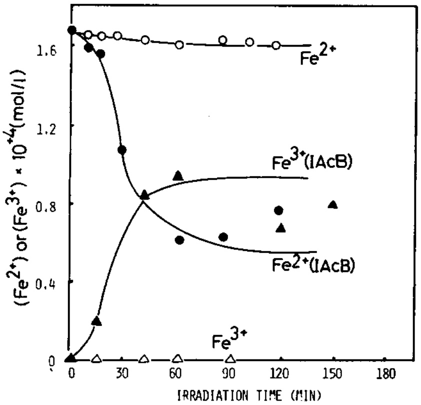


Fig. 9. Variation in concentrations of Fe^{2+} and Fe^{3+} in photoreaction of IAcB with $FeCl_2$ (at 17°C).

of $FeCl_2$) and 0.21 (in the presence of $FeCl_3$) as shown in Table V. These are considerably lower than the theoretical value (1.32).

Recently, Kubota and Ogiwara[10b,10c] have reported that Fe^{2+} adsorbed on cellulose increases the degree of grafting in photograft polymerization of MMA. This appears to imply a photochemical reaction between a hydroxy group and Fe^{2+}, but we found that any appreciable extent of photograft polymerization onto poly(vinyl alcohol) was not caused by Fe^{2+}, at least under our condition. Thus, the effect of Fe^{2+} on the photograft polymerization onto PVAcB-1 which contains hydroxy groups should differ in the nature from Kubota et al.'s observation.

Experimental results using IAcB as a model compound for PVAcB showed that the coexistence of $FeCl_2$ and IAcB resulted in a remarkable increase in the polymerization rate, as shown in Table VI. In addition, Figure 9 shows Fe^{2+} is oxidized to Fe^{3+} by irradiation with UV light in the presence of IAcB. From these results, we propose an oxidation–reduction reaction, (1) or (2), between thiosulfate group and Fe^{2+}, though the role of irradiation is unclear:

$$RSSO_3Na + Fe^{2+} \xrightarrow{h\nu} RS\cdot + {}^{-}SO_3Na + Fe^{3+} \qquad (1)$$

$$RSSO_3Na + Fe^{2+} \xrightarrow{h\nu} RS^{-} + \cdot SO_3Na + Fe^{3+} \qquad (2)$$

The accelerated rate of polymerization in the presence of $FeCl_2$ is explicable by either of the reactions. Reaction (2) is preferred for the interpretation of the reduced grafting efficiency but seems not to explain the enhanced degree of grafting. This apparent discrepancy, however, is resolved well by assuming a further reaction (3) between the reaction products:

$$RS^{-} + Fe^{3+} \rightarrow RS\cdot + Fe^{2+} \qquad (3)$$

Introduction of reaction (3) leads to a reasonable interpretation of the following experimental results: an increase in the degree of grafting with reaction time in the presence of $FeCl_2$ exceeded that in the absence of $FeCl_2$, as shown in Figure 7.

Although reaction (1) is more favorable than reaction (2) with regard to the degree of grafting, the reduced grafting efficiency in the presence of $FeCl_2$ seems not to be explained by reaction (1), even if reaction (4) is assumed instead of reaction (3):

$$^{-}SO_3Na + Fe^{3+} \rightarrow \cdot SO_3Na + Fe^{2+} \qquad (4)$$

If this reaction were possible, grafting efficiency should reduce with reaction time.

The addition of $FeCl_3$, on the other hand, led a lowering of both degree of grafting and grafting efficiency with a slight increase in the total conversion. This may be due to the well-known dual function of $FeCl_3$ as initiator for photopolymerization[11] and as retarder for radical polymerization.[12] Termination of growing graft polymer radicals by $FeCl_3$ should result in a decrease in the degree of grafting, because the radicals should propagate further if they were not terminated by $FeCl_3$.

Another function of $FeCl_3$ as initiator should result in an increase in the formation of homopolymer (and hence an increase in the total conversion) without affecting the formation of graft polymer. As Fe^{3+} changes to Fe^{2+} after playing a role as initiator or as retarder, the effect of Fe^{2+} will increase gradually with reaction time. The reduction of grafting efficiency with reaction time, which is shown Figure 8, might be due to the contribution of reaction (2) caused by Fe^{2+}. A slight increase in the total conversion observed in the presence of $FeCl_3$ is presumably a result of an inadvertent balance of the dual functions of $FeCl_3$. The fact that the number of sulfonate groups per polymer chain was quite less than the theoretical value seems to be another evidence supporting the function of $FeCl_3$ as initiator and/or retarder. Even in the case of $FeCl_2$, the number was considerably less than the theoretical value. This may be due to the effect of Fe^{3+} converted from Fe^{2+}.

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