Effect of Ultrasonic Irradiation on Ceric-Salt-Initiated Grafting of Methyl Methacrylate onto Regenerated Cellulose Film

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ABSTRACT: Effect of ultrasonic irradiation on ceric salt (Ce^{4+})-initiated grafting of methyl methacrylate (MMA) on regenerated cellulose film (thickness = 20 μm) was investigated under an air atmosphere in water solvent at 60°C. The grafting system with the ultrasonic irradiation was characterized by higher percentage of grafting and graft efficiency than the system without the irradiation. Reaction of cellulose with Ce^{4+} was also accelerated by the ultrasonic irradiation. No accelerating effect of grafting due to the ultrasonic irradiation was observed for the system under reduced pressure of 5 torr. The effect of the ultrasonic irradiation on the average molecular weight of MMA-grafted chains was also studied. Moreover, the surface layer of the resulting grafted films was examined by attenuated total reflection–infrared (ATR–IR) measurement and scanning electron microscopy (SEM) observation. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 251–258, 1999

Key words: grafting; methyl methacrylate; regenerated cellulose film; ultrasonic irradiation

INTRODUCTION

It is well known that ultrasound induces mechanical, thermal, and/or oxidative effects to materials in the liquid. The phenomenon is generally considered to be due to the cavitation[1,2] generated by the sound wave passing through the liquid. The ultrasonic effect has been applied to polymer reaction and synthesis, such as ultrasonically initiated polymerization[3,4] of vinyl monomers and degradation[5,6] of polymer materials. It was found in the former case that ultrasound directly affects the vinyl monomers to initiate polymerization, even in the system without any initiators. It was reported, moreover, that polymerization of organosilanes[7] with metallic sodium is facilitated with the ultrasonic irradiation, leading to promoted rate of polymerization and yield.

With degradation of polymers, on the other hand, the degree of polymerization was reduced when ultrasound was irradiated to the polymer solution. Various factors[8–12] affecting the polymer degradation due to the ultrasonic irradiation have been investigated in terms of ultrasonic intensity and frequency, nature of solvent, irradiation temperature, pressure, and so on. It was found, furthermore, that the formation of polymer radicals[13,14] is accompanied by the ultrasonically induced degradation, and the resulting polymer radicals can initiate polymerization of vinyl monomers to yield copolymers.[15] Recently, Price and Clifton[16] observed that surface modification of polyethylene film could be done by ultrasonic irradiation in the presence of persulfates.

Most effects of the ultrasonic irradiation on polymer reaction and synthesis described above are gen-

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erally attributed to the cavitation phenomenon; the formation and implosive collapse of small bubbles as the ultrasound wave passes through the solvent. The implosive collapse of cavitation bubbles induces localized high temperature and pressure and/or jet of liquid in the reaction system. The latter causes high shear gradient force and rapid mass transfer and diffusion. These functions of ultrasound closely relate with the above effects on polymer reaction and synthesis.

In the present study, the functions of ultrasound, such as mass transfer and diffusion, were applied to polymer reaction in a heterogeneous system. We focused on grafting as the polymer reaction, which is useful means for modification and functionalization of polymer materials. We have investigated grafting of vinyl monomers on wood pulp as a cellulose sample in ceric-salt-initiated,[17,18] hydrogen peroxide–metallic ion-initiated,[19,20] and photoinitiated[21,22] systems. In these heterogeneous systems, diffusion of initiator and monomer into cellulose substrate is considered to be most important factor for the effective performance of grafting reaction. This article deals with the effect of ultrasonic irradiation on ceric-salt-initiated grafting of methyl methacrylate (MMA) on cellulose film under air atmosphere in terms of grafting behavior, reaction of cellulose with ceric salt, average molecular weight of MMA-grafted chains, and distribution of grafted chains of surface layer of the resulting grafted films.

EXPERIMENTAL

Materials

Commercially available regenerated cellulose film (cellophane) with a thickness of 20 μm was used as a film sample (3 $\times$ 10 cm), which was extracted with hot methanol for 24 h to remove additives. The extraction resulted in about a 10% decrease in the film weight. Commercial dissolving pulp from softwoods was used as a fibrous sample. Ceric ammonium nitrate (Ce^{4+}), ferrous sulfate, and *o*-phenanthroline were reagent grade. MMA and acrylonitrile (AN) were purified by distillation under reduced and normal pressures, respectively.

Grafting

Grafting was carried out at 60°C under air atmosphere in a Pyrex glass tube containing the film sample, 24 mL water, known quantities of MMA, and 6 mL aqueous solution of nitric acid (5 m*M*), in which known quantities of Ce^{4+} were dissolved. Grafting under reduced pressure was performed in an evacuated (5 torr) and sealed Pyrex glass tube. Ultrasonic irradiation was carried out using an ultrasonic cleaning bath, model NS80-1.5u of Nihonseiki seisakusho Ltd. (bath size, 150 $\times$ 135 $\times$ 100 mm; nominal frequency, 28 kHz; power output, 80 W).

With grafting under a stirring operation (stirring rate = 600 rpm), grafting was carried out using a film sample (3 $\times$ 10 cm), which was cut into small pieces (about 10 $\times$ 10 mm), without ultrasonic irradiation under an air atmosphere. In the case of grafting on the pulp sample, 0.20 g sample was used in the same grafting system as that using the film sample described above section.

Polymerized film was extracted with acetone and *N,N′*-dimethylformamide for 24 h to remove homopolymers of poly(MMA) and polyAN, respectively. The percentage of grafting, the percentage of homopolymer, and graft efficiency were calculated by the following equations.

$$\text{Grafting (\%)} = \frac{\text{weight of grafts}}{\text{weight of original film}} \times 100$$

$$\text{Homopolymer (\%)} = \frac{\text{weight of homopolymer}}{\text{weight of original film}} \times 100$$

$$\text{Graft efficiency} = \frac{\text{weight of grafts}}{\text{weights of grafts and homopolymer}} \times 100$$

Reaction of Cellulose with Ce^{4+}

Reaction of cellulose with Ce^{4+} was carried out at 60°C in the same system as that of grafting in the absence of the MMA monomer described in the above section. The amount of Ce^{4+} in an aqueous solution was determined by adding a given amount of ferrous sulfate and backtitration with Ce^{4+} with *o*-phenanthroline as an indicator.

Average Molecular Weight of MMA-Grafted Chains

MMA-grafted film was treated with 72% sulfuric acid[23] to isolate poly(MMA) as the grafted chains. The average molecular weight of grafted chains

was determined from the viscosity of benzene solution at 30°C using the following equation[24]:

$$[\eta](\mathrm{dL/g}) = 8.69 \times 10^{-5} \cdot Mn^{0.76}$$

The molar number of grafted chains per 100 g of cellulose calculated from the percentage of grafting and the average molecular weight of grafted chains was indicated as the number of grafted chains.

Measurement of ATR–IR Spectra

ATR–IR spectra of the surface layer of grafted film were measured with an IR spectrometer model MAGNA-IR750 of Nikolet. The absorbance ratio of the carbonyl peak (stretching, 1730 cm^{-1}) of MMA-grafted chains to the ether peak (stretching, 900 cm^{-1}) of cellulose was obtained.

SEM Observation

Observation of surface of MMA-grafted film was performed by a scanning electron microscope, model ESA-2000 of ELIONIX.

RESULTS AND DISCUSSION

In a grafting reaction, a deaerated system is generally employed to remove oxygen in the system, which inhibits a radical polymerization of vinyl monomer. It was observed in previous articles[25] that Ce^{4+}-initiated grafting of MMA and AN on bleached sulfate pulp from softwood easily proceeds under an air atmosphere. In this study, therefore, the grafting of MMA on regenerated cellulose film was also carried out under air atmosphere because of the simple polymerization procedure without the oxygen removal process. Figure 1 shows the effect of Ce^{4+} concentration on the grafting reaction. The grafting proceeded even under the polymerization conditions at 60°C for 5 min in an air atmosphere. The percentage of grafting in the system without ultrasonic irradiation (unirradiated system) reached a certain level at the Ce^{4+} concentration of about 1 mmol/L, and then no large increase in the percentage of grafting was recorded when a higher Ce^{4+} concentration was used. The percentage of grafting in the system with ultrasonic irradiation (irradiated system) was higher in the whole range of Ce^{4+} concentration examined than that of the unirradiated system, showing that the ultrasonic irradiation markedly promotes Ce^{4+}-initiated grafting of MMA on regenerated cellulose film. The graft efficiencies in the unirradiated system decreased with an increase in the Ce^{4+} concentration, being less than 60% in the range of Ce^{4+} concentrations higher than about 3 mmol/L. Polymerization of MMA initiated by Ce^{4+} was examined at 60°C for 30 min using a Ce^{4+} and MMA concentration of 5.0 mmol/L and 0.3 mol/L, respectively, and water solvent, and the conversion of 26.2% was recorded. This suggests that Ce^{4+}-induced homopolymerization of MMA proceeds in the present grafting system. It was found, on the other hand, that the graft efficiency of the irradiated system is higher than 90% in the whole range of Ce^{4+} concentration used, showing a preferential formation of grafted polymer. Figure 2 presents the relationship between both the percentage of grafting and graft efficiency and MMA concentration. Again, the percentage of grafting and the graft efficiency were confirmed to be higher for the irradiated system than the unirradiated one. Thus, the ultrasonic irradiation remarkably accelerated Ce^{4+}-initiated grafting of MMA on regenerated cellulose film, which was characterized by the graft efficiency higher than 90%.

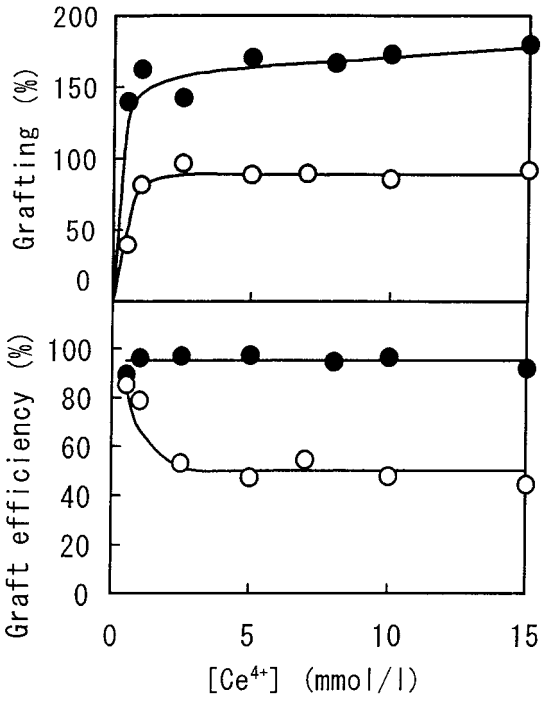

Figure 1 Effect of Ce^{4+} concentration on grafting of MMA onto cellulose film {grafting, 5 min; [MMA] = 0.31 mol/L}: (○) without irradiation; (●) with irradiation.

The high graft efficiency of the irradiated system is supposed to be originated in the retarda-

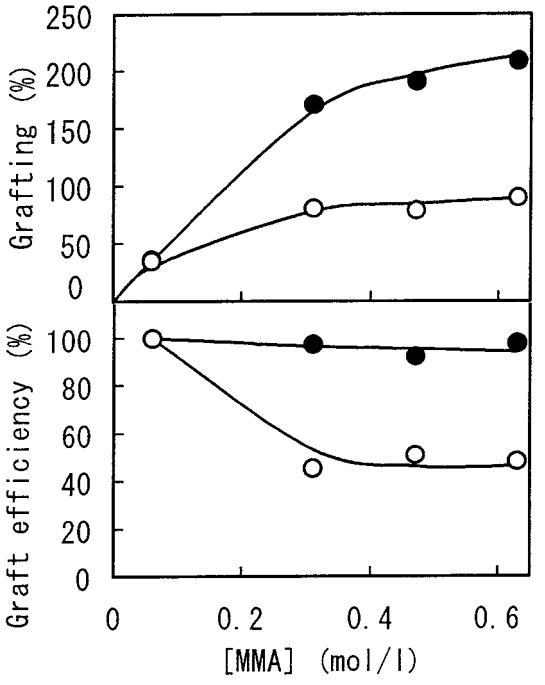

Figure 2 Effect of monomer concentration on grafting of MMA onto cellulose film {grafting, 5 min; [Ce^{4+}] = 5.0 mmol/L}: (○) without irradiation; (●) with irradiation.

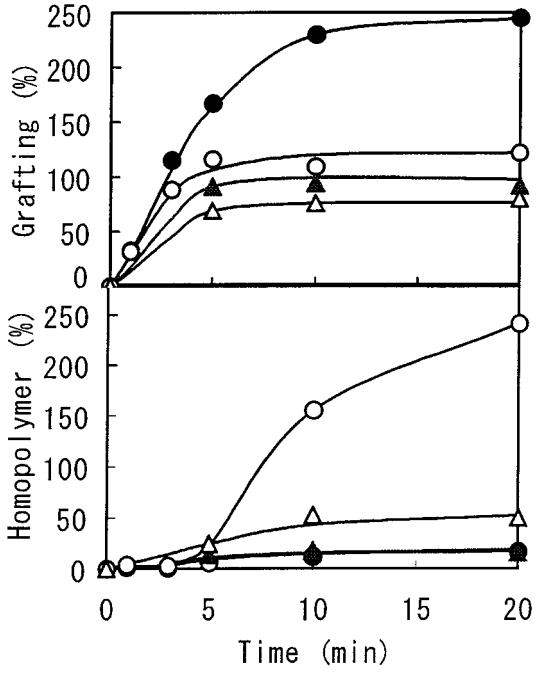

Figure 3 Effect of air bubbling on grafting of MMA onto cellulose film {[MMA] = 0.31 mol/L; [Ce^{4+}] = 5.0 mmol/L}: (○) without irradiation; (●) with irradiation; (△) without irradiation, with air bubbling; (▲) with irradiation, with air-bubbling.

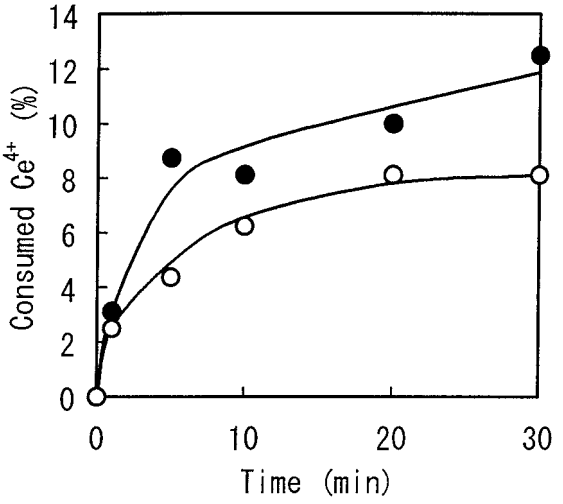

Figure 4 Reaction of cellulose film with ceric salt initiator at 60°C {[Ce^{4+}] = 5.0 mmol/L}: (○) without irradiation; (●) with irradiation.

tion effect of homopolymerization of MMA due to oxygen dissolved in the system since the present grating reaction is performed under air atmosphere. In order to understand the effect due to the dissolved oxygen, grafting of MMA on regenerated film was carried out in the system with air bubbling (Fig. 3). The percentage of grafting of both the irradiated and unirradiated systems was reduced by the air bubbling, and the magnitude was larger for the former system than the latter

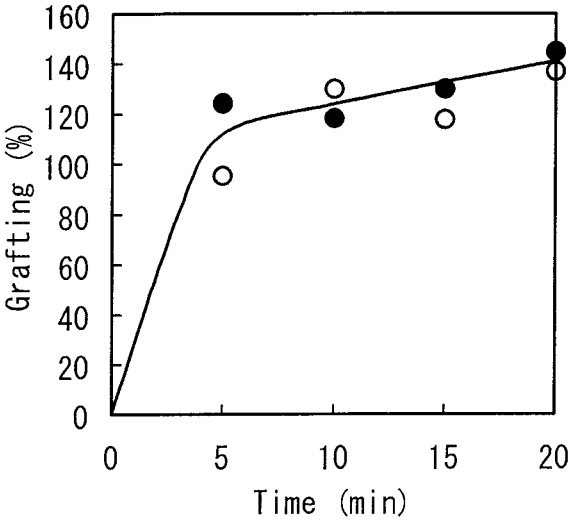

Figure 5 Effect of irradiation on grafting of MMA on cellulose film under reduced pressure at 60°C {[MMA] = 0.31 mol/L; [Ce^{4+}] = 5.0 mmol/L; pressure = 5 torr}: (○) without irradiation; (●) with irradiation.

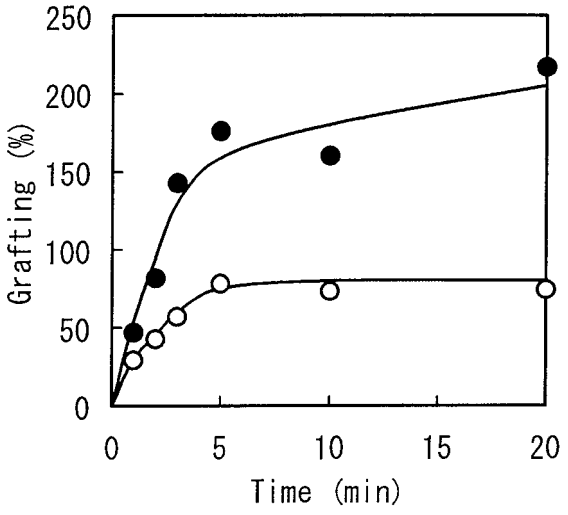

Figure 6 Effect of stirring by magnetic stirrer on grafting of MMA on cellulose film in the system without ultrasonic irradiation at 60°C {[MMA] = 0.31 mol/L; [Ce^{4+}] = 5.0 mmol/L; stirring, 600 rpm}: (○) without stirring; (●) with stirring.

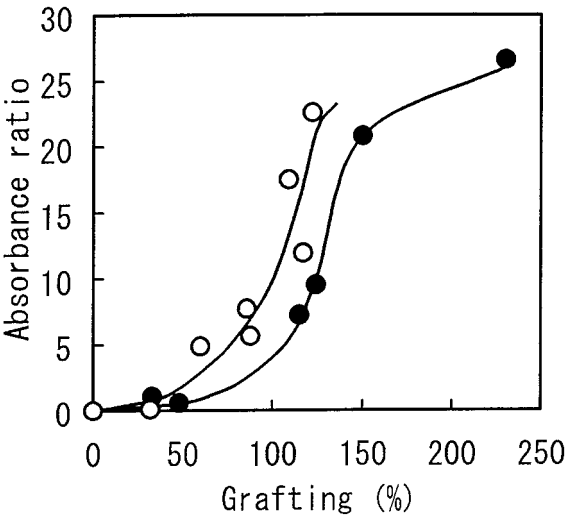

Figure 7 Changes in absorbance ratio of the carbonyl peak at 1730 cm^{-1} to the ether peak at 900 cm^{-1} with the percentage of grafting in MMA-grafted cellulose film: (○) without irradiation; (●) with irradiation.

one. On the other hand, the percentage of homopolymer in the unirradiated system largely decreased by the air bubbling though the value was higher than that of the irradiated system. The percentage of homopolymer in the irradiated system was very low, which was hardly affected by the air bubbling. It was thus found that oxygen dissolved in the polymerization system remarkably retards the formation of both grafted polymer and homopolymer, the extent of which is emphasized by the ultrasonic irradiation. This is inferred to be originated in the enhanced reaction between dissolved oxygen and growing polymer radicals in the system by ultrasonic irradiation.

Figure 4 shows the effect of ultrasonic irradiation on reaction of cellulose with Ce^{4+}. The vertical axis of the figure is the amount of consumed Ce^{4+}. The amount increased with the reaction time, and the extent of the increase was larger for the irradiated system than the unirradiated one, indicating that the ultrasonic irradiation accelerates the reaction of cellulose with Ce^{4+}. It is generally considered that Ce^{4+} forms complex with alcohol,[26] which then decomposes to yield an alcohol radical according to the following equation:

$$RCH_2OH + Ce^{4+} \overset{K}{\rightleftarrows} \text{Complex} \overset{K_d}{\longrightarrow} R\dot{C}HOH + Ce^{3+} + H^+$$

Table I Average Molecular Weight of MMA-Grafted Chains

Ultrasonic Irradiation	Grafting (%)	Grafting Mn × 10^{-4}	Number of Grafts (mmol/100 g cell)
Without irradiation	61.7	34.4	0.179
	117.8	67.8	0.174
With irradiation	62.2	30.4	0.205
	115.0	50.0	0.230
	295.0	94.4	0.313

The average molecular weight of poly(MMA) was determined from the viscosity of benzene solution at 30°C.

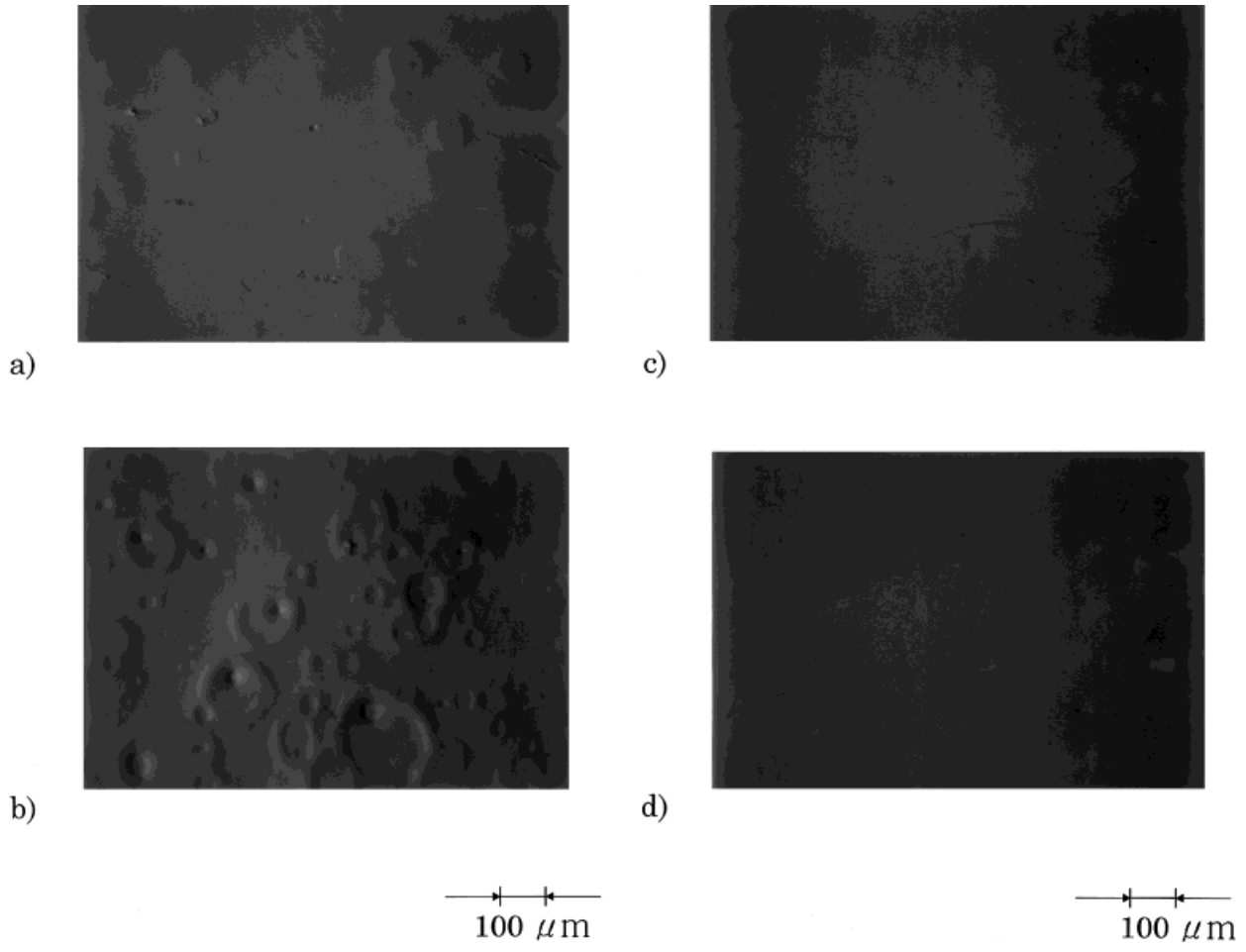

Figure 8 SEM photographs of surface of MMA-grafted cellulose films: (a) without irradiation, grafting = 63.5%; (b) without irradiation, grafting = 116.2%; (c) with irradiation, grafting = 63.9%; (d) with irradiation, grafting = 117.6%.

where K and K_d denote the equilibrium constant and decomposition rate constant, respectively. In the present system, the ultrasonic irradiation is conceivable to promote the above reaction.

Figure 5 shows the effect of ultrasonic irradiation on grafting under reduced pressure. There was no large difference in the percentage of grafting between the unirradiated and irradiated systems, and no accelerating effect of the grafting reaction by the ultrasonic irradiation was observed. The result obtained here coincides with the fact[27] that the cavitation phenomenon is hard to generate under reduced pressure. Accordingly, the accelerating effect of grafting reaction by ultrasonic irradiation was confirmed to be based on cavitation phenomenon. Figure 6 presents the effect of stirring on grafting in the unirradiated system. The percentage of grafting was clearly raised by the stirring with 600 rpm. This suggests that mass transfer and diffusion are important factors for the present grafting system. So, the accelerating effect of grafting reaction by the ultrasonic irradiation may be much due to the functions of ultrasound, such as mass transfer and diffusion. Ultrasound makes the diffusion of Ce^{4+} into film substrate easy, resulting in a promoted formation of cellulose radicals capable of initiating grafting. Moreover, ultrasound may also assist the dispersion of MMA monomer to water solvent to accelerate its diffusion into film substrate. It is supposed accordingly that the accelerating effect of the diffusion of Ce^{4+} and MMA monomer into film substrate by ultrasound overcomes that of the retardation of formation of grafted polymer due to dissolved oxygen, leading to higher percentage of grafting in the irradiated system compared to the unirradiated one, which is shown in Figures 1 and 2.

Table II Effect of Ultrasonic Irradiation (USI) on Ce^{4+}-Initiated Grafting on Cellulose

Monomer	Cellulose	Grafting Time (min)	Grafting (%)		Graft Efficiency (%)	
			Without USI	With USI	Without USI	With USI
Acrylonitrile[a]	film	5	32.8	46.4	58.8	84.8
		10	44.1	56.6	22.0	34.2
		20	45.0	54.0	12.1	24.5
		30	44.7	54.1	11.3	23.7
Methyl methacrylate[b]	pulp	5	117.4	210.0	73.1	82.5
		10	132.2	239.7	65.4	78.4
		20	177.4	243.3	61.4	73.7
		30	179.3	279.4	62.9	76.8

Grafting was carried out at 60°C using Ce^{4+} concentration of 5.0 mmol/L under air atmosphere.
[a] [AN] = 0.51 mol/L.
[b] [MMA] = 0.31 mol/L.

Table I shows the effect of ultrasonic irradiation on average molecular weight of MMA-grafted chains. The molecular weight of the irradiated system was slightly lower than that of the unirradiated one. As described later, it was found from the examination on ultrasonic irradiation to MMA-grafted film that degradation of MMA-grafted chains is hard to create by the ultrasound source used in this study. It is supposed, therefore, that the result is ascribed to larger formation of initiation site for grafting on cellulose substrate in the irradiated system compared to the unirradiated one. This is supported by the fact that the number of grafted chains (Table I), which was calculated from the percentage of grafting and the average molecular weight of grafted chains, was higher for the irradiated system than the unirradiated one.

MMA-grafted chains of surface layer of the grafted films (unirradiated and irradiated samples) prepared in the unirradiated and irradiated systems, respectively, were examined by ATR–IR measurement, and the results are shown in Figure 7. The vertical axis of the figure is the absorbance ratio of the carbonyl peak of MMA-grafted chains at 1730 cm^{-1} to the ether peak of cellulose substrate at 900 cm^{-1}. The absorbance ratio increased with an increase in the percentage of grafting, and the magnitude was lower for the irradiated sample than the unirradiated one. This suggests that density of MMA-grafted chains in surface layer of grafted film is lower for the irradiated sample compared to that of the unirradiated one, showing easier penetration of MMA-grafted chains into the film substrate in the irradiated system.

Figure 8 shows SEM observation of surface appearance of MMA-grafted films. The unirradiated sample showed rough surface, the extent of which increased markedly with the percentage of grafting. On the other hand, the surface appearance of the irradiated sample was flat. It is inferred that the difference in the surface structure between the 2 samples closely relates with penetration of grafted chains into film substrate, which is shown in Figure 7. As grafting reaction proceeds, with the unirradiated system, the film surface becomes rich in the component of MMA-grafted chains, and the accumulation of the grafted layer on the film surface leads to a rough structure. The grafted film (grafting = 117.0%) with a rough surface structure prepared in the unirradiated system was subjected to the ultrasonic irradiation at 60°C for 10 min in water. There was no large decrease in the weight of grafted film, and the surface appearance remained unchanged (a rough structure) by the irradiation. This suggests that degradation of grafted chains due to ultrasonic irradiation does not occur in the present system, and the generation of flat surface, which is observed for the irradiated sample, does not relate to the degradation. It is plausible that ultrasonic irradiation accelerates the diffusion of initiator and monomer into film substrate, and the grafted chains penetrate easily into the film inside to yield flat surface.

Table II shows the grafting of AN on regener-

ated cellulose film. The percentage of grafting and the graft efficiency were higher for the irradiated system than the unirradiated one. The table also includes the results of grafting of MMA on a fibrous pulp sample. Again, a higher percentage of grafting and graft efficiency were afforded for the irradiated system compared to the unirradiated one. Thus, the ultrasonic irradiation was found to be useful for the grafting using the AN monomer and the fibrous cellulose sample.

Based on the above investigations, we concluded that the acceleration effect of Ce^{4+}-initiated grafting of MMA onto cellulose film by ultrasonic irradiation is mainly ascribed to the functions of ultrasound, such as mass transfer and diffusion, which are induced by cavitation phenomenon, and the ultrasonic irradiation is a useful means for the effective performance of the grafting reaction on cellulose in a heterogeneous system.

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