

Gas-Phase-Assisted Surface Polymerization of Methyl Methacrylate with Fe(0)/TsCl Initiator System

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ABSTRACT: To obtain a high polymer coated Fe(0) surface, gas-phase-assisted surface polymerization (GASP) of methyl methacrylate (MMA) was investigated using a zero-valent iron (Fe(0))/*p*-toluene sulfonylchloride (TsCl) initiator system, resulting in successful high polymer production on the solid surface. GASP was found to be initiated by radical species that might have been generated via redox reactions with Fe(0), Fe(II), Fe(III), and TsCl. From ¹H-NMR analysis, the *p*-toluene sulfonyl group was found at one end of the polymer chain. The molecular weight of obtained PMMA

drastically decreased with increase in the composition ratio of Fe(0) in the initiator system, and increased with increase in polymer yield. From the results, it was assumed that the physically controlled polymerization of MMA proceeded by immobilized active species at gas–solid interfaces. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1879–1886, 2007

Key words: gas-phase-assisted polymerization; atom transfer radical polymerization; Fe-based catalyst; physically controlled polymerization; radical polymerization; surfaces

INTRODUCTION

Extremely thin polymer coating of metallic surfaces is one method of fine coating that is attracting great interest. It has many industrial applications, an important one being the anticorrosive treatment of parts to be used in automobiles, ships, and electric and electronic devices. Intricate mechanisms, powders and device parts in particular, often require a coating to a precise pattern and depth of a micrometer or less, making polymer coatings capable of this accuracy an attractive proposition.

Many reports on radical polymerization assisted by metallic surfaces have been published. Otsu et al.^{1,2} reported that a simple system zero-valent metal {Me(0)} and carbon tetrachloride could initiate the polymerization of methyl methacrylate (MMA) and styrene (St) in solution. Matyjaszewski et al. used a metal halide/ligand/Me(0) system for the atom transfer radical polymerization (ATRP) of vinyl monomers in bulk, resulting in the preparation of well-defined polymers.³ Percec et al. found that mixtures of Cu₂O/Cu(0)/ligand/phase transfer catalyst functioned as a simple initiation system for the living radical polymerization of butyl meth-

acrylate in solution.⁴ Destarac et al. also reported on the considerable acceleration effect of Cu(0) on the ATRP of MMA with CuCl/bipyridine/polychloroalkane.⁵

ATRP has been gaining popularity as a method of preparing novel polymers based on its controllable polymerization mechanism.^{6,7} In the ATRP process, the growing chain end is kept in an equilibrium state between active and dormant species. The metal complex, consisting of metal halide and ligand, acts as a catalyst functioning in the redox equilibrium between the oxidation and reduction states.⁸ Almost all the studies of ATRP have investigated initiator systems and monomers in solution or bulk, focusing on control of the propagation, and clarification of the kinetics.⁹ It is well known that complexes of transition metals, including ruthenium, iron, copper, nickel, palladium, rhenium, and molybdenum, are suitable as ATRP catalysts. In particular, iron-based catalysts, e.g., initiator/FeX₂/2,2'-bipyridine (X: halogen), are attractive because they are economical and nontoxic. This means, iron-based catalysts have been extensively investigated for their practical use in actual applications.^{3,10,11}

Although ATRP is promising as a precise polymerization technology, large amounts of solvent are required for the polymerization and purification processes. Gas-phase-assisted surface polymerization (GASP), on the other hand, is a controllable surface modification technology that is solvent-free.^{12–15} If GASP could be combined with ATRP technology to achieve precise coatings of great accuracy,¹² then this would

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be an ideal method particularly appropriate in the precise modification of metal surfaces. However, thus far, there has been no report dealing with ATRP in a gas phase. Previously, we found that a simple system zero-valent iron (Fe(0))/methyl α -bromophenylacetate could initiate a physically controlled polymerization of MMA and St on metal surfaces without any oxidized Fe(II)/Fe(III) species and ligand.¹⁶ However, only low molecular weight polymers, of less than 7400 in M_n , were obtained by the initiator system. These results interested us because if the molecular weight could be increased then the GASP process could have potential applications in many fields.

In this study, to produce a high polymer on Fe(0) surface and to clarify the polymerization behavior of GASP with a Fe(0)-based initiator system, various Fe(0)-based initiator systems were investigated for the polymerization of MMA. Consequently, successful polymer production was achieved by GASP with a Fe(0)/*p*-toluene sulfonylchloride (TsCl) as a totally solid-type initiator system, and it was demonstrated that physically controlled radical polymerization proceeded at the gas–solid interface.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA, > 99%, Tokyo Chemical Industry Co. (TCI)) was purified by distillation under reduced pressure from CaH₂ just before polymerization. Iron powder (Fe(0), diameter < 45 μ m, Wako Pure Chemical Industries (Wako)), α -iron(III) oxide (Fe₂O₃, 99.9%, Wako), iron(II) bromide (Fe(II)Br₂, Aldrich), *p*-toluene sulfonylchloride (TsCl, Wako), and 4-*tert*-butylcatechol (TCI) were used as received. Many other kinds of organic halides were purchased from TCI and used as received. All other reagents were commercially obtained and used as received.

Characterization methods

¹H-NMR spectra were measured on a 400-MHz Varian INOVA 400 VLX spectrometer. Chloroform-*d* (CDCl₃) was used as a solvent. Chemical shift was reported as a δ value (ppm) relative to the signal of tetramethylsilane (TMS) that acted as an internal standard in CDCl₃ unless otherwise noted. Fourier transform infrared (FTIR) spectroscopy was performed using a JASCO FT-IR 460 plus spectrometer.

Number- and weight-average molecular weights (M_n and M_w , respectively) of the polymer were measured on a TOSOH HLC-8220 gel permeation chromatography (GPC) system with refractive index (RI) and ultraviolet (UV, 254 nm) detectors under the following conditions: TSK gel super HM-H linear column (linearity range, 1×10^3 – 8×10^6 ; molecular weight exclusion limit, 4×10^8), chloroform (HPLC grade)

eluent at a flow rate of 0.6 mL min⁻¹, and column temperature of 40°C. The calibration curve for GPC analysis was obtained using polystyrene (PSt) standards with a low polydispersity (5.00×10^2 , 1.05×10^3 , 2.50×10^3 , 5.87×10^3 , 9.49×10^3 , 1.71×10^4 , 3.72×10^4 , 9.89×10^4 , 1.89×10^5 , 3.97×10^5 , 7.07×10^5 , 1.11×10^6 , TOSOH Corp.). By using $[\eta]M$ as a universal calibration parameter,¹⁷ the PSt calibration was converted into one for PMMA by the relationship

$$\log M_1 = \log(K_2/K_1)/(1 + a_1) + \{(1 + a_2)/(1 + a_1)\} \log M_2 \quad (1)$$

where K_1 , K_2 (mL g⁻¹), a_1 , and a_2 are the Mark-Houwink-Sakurada equation parameters for PMMA (subscript 1) and PSt (subscript 2) respectively. The Mark-Houwink-Sakurada equations used for the PMMA and PSt were as follows:

$$\text{PMMA}^{18} \quad [\eta] = 0.43 \times 10^{-4} M_1^{0.80} \quad (2)$$

$$\text{PSt}^{19} \quad [\eta] = 0.49 \times 10^{-4} M_2^{0.796} \quad (3)$$

X-ray photoelectron spectroscopy (XPS) spectra were recorded on a PHI 5800 (Physical Electronics Co.) using an Al K α X-ray source, with the X-ray beam set for measuring the binding energy at 14 kV and 350 mW with a takeoff angle of 45°, and an analyzer chamber pressure in the range of 10⁻⁹–10⁻¹⁰ Pa.

Bulk polymerization of MMA with Fe(0)/organic halides

In a typical procedure, Fe(0) powder (0.5 g) was added into a glass tube reactor (16 mm in diameter and 200 mm in length). The reactor, after sealing with a rubber septum, underwent three cycles of degassing *in vacuo*, followed by backfilling with argon (Ar) through a syringe. Monomer (MMA [5.0 mL, 47.19 mmol]) and initiator (alkyl halide [0.5 mL]) were added via an Ar-purged syringe. After bubbling Ar through the solution for 1 min, the reactor was immersed in a shaking water-bath thermostated at 60°C to start polymerization. After 10 h, the reactor was taken out, and the contained product was dissolved in CHCl₃ (3 mL), filtered to separate it from the iron powder, precipitated with methanol of 80 mL, and isolated by filtration. The product was dried under a reduced pressure for 24 h at 25°C, weighed, and then analyzed by FTIR, ¹H-NMR, and GPC. Initiator efficiency was calculated as a ratio of the number of obtained polymer chains, yield/ M_n , to the used molar quantity of initiator and expressed in terms of yield/ M_n /initiator (mol mol⁻¹).

General procedure of GASP

In a typical procedure, GASP was carried out in a H-shaped glass tube reactor with a vacuum cock and a

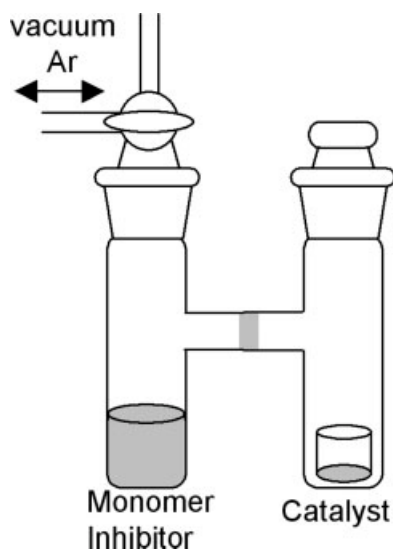


Figure 1 H-shaped glass tube reactor for GASP.

glass filter separator (pore size, 20–30 μm) at the bridge section (Fig. 1), as described in previous reports.^{12–14} A solution of TsCl (22 mg, 0.13 mmol) in diethyl ether (0.5 mL) and Fe(0) powder (50 mg) was added in a glass pan (bottom surface area, 154 mm^2 ; height, 40 mm). The glass pan was dried for 1 h at ambient temperature and then set in one of the bottom legs of the H-shaped glass tube reactor. A solution of MMA (0.5 mL) and 4-*tert*-butylcatechol (~ 20 mg) was added in the other bottom leg of the reactor. The reactor was degassed by three freeze-pump-thaw cycles and then sealed under a saturated atmosphere of MMA. Polymerization was carried out under a saturated vapor pressure of MMA (2.35×10^4 Pa) in a thermostated oven at 60°C. After 5 h, the polymerization was

stopped, and the product was dissolved in CHCl_3 (3 mL), filtered to separate it from the iron powder, precipitated with methanol of 80 mL, and isolated by filtration. The product was dried under reduced pressure for 24 h at 25°C, weighed, and then analyzed by FTIR, $^1\text{H-NMR}$, and GPC. Initiator efficiency was calculated in the same manner as the bulk polymerization.

RESULTS AND DISCUSSION

Bulk polymerization of MMA with simple initiator system: Fe(0)/organic halides

In a previous report,¹⁶ it was found that a simple initiator system Fe(0)/methyl α -bromophenylacetate (MBP) was able to initiate the radical polymerization of MMA on iron powder surfaces in a gas phase, suggesting a physically controlled polymerization behavior; that is, it was shown that the molecular weight of the obtained polymer increased with increase in its yield. However, the number-average molecular weight (M_n) of the obtained polymer was lower than 7400 even after 24 h at 60°C, suggesting a slow propagation process. To obtain a polymer having a higher molecular weight, through efficient initiation and controlled propagation, various initiator systems, Fe(0)/organic halides, were evaluated for their ability to initiate the radical polymerization of MMA in bulk. Results are listed in Table I.

All the systems, except for the reference without an initiator, were able to initiate the polymerization of MMA to give polymers with different yields and molecular weights in a range of $M_n = 32,000$ – $1,121,000$. Previously, it was reported that the polymerization rate and polydispersity index (PDI) value of resulting

TABLE I
Polymerization of MMA with Fe(0)/Organic Halides in Bulk

Run	Initiator ^b		Yield (wt %)	GPC		Initiator efficiency (10^5)
	Type	Amount (mmol)		M_n	PDI	
Ref. ^a	None	–	0	–	–	–
1-1	MBP	3.18	8.47	188,000	1.6	67
1-2	MC	4.39	8.69	830,000	1.4	11
1-3	BAEE	3.36	8.82	105,000	1.9	118
1-4	BzCl	4.34	4.16	263,000	3.8	17
1-5	4-FBB	4.01	1.86	779,000	1.7	3
1-6	1,6-DBH	3.25	0.56	292,000	1.7	3
1-7	CHCl_3	6.25	7.63	1,121,000	1.5	5
1-8	CCl_4	5.18	7.44	616,000	1.8	11
1-9	TsCl	2.62	11.85	32,000	2.1	667

Reaction conditions: All the reactions were carried out with MMA, 5 mL (47.19 mmol); Fe(0), 0.5 g; and organic halide, 0.5 mL at 60°C for 10 h in bulk.

^a Reaction time, 15 h.

^b MBP, methyl α -bromophenylacetate; MC, methyl 2-chloropropionate; BAEE, 2-bromoisobutyric acid ethyl ester; BzCl, benzyl chloride; 4-FBB, 4-fluorobenzyl bromide; 1,6-DBH, 1,6-dibromohexane; TsCl, *p*-toluenesulfonyl chloride.

polymers on ATRP varied depending on the kind of organic halides used as initiators.²⁰ The esters having a halogen atom on the α -carbon, such as MBP, methyl 2-chloropropionate, and 2-bromoisobutyric acid ethyl ester, showed relatively higher yield (8–9 wt %) and initiator efficiency ($11\text{--}118 \times 10^{-5}$) (runs 1-1–3 in Table I). The initiator efficiency was calculated as a ratio of the number of obtained polymer chains, yield/ M_n , to the used molar quantity of initiator. Although two benzyl halides and one alkyl halide were of low activity and low initiator efficiency ($3\text{--}17 \times 10^{-5}$), they gave relatively higher molecular weight polymers (runs 1-4–6 in Table I). Multisubstituted methane halides, CCl_4 and CHCl_3 , gave polymers having both a high yield and high molecular weight (runs 1-7–8 in Table I), but with an initiator efficiency of less than 11×10^{-5} , suggesting that organic halides with a lower oxidation-activity give higher molecular weight polymers. This may be because in such a system a trace amount of Fe(II)/(III) halides was formed and the propagation continued without frequent termination or atom transfer reactions. This catalytic feature means that the controlling of the polymer's molecular weight and its distribution is difficult.

In comparison with the above-mentioned liquid-type organic halides, a solid-type organic halide *p*-toluenesulfonyl chloride (TsCl), exhibited the highest yield and the lowest molecular weight of the polymer (run 1-9 in Table I). It also showed the highest initiator efficiency of 667×10^{-5} . The initiator TsCl has been reported as an active initiator for ATRP in a liquid phase,²¹ and our results confirmed that TsCl, with its high activity and efficiency, was the obvious choice as the initiator for controlling GASP.

GASP of MMA with Fe-compound/TsCl systems

The GASP of MMA with TsCl as the initiator was carried out on the Fe(0) powder surface under a saturated vapor pressure of MMA (2.35×10^4 Pa) at 60°C. Results are listed in Table II.

During the GASP of MMA, the surface color of Fe(0) powder changed from gray to dark red, which indicated the formation of oxidized species, Fe(II) and/or Fe(III) chlorides on the Fe(0) surface as previously reported when using the Fe(0)/MBP system.¹⁶ A large amount of deposit was found on the Fe(0) powder surface with a simple system Fe(0)/TsCl without ligand (run 2-1). Interestingly, this system gave a high molecular weight polymer of 36,000 M_n , showing a high initiator efficiency of 0.0221 in comparison with the result in the liquid phase (Table I). These results suggest that the effective initiation and propagation by the Fe(0)/TsCl system were achieved in the gas phase, because TsCl was concentrated on the Fe(0) surface, not dispersed in the liquid monomer phase. Both components of Fe(0) and TsCl were essential for the GASP, because no polymer deposition was obtained without Fe(0) or TsCl (run 2-2–3). Moreover, the ATRP is generally inhibited by paramagnetic species in a way similar to the conventional radical polymerization in a liquid phase.²² The GASP with the simple system Fe(0)/TsCl was also suppressed by the addition of a radical trapping reagent, 4-*tert*-butylprocatechol (run 2-4). This result must indicate that the GASP with the Fe(0)/TsCl system proceeded by a radical mechanism. Production of a small amount of polymer may be due to the deposition accumulated on the trapping reagent.

A relatively high deposition was observed with the iron dibromide Fe(II)Br₂/TsCl system, but the molecular weight of the product was very low (run 2-5), suggesting that the excess concentration of active species was causing effective termination reactions. In the case of the oxidized iron (Fe₂O₃)/TsCl system, the polymer yield was poor and molecular weight was also very low (run 2-6). The formation of active species on the Fe₂O₃ powder surface must be very slow, because the change in the surface color of the Fe₂O₃ powder to red was hardly observed, in contrast to the Fe(0)/TsCl system. Thus, the Fe₂O₃/TsCl system inevitably shows a much poorer GASP activity. Per-

TABLE II
GASP of MMA with Fe-Compound/TsCl System

Run	Catalyst			Time (h)	Yield (mg)	GPC		Initiator efficiency
	Type	Amount (mg)	TsCl ($\mu\text{mol mm}^{-2}$)			M_n	M_w	
2-1	Fe(0)	50.1	0.75	5	91.92	36,000	60,000	0.0221
2-2	Fe(0)	78.1	–	24	0	–	–	–
2-3	–	–	0.76	5	0	–	–	–
2-4	Fe(0) ^a	50.0	0.68	5	19.39	360	440	–
2-5	Fe(II)Br ₂	46.1	0.52	5	48.15	220	230	–
2-6	Fe ₂ O ₃	50.4	0.72	5	6.38	220	240	–

Polymerization conditions: MMA 2.0 mL, at 60°C.

^a GASP was carried out in the presence of 4-*tert*-butylprocatechol (0.30 mmol) as a radical trapping agent on Fe(0) powder surface.

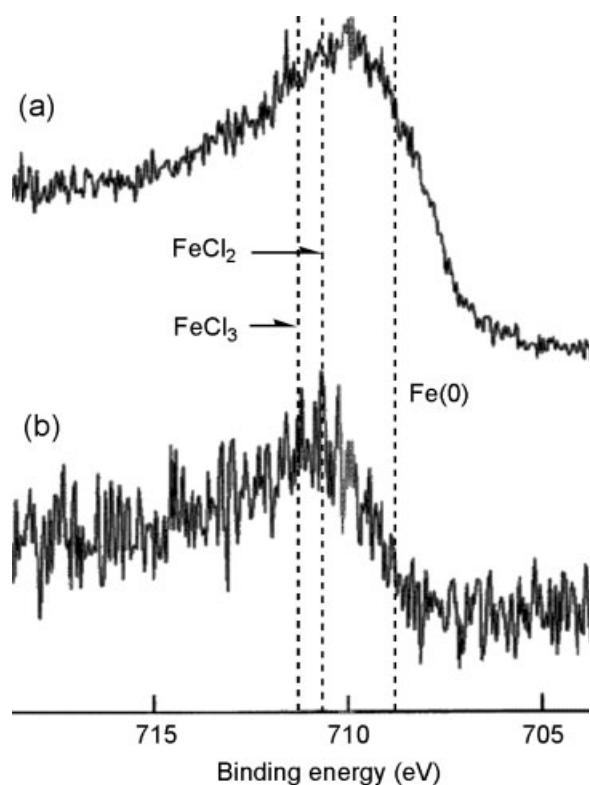


Figure 2 XPS spectra of Fe(0)/TsCl catalyst before (a) and after GASP (b).

cec et al. reported that on ATRP of butyl methacrylate and St using Cu(0) and Cu₂O, the formation of CuCl was slower in the case of Cu₂O than in the case of Cu(0).⁴ These results suggest that the combination of Fe(0)/TsCl would be a more appropriate system for the GASP of MMA, than are the other initiator systems.

The Fe(0) powder surface in the polymerization system with Fe(0)/TsCl was observed with an X-ray photoelectron spectrometer (XPS) before and after the GASP of MMA (Fig. 2). Figure 2(a) shows the XPS spectrum of the catalyst surface before the polymerization, in which the intensity peak of the binding energy was observed at 710 eV. Considering that the binding energy values of Fe(0), Fe(II)Cl₂, and Fe(III)Cl₃ are 708.7,²³ 710.6,²⁴ and 711.3 eV,²⁴ respectively, this observed binding energy value suggests that a mixture of Fe(0) and its oxidized species must be present on the iron powder surface before GASP. After the GASP, the intensity peak shifted to a higher binding energy value of around 711 eV [Fig. 2(b)]. This means that the iron powder surface was covered by the oxidized Fe(II) and/or Fe(III) species during the GASP process.³

GPC results listed in Table II indicate that the deposited polymer obtained with the simple initiator system, Fe(0)/TsCl, has a significantly high molecular weight than those obtained with other systems. The deposited polymer on the Fe(0) powder surfaces was

completely dissolved in chloroform and tetrahydrofuran. Its chemical structure was characterized by FTIR, ¹H-NMR, and GPC analyses. FTIR spectrum of the deposits showed a sharp peak at 1730 cm⁻¹ assigned to λ_{C=O}. Figure 3 shows the ¹H-NMR spectrum of a deposited polymer obtained by GASP at 60°C for 1 h with Fe(0)/TsCl (50 mg/0.65 μmol mm⁻²). In this spectrum, all the main signals (d and e) were assigned to corresponding protons in a repeating unit; specifically, a sharp singlet e at 3.53 ppm and complex signals d in a range of 0.77–1.95 ppm were assigned to –COOCH₃ and (–CH₂– + –CH₂–C(CH₃)<), respectively. These results show clearly that the deposit on the Fe(0) powder surface is a high molecular weight PMMA.

In Figure 3, in addition to the main signals, some minor signals were observed at 2.43 (a), 7.34 (b), and 7.86 ppm (c), which were assigned to protons on methyl and phenyl groups that originated from the initiator TsCl as shown in Figure 3. If each polymer chain has one *p*-toluenesulfonyl group at one of the chain ends, the *M_n* value of the polymer can be calculated from the integral intensity value by comparing it with that of main chain protons. The calculated *M_n* value was 18,000 based on the integral intensity values of the signals at 7.86 and 3.65 ppm, a value very similar to the *M_n* = 17,800 obtained from GPC analysis. This means that in this GASP the chain transfer reactions and terminations scarcely occurred except in the initial stage, where some termination reactions

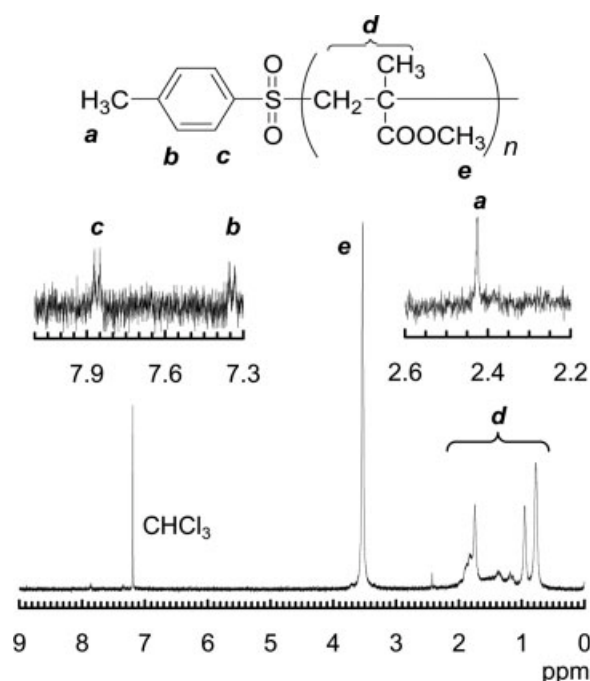
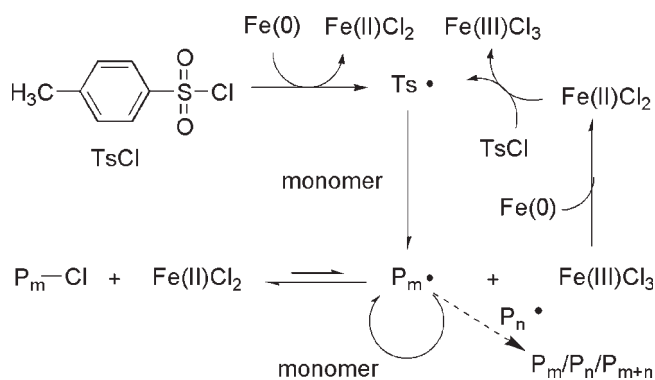


Figure 3 ¹H-NMR spectrum of a deposited polymer during GASP with Fe(0)/TsCl (50.0 mg/0.65 μmol mm⁻²) system at 60°C for 1 h.



Scheme 1 Polymerization of MMA with the Fe(0)/TsCl system.

must occur because of the high concentration of active species on the solid surfaces.

From the above-mentioned results, it is considered that the GASP of MMA with the Fe(0)/TsCl system is initiated by radical species from TsCl via an oxidation reaction of iron species, and that it is controlled by an equilibrium between Fe(II)Cl₂ and Fe(III)Cl₃, as shown in Scheme 1.

GASP of MMA with various feed ratios of Fe(0)/TsCl

GASP of MMA was carried out with various compositions of the Fe(0)/TsCl system at 60°C for 5 h. The results are listed in Table III. The yield and molecular weight of obtained polymers changed depending on the composition of the system. Under low composition ratios of Fe(0) against TsCl (run 3-1–3), products having high molecular weights were consistently obtained, although both the yield and initiator efficiency were low. With increase in the composition of Fe(0) in the feed (run 3-4–5), the polymer yield drastically increased, but the molecular weight value suddenly decreased, accompanying the marked increase in PDI value. It is noteworthy that the initiator efficiency rapidly increased up to 0.80 from ~ 0.002. These results suggest a discontinuous change in the polymerization process on the solid surface. This sudden change may be the cause of some of the results

being out of order, such as that of run 2-1, in comparison with the ordered results in Table III. From a general viewpoint, the tendency of the change is reasonable, because the generation of active species, Ts•, from TsCl is promoted by Fe(0), after which the active species accelerate the initiation and subsequent propagation reactions, resulting in an increase in the polymer yield. The generation of a large number of active species may also accelerate the termination by disproportionation or recombination to produce dead-end products, P_m/P_n/P_{m+n}, as shown in Scheme 1. The results, showing a production of oligomers and wide PDI values in run 3-4–5, must be caused by the generation of a large amount of active species. On the other hand, in the case of lower feed ratios of Fe(0) to TsCl (run 3-1–3), higher molecular weight polymers with relatively lower PDI values were consistently obtained, with polymer yield being depressed.

Taking into consideration the previous results of GASP,^{12–14,16} the molecular weight and PDI value of obtained polymers are considered to be affected by various factors, which include not only the composition ratio of the initiator system, but also the homogeneity of substrate/deposit surfaces. In the previous report,¹² it was found that the deposition rate of PMMA increased with reaction time, suggesting the enhancement of the polymerization by the increase in surface roughness. In this study, in the lower feed ratio of Fe(0) powder (run 3-1–3), it is considered that the propagation process is controlled by a constant surface concentration of active species, resulting in a similar low yield and high molecular weight polymer production. On the other hand, in cases where a large amount of Fe(0) powder was used (run 3-4–5), many active species will be generated on the powder surface. Moreover, not only many more gaseous monomers must be adsorbed on the Fe(0) powder surface, but they must also be absorbed into the interstitial spaces of the powder. Thus, because of the remarkably high concentration of active species, enhanced polymerization is achieved at the cost of molecular weight.

If active species at growing chain-ends are immobilized on deposit surfaces and prevented from inter-

TABLE III
GASP of MMA with Various Compositions of Fe(0)/TsCl System

Run	Fe(0) (mg)	TsCl ($\mu\text{mol mm}^{-2}$)	Yield (mg)	GPC		Initiator efficiency
				M_n	M_w	
3-1	0.1	0.53	21.80	120,000	300,000	0.00223
3-2	1.5	0.53	15.92	140,000	294,000	0.00139
3-3	5.3	0.53	18.65	100,000	250,000	0.00228
3-4	10.0	0.53	39.26	8,200	58,200	0.0587
3-5	99.6	0.54	73.40	1,100	20,600	0.802

Polymerization conditions: MMA 2.0 mL, at 60°C for 5 h.

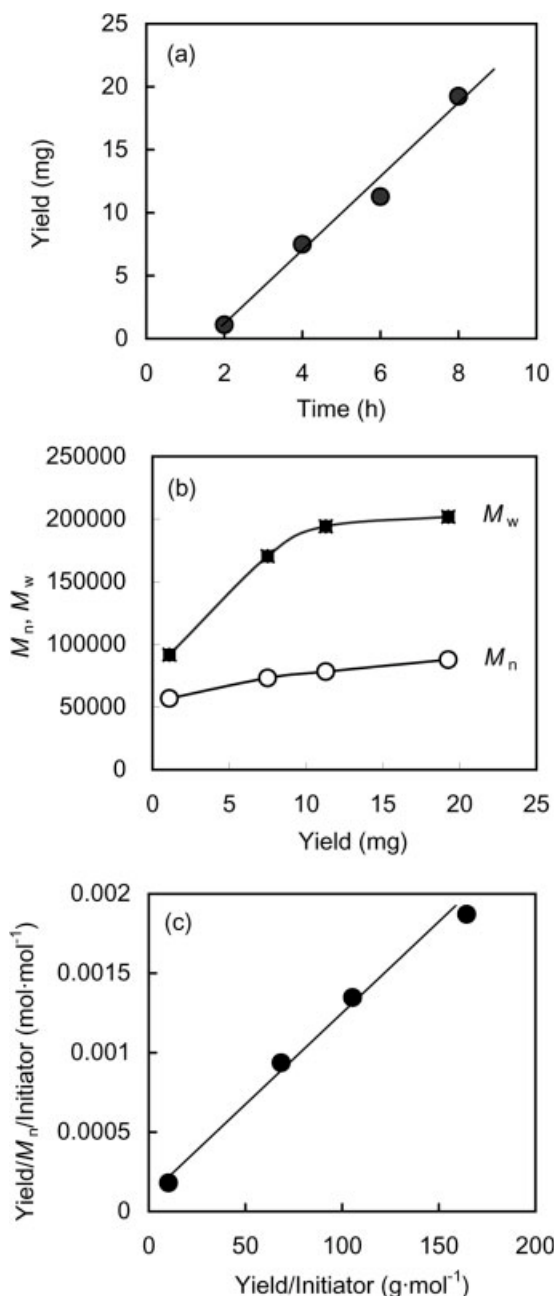


Figure 4 Time-course test of GASP of MMA with Fe(0)/TsCl (2.0 mg/0.53 $\mu\text{mol mm}^{-2}$) at 60°C. Changes in (a) polymer yield, (b) M_n and M_w , and (c) initiator efficiency.

acting with other active species, the termination reactions will be suppressed, allowing the propagation reaction to continue, producing an increase in the molecular weight with reaction time.¹⁶ To determine the propagation behavior of the active chain ends on the deposit surfaces, a time-course test of GASP was conducted with Fe(0)/TsCl (2.0 mg/0.53 $\mu\text{mol mm}^{-2}$) at 60°C. The results are illustrated in Figure 4. A linear increase in the polymer yield with reaction time was observed [Fig. 4(a)]. The M_n value was gradually increased with increase in the polymer yield [Fig. 4(b)].

In Figure 5, GPC profiles of polymers obtained at 2 and 8 h are shown. Clearly, the profile shifts to a higher molecular weight region with time. These results indicate the living nature of GASP of MMA on the Fe(0) surface and, except for their high molecular weight production, they are similar to the previous results with the Fe(0)/MBP system.¹⁶ In Figure 4(b), it was found that the M_w value rapidly increased, with consequent increase in the PDI value [Fig. 4(b)]. This result suggests that the actual propagation rates of the active species on the surface are not equal, reflecting the heterogeneity of the initiation and propagation processes.

In Figure 4(c), a relationship between the yield/ M_n /initiator (mol mol⁻¹) and yield/initiator (g mol⁻¹) is depicted. This relationship reveals the change in the initiator efficiency. The initiator efficiency gradually and linearly increased with the polymer yield; however, its value was much lower than 1.0. The gradual increase in the initiator efficiency is consistent with the widening of the PDI value with time in Figure 4(b). If, in this GASP process, chain transfer reactions occur in the same way as for a conventional free radical polymerization process, the initiator efficiency value will be greater than 1.0. Thus, the above-mentioned results suggest, importantly, that the chain transfer reactions are suppressed or inhibited during the GASP of MMA with Fe(0)/TsCl.

Process of GASP on Fe(0) surface

The above-mentioned results demonstrate that the GASP of MMA with the Fe(0)/TsCl system is a physically controlled process at the gas–solid interface. A plausible process for the GASP is illustrated in Scheme 2. First, the Fe(0) surface is oxidized by TsCl to produce Fe(II)Cl₂ and Fe(III)Cl₃ species, accompanying the initiator radical species, Ts·. The initiator radicals react with monomers afforded from the gas phase to change into active propagating species. As

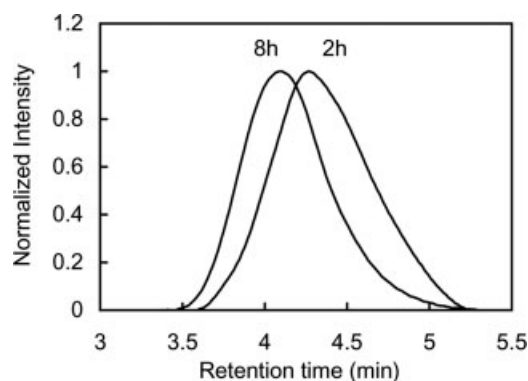
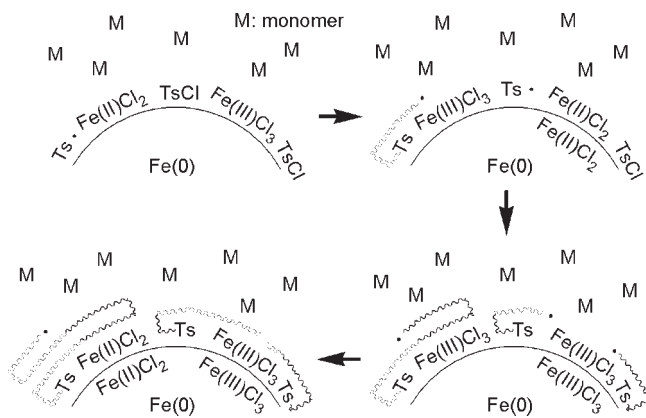


Figure 5 Changes in GPC profile of PMMA in time-course test of GASP with Fe(0)/TsCl (2.0 mg/0.53 $\mu\text{mol mm}^{-2}$) at 60°C.



Scheme 2 Plausible process of GASP of MMA with TsCl as on Fe(0) surface.

the propagation reaction proceeds, the metallic and reactor-bottom surfaces are covered by the polymer chains after which a further accumulation occurs on this earlier formed polymer layer to produce the polymer deposits. During this multilayer accumulation, the active propagating species must be immobilized on the surface if the propagation reaction is to progress, resulting in a physically controlled polymerization process on the Fe(0) powder surfaces.

CONCLUSIONS

GASP of MMA with Fe(0)/TsCl initiator systems resulted in the production of high molecular weight polymers on solid surfaces. From the suppression effect of a radical trapping reagent, it was found that the GASP by Fe(0)/TsCl proceeded by a radical mechanism according to the ATRP mechanism. The composition ratio of Fe(0) to TsCl affected the yield and molecular weight of obtained polymers, and the initiator efficiency. When the lower ratios of Fe(0)/TsCl were employed, high molecular weight polymers were obtained with low yields. On the time-course test, it was found that the M_n value increased with the polymer yield, and that the initiator efficiency was at a very low level of less than 1.0. These results suggest that a physically controlled radical po-

lymerization of MMA by the immobilized active species could be made to proceed at gas–solid interfaces.

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