

Effect of Sparteine on the Photopolymerization of Methyl and Ethyl Methacrylates with Bis(cyclopentadienyl)titanium Dichloride in a Water–Methanol Mixture

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ABSTRACT: The photopolymerization of methyl methacrylate (MMA) with bis(cyclopentadienyl)titanium dichloride (Cp_2TiCl_2) in a H_2O – MeOH [1 : 1 (v/v)] mixture was examined at 40°C in the presence of 2,2'-bipyridyl (Bipy), 1,10-phenanthroline (Phen) or sparteine (Spr) as the chelating reagent. The presence of these chelating reagents retarded the photopolymerization. Poly(MMA)s formed in the presence of them were found to contain a considerable fraction of the benzene-insoluble part, in contrast to the ones in the absence of them. Spr was the most effective for formation of the insoluble part. The benzene-insoluble poly(MMA) was insoluble in usual organic solvents including acetone, tetrahydrofuran, ethyl acetate, and dimethyl sulfoxide, suggesting crosslinking. However, poly(MMA) reproduced by hydrolysis of the insoluble part followed by methylation was soluble in usual organic solvents, indicating no crosslinking between polymer main chains. The insoluble part was thermally more stable than the soluble part. Polymerization of ethyl methacrylate in the presence of Spr gave similar results. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 815–822, 2001

Key words: photopolymerization; Cp_2TiCl_2 ; methacrylate; sparteine

INTRODUCTION

Some combined systems of metallocenes and organic halides or acid anhydrides were reported to initiate radical polymerizations of vinyl monomers, although the metallocenes alone show little initiating activity.^{1–5} Living radical polymerization characters were found in the polymerization of methyl methacrylate (MMA) initiated with the binary system of cobaltocene and bis(ethyl acetate) copper (II) in acetonitrile.^{6–8}

In the preceding articles,^{9,10} we found that bis(cyclopentadienyl)titanium dichloride (Cp_2TiCl_2)

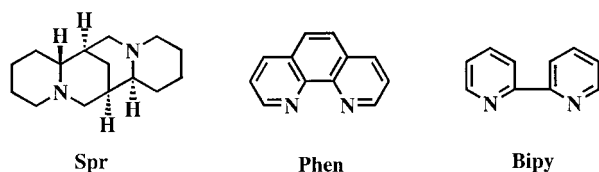
serves as an effective initiator for the radical polymerization of MMA in a water–methanol (H_2O – MeOH) mixture, and that the polymerization is profoundly accelerated, even by irradiation of a 15-W fluorescent room lamp, although Cp_2TiCl_2 was reported to act scarcely as a photoinitiator for MMA in bulk.¹¹ It is of great interest that the resulting poly(MMA) contains a considerable fraction of novel solubility characters; soluble in benzene and toluene, but insoluble in tetrahydrofuran (THF), acetone, methyl ethyl ketone (MEK), ethyl acetate, acetonitrile, dimethyl sulfoxide (DMSO), and *N,N*-dimethylformamide (DMF). Similar results were observed for the polymerization of ethyl methacrylate (EMA) with Cp_2TiCl_2 in an H_2O – MeOH mixture.¹²

In the present article we have investigated the effects of diamine chelating reagents [especially

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Scheme 1

sparteine (Spr)] on the polymerizations of MMA and EMA with Cp_2TiCl_2 in a H_2O -MeOH mixture, and found that a considerable fraction of the resulting polymers are insoluble even in benzene and toluene. 1,10-Phenanthroline (Phen) and 2,2'-bipyridyl (Bipy) were examined as chelating reagent along with Spr (Scheme 1).

EXPERIMENTAL

Commercial MMA and EMA were freed from inhibitor by treatment with a 5% NaOH aqueous solution, dried over anhydrous sodium sulfate, and distilled. MeOH was used after distillation. Ion-free water was used.

Cp_2TiCl_2 (supplied from Nichia Chemical Industries, Tokushima, Japan), Bipy (purchased from Wako Pure Chemical Industries, Ltd.), Phen as monohydrate (purchased from Wako Pure Chemical Industries, Ltd.), and Spr (purchased from Sigma Chemical Co.) were used as received. Dimethyl 2,2'-azobis(isobutyrate) (MAIB) was recrystallized from MeOH.

Polymerizations of MMA and EMA were conducted in degassed and sealed glass tubes at 40°C without shaking under irradiation of a 15-W fluorescent room lamp (Toshiba FL 15EX-N-H) from a distance of 60 cm. The resulting polymers were isolated by pouring the polymerization mixtures into a large excess of MeOH containing small amounts of 4-*tert*-butylcatechol as inhibitor and HCl. The precipitated polymers were filtered, dried under vacuum, and weighed. Poly(MMA) and poly(EMA) were further divided into soluble and insoluble parts in benzene.

Poly(MMA) was hydrolyzed according to the method of Loebel et al.¹³ Poly(MMA) was added into concentrated sulfuric acid and was allowed to stand for a week at room temperature. The homogeneous reaction mixture was poured into a large amount of ice water. Resulting poly(methacrylic acid) as precipitate was separated by centrifugation and washed with water. The poly(methacrylic acid) was purified by reprecipitation

using a methanol (solvent)-ether (nonsolvent) system and was methylated with diazomethane prepared from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide,¹⁴ reproducing poly(MMA).

IR spectra were obtained with a Perkin-Elmer 1600 FTIR spectrometer. $^1\text{H-NMR}$ spectra were observed in deuteriochloroform with a JEOL GX-400 (400 MHz) spectrometer. Gel permeation chromatography (GPC) was performed with a Toso HLC-802H chromatograph at 38°C using THF as eluent. The number-average (\bar{M}_n) and weight-average (\bar{M}_w) molecular weights were estimated from the GPC results by calibration with polystyrene standards. Dynamic thermogravimetry (TG) of polymers was performed in a nitrogen atmosphere (flow rate: 20 mL/min) on a Shimadzu TG-50 thermogravimeter at a heating rate of $10^\circ\text{C}/\text{min}$. A differential scanning calorimeter (DSC) (Shimadzu DSC-50) was used for thermal analysis of the polymers (heating rate: $10^\circ\text{C}/\text{min}$).

RESULTS AND DISCUSSION

Photopolymerization of MMA with Cp_2TiCl_2 in a H_2O -MeOH Mixture in the Presence of Diamine Chelating Reagents

As described in the preceding article,¹⁰ the photopolymerization of MMA with Cp_2TiCl_2 in an H_2O -MeOH mixture gives a considerable fraction of THF-insoluble poly(MMA). The THF-insoluble poly(MMA) shows novel solubility characters. To see the effects of diamine chelating reagents on the polymerization, the photopoly-

Table I Effect of Chelating Reagents on the Photopolymerization of MMA with Cp_2TiCl_2 in an H_2O -MeOH [1 : 1 (v/v)] Mixture at 40°C for 10 h^a

Chelating Reagent	Total Yield (%)	Fraction (%)	
		Benzene Soluble	Benzene Insoluble
None	82.9	100 ^b	0
Spr	53.0	32	68
Bipy	62.8	77	23
Phen	10.0	94	6

^a [MMA] = 0.935 mol/L, [Cp_2TiCl_2] = 1.5×10^{-3} mol/L, [chelating reagent] = 3.0×10^{-3} mol/L.

^b This fraction contained acetone-soluble (61%) and -insoluble (39%) parts.

Table II Solubility of the Benzene-Soluble and -Insoluble Parts of Poly(MMA) Formed in the Photopolymerization with the Cp_2TiCl_2/Spr System in an $H_2O-MeOH$ [1 : 1 (v/v)] Mixture at 40°C for 10 h^a

Solvent	Benzene Soluble	Benzene Insoluble	Radical ^b Poly(MMA)
Benzene	Soluble	Insoluble	Soluble
Toluene	Soluble	Insoluble	Soluble
Chloroform	Soluble	Insoluble	Soluble
THF	Soluble	Insoluble	Soluble
Ethyl acetate	Soluble	Insoluble	Soluble
Acetone	Soluble	Insoluble	Soluble
Methyl ethyl ketone	Soluble	Insoluble	Soluble
Acetonitrile	Insoluble	Insoluble	Soluble
Dimethylformamide	Soluble	Insoluble	Soluble
Dimethylsulfoxide	Soluble	Insoluble	Soluble

^a [MMA] = 0.935 mol/L, [Cp_2TiCl_2] = 1.5×10^{-3} mol/L, [Spr] = 1.5×10^{-3} mol/L.

^b Prepared by the polymerization with MAIB at 40°C in benzene.

merization of MMA with Cp_2TiCl_2 in a $H_2O-MeOH$ [1 : 1 (v/v)] was carried out at 40°C for 10 h in the presence of Spr, Phen, or Bipy as chelating reagent, where the concentrations of MMA, Cp_2TiCl_2 and chelating reagents were 0.935, 1.5×10^{-3} and 3.0×10^{-3} mol/L, respectively. The resulting poly(MMA) precipitated during the photopolymerization.

Table I summarizes the results obtained together with those of the polymerization in the absence of a chelating reagent. Thus, the presence of chelating reagents, especially Phen, retarded the photopolymerization. Further, the resulting poly(MMA)s were observed to contain a benzene-insoluble part, while poly(MMA) formed in the absence of chelating reagents was completely soluble in benzene. The latter benzene-soluble poly(MMA) contained acetone-soluble (61%) and insoluble (39%) parts as described in the previously.¹⁰ Poly(MMA)s obtained in the presence of chelating reagents were fractionated into benzene-soluble and insoluble parts. The fraction of benzene-insoluble part depended on the chelating reagent used.

Table II shows the solubility of benzene-soluble and insoluble parts formed in the presence of Spr. For comparison, the results of poly(MMA) separately obtained in the polymerization with MAIB in benzene are also presented in the table. Thus, the benzene-insoluble part was found to be insoluble in any organic solvents used here, suggesting crosslinking. However, the insoluble part was dissolved in sulfuric acid, probably with hydrolysis, indicating no crosslinking between polymer main chains.

Table III presents the photopolymerization results observed at 40°C when the concentrations of Bipy and Phen were varied.

The polymer yield decreased with increasing Bipy concentration. The fraction of the benzene-insoluble part was about 20% of the total yield for most of the Bipy concentrations used though a much higher fraction (43%) of the insoluble part was observed for a low Bipy concentration (1.0×10^{-3} mol/L).

Table III Photopolymerization of MMA with the $Cp_2TiCl_2/Bipy$ and $Cp_2TiCl_2/Phen$ Systems in an $H_2O-MeOH$ [1 : 1 (v/v)] Mixture at 40°C for 10 h^a

Chelating Reagent	[Chelating Reagent] $\times 10^3$ (mol/L)	Total Yield (%)	Fraction (%)	
			Benzene Soluble	Benzene Insoluble
Bipy	0	82.9	100 ^b	0
	1.0	93.4	57	43
	1.5	64.3	84	16
	2.0	53.5	79	21
	3.0	53.0	77	23
Phen	6.0	15.2	80	20
	1.0	23.1	99	1
	1.5	13.7	97	3
	3.0	10.0	94	6
	4.5	4.1	—	—
	6.0	3.8	—	—

^a [MMA] = 0.935 mol/L; [Cp_2TiCl_2] = 1.5×10^{-3} mol/L.

^b This fraction contained acetone-soluble (61%) and -insoluble (39%) parts.

Table IV Photopolymerization of MMA with Cp_2TiCl_2 in an H_2O -MeOH [1/1 (v/v)] Mixture in the Presence of Spr at 40°C for 10 h^a

[Spr] $\times 10^3$ (mol/L)	Total Yield (%)	Fraction (%)		Benzene-Soluble Part		
		Benzene Soluble	Benzene Insoluble	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w \times 10^{-5}$	\bar{M}_w/\bar{M}_n
0	82.9	100 ^b	0	4.88	14.9	3.0
0.1	82.6	57	43	3.94	10.7	2.5
0.3	82.5	56	44	4.31	11.0	2.4
0.5	82.3	52	48	3.63	10.9	2.8
0.8	80.9	49	51	4.05	11.1	2.6
1.0	78.5	49	51	5.99	13.2	2.2
1.5	70.9	44	56	4.88	13.7	2.8
2.0	67.5	37	63	5.77	13.8	2.4
3.0	52.8	33	67	5.41	13.7	2.5
3.5	38.7	55	45	8.83	20.3	2.3
4.0	31.6	61	39	7.43	16.4	2.2
5.0	28.1	64	36	4.58	15.7	3.4
6.0	24.7	80	20	8.36	17.2	2.1
7.0	9.0	83	17	4.57	15.4	3.4

^a [MMA] = 0.935 mol/L, $[\text{Cp}_2\text{TiCl}_2] = 1.5 \times 10^{-3}$ mol/L.

^b This fraction contained acetone-soluble (61%) and -insoluble (39%) parts.

The photopolymerization was more retarded by Ph_{en}. The retardation effect observed became more remarkable with increasing Ph_{en} concentration. The total yield of 82.9% in the absence of Ph_{en} was profoundly reduced to 3.8% at $[\text{Phen}] = 6.0 \times 10^{-3}$ mol/L. The benzene-insoluble fraction, being very small (less than 10%), tended to increase with the phen concentration.

Effect of Spr on the Photopolymerization of MMA with Cp_2TiCl_2 in an H_2O -MeOH [1 : 1 (v/v)] and Characterization of Resulting Poly(MMA)

Among the chelating reagents, Spr caused the most effective formation of the benzene-insoluble part in the photopolymerization, leading us to examine in more detail the effect of Spr on the photopolymerization.

The photopolymerization of MMA (0.935 mol L⁻¹) with Cp_2TiCl_2 (1.5×10^{-3} mol/L) in an H_2O -MeOH [1 : 1 (v/v)] was performed at 40°C for 10 h on varying the Spr concentration. The results obtained are summarized in Table IV. Similar to the cases of Bipy and Ph_{en}, the total polymer yield decreased with increasing Spr concentration. However, the fraction of benzene-insoluble part showed a maximum on varying the Spr concentration. The maximum fraction (67%) of insoluble part was observed at $[\text{Spr}] = 3.0 \times 10^{-3}$ mol/L

(two times $[\text{Cp}_2\text{TiCl}_2] = 1.5 \times 10^{-3}$ mol/L), suggesting formation of a 1 : 2 complex of Cp_2TiCl_2 and Spr. This finding conforms the fact that a yellow precipitation was formed by adding double a molar quantity of Spr (3.0×10^{-3} mol/L) to a solution of Cp_2TiCl_2 (1.5×10^{-3} mol/L) in an H_2O -MeOH [1 : 1 (v/v)]. The \bar{M}_n values of benzene-soluble parts were in the range of 3.6 – 8.4×10^5 , and the \bar{M}_w/\bar{M}_n values ranged from 2.1 to 3.4.

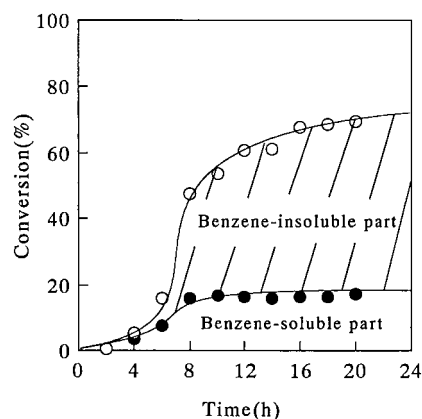


Figure 1 Time-profiles for the yields of benzene-soluble and -insoluble parts in the photopolymerization of MMA with the Cp_2TiCl_2 /Spr system in a MeOH- H_2O [1 : 1 (v/v)] mixture at 40°C; [MMA] = 0.935 mol/L, $[\text{Cp}_2\text{TiCl}_2] = 1.5 \times 10^{-3}$ mol/L, $[\text{Spr}] = 3.0 \times 10^{-3}$ mol/L.

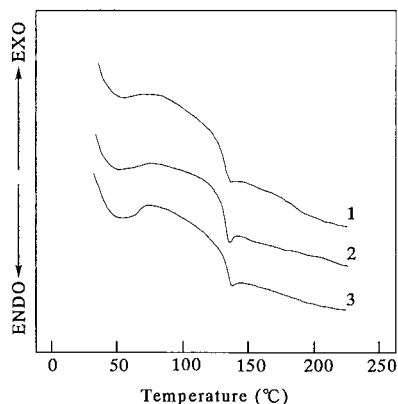


Figure 2 DSC curves of (1) benzene-soluble and (2) -insoluble parts of poly(MMA) formed in the photopolymerization of MMA with the $\text{Cp}_2\text{TiCl}_2/\text{Spr}$ system in a $\text{MeOH-H}_2\text{O}$ [1 : 1 (v/v)] mixture at 40°C and (3) poly(MMA) formed in the MAIB-initiated polymerization in benzene at 40°C .

Figure 1 shows time profiles for the total yield and the fractions of benzene-soluble and -insoluble parts in the photopolymerization of MMA (0.935 mol/L) with Cp_2TiCl_2 ($1.5 \times 10^{-3} \text{ mol/L}$) at 40°C in an $\text{H}_2\text{O-MeOH}$ [1 : 1 (v/v)] in the pres-

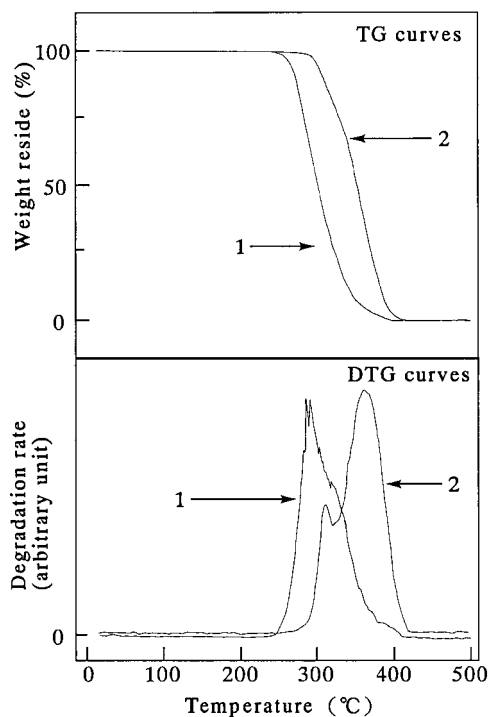


Figure 3 TG and DTG curves of (1) benzene-soluble and (2) -insoluble parts of poly(MMA) formed in the photopolymerization of MMA with the $\text{Cp}_2\text{TiCl}_2/\text{Spr}$ system in a $\text{MeOH-H}_2\text{O}$ [1 : 1 (v/v)] mixture at 40°C .

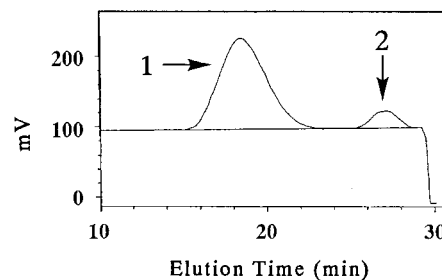


Figure 4 GPC curve of reproduced poly(MMA).

ence of Spr ($3.0 \times 10^{-3} \text{ mol/L}$). Thus, most of the polymer formed after polymerization for about 8 h was benzene insoluble.

Figure 2 shows DSC curves of the benzene-soluble and -insoluble parts, together with that of poly(MMA) formed by the MAIB (typical azoinitiator)-initiated polymerization. Little difference was observed in the glass transition temperatures of these three poly(MMA)s. As shown in Figure 3, however, different TG and differential thermogravimetric (DTG) curves were observed for the soluble and insoluble parts. The latter was thermally more stable than the former. This difference results probably from different modes of initiation of depolymerization.^{15,16}

To pursue the origin of insolubility, the insoluble part obtained in the photopolymerization of MMA (0.935 mol/L) with Cp_2TiCl_2 ($1.5 \times 10^{-3} \text{ mol/L}$) in the presence of Spr ($3.0 \times 10^{-3} \text{ mol/L}$) (see Table IV) was allowed to be hydrolyzed in concentrated sulfuric acid. The resulting poly(methacrylic acid) was methylated by diazomethane in benzene to yield poly(MMA).

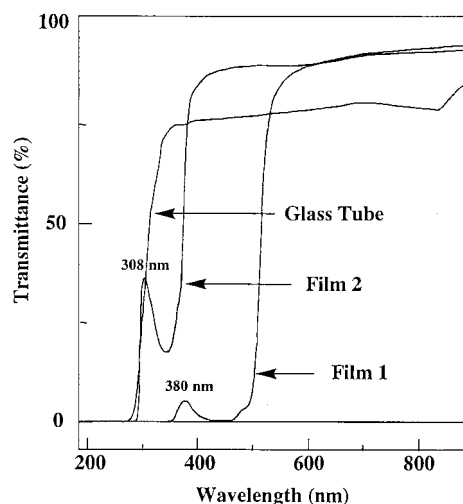


Figure 5 UV spectra of films and glass tube.

Table V Effect of Optical Film Filter on the Photopolymerization of MMA with the Cp₂TiCl₂/Spr System in an H₂O–MeOH [1 : 1 (v/v)] Mixture at 40°C for 10 h^a

Film Filter	Total Yield (%)	Fraction (%)	
		Benzene Soluble	Benzene Insoluble
None	57.7	33	67
Film 1	0.3	—	—
Film 2	22.6	34	66

^a [MMA] = 0.935 mol/L, [Cp₂TiCl₂] = 1.5 × 10⁻³ mol/L, [Spr] = 3.0 × 10⁻³ mol/L.

The reproduced poly(MMA) was found to be soluble in all the solvents used, that is, chloroform, benzene, toluene, THF, ethyl acetate, MEK, acetonitrile, DMF, and DMSO, similar to poly(MMA) formed in the MAIB-initiated polymerization. Further, the tacticity (mm = 3.5, mr = 35.5, rr = 61.0) of reproduced poly(MMA) was closely similar to that (mm = 3.7, mr = 34.5, rr = 61.8) of poly(MMA) obtained with MAIB.

Figure 4 shows the GPC curve of the reproduced poly(MMA). Higher ($\bar{M}_n = 3.0 \times 10^5$, $\bar{M}_w/\bar{M}_n = 2.4$) and lower ($\bar{M}_n = 1.2 \times 10^3$, $\bar{M}_w/\bar{M}_n = 1.4$) molecular weight parts were observed. Although low molecular weight poly(MMA) ($\bar{M}_n =$ less than ca. 3×10^3) is usually soluble in methanol, attempted separation of the two parts was not successful. The observed MeOH-insoluble poly(MMA) with a low molecular weight may be related to the origin of insol-

ubility of poly(MMA) formed in the present photopolymerization. It is noteworthy that \bar{M}_n (3.5×10^5) of the reproduced poly(MMA) was considerably lower than that (5.4×10^5) of the benzene-soluble part formed in the same photopolymerization (see Table IV).

To examine the effect of wavelength of irradiation light, the photopolymerization system was covered with polymer film as optical filter during the polymerization. Two kinds of films [Film 1 (FTER5253, Achilles) and Film 2 (FTEP3757, Achilles)] were used, and their UV spectra are shown in Figure 5, together with that of glass tube employed for the photopolymerization. The polymerization results are presented in Table V. Thus, the photopolymerization was found to be almost inhibited by Film 1, which can cut off the light of wavelength shorter than 500 nm, indicating that the light of wavelength longer than 500 nm is ineffective for the present photopolymerization. The use of Film 2 caused a significant decrease in the total polymer yield, although the fraction of benzene-insoluble part was little changed. Comparison of the spectra of Film 2 and glass tube suggests that the light in the wavelength range of 280–400 nm is effective for the present photopolymerization.

Effect of Spr on the Photopolymerization of EMA with Cp₂TiCl₂ in an H₂O–MeOH [1 : 1 (v/v)] and Characterization of Resulting Poly(EMA)

Table VI summarizes the results obtained in the photopolymerization of EMA (0.40 mol/L) with

Table VI Photopolymerization of EMA with Cp₂TiCl₂ in an H₂O–MeOH [1 : 1 (v/v)] Mixture in the Presence of Spr at 40°C for 10 h^a

[Spr] × 10 ³ (mol/L)	Total Yield (%)	Fraction (%)		Benzene-Soluble Part		
		Benzene Soluble	Benzene Insoluble	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w \times 10^{-5}$	\bar{M}_w/\bar{M}_n
0	90.3	100 ^b	0	5.80	14.5	2.3
0.05	91.3	31	69	6.43	14.8	2.1
0.1	89.3	35	65	5.10	13.4	2.5
0.3	80.9	36	64	5.96	15.1	2.4
0.5	63.2	42	58	6.23	16.0	2.4
0.8	60.4	39	61	7.27	17.0	2.2
1.0	27.5	50	50	7.93	18.5	2.2
1.5	3.1	84	16	5.07	15.8	2.9
2.0	0.3	—	—	—	—	—

^a [EMA] = 0.4 mol/L, [Cp₂TiCl₂] = 0.5 × 10⁻³ mol/L.

^b This fraction contained acetone-soluble (32%) and -insoluble (68%) parts.

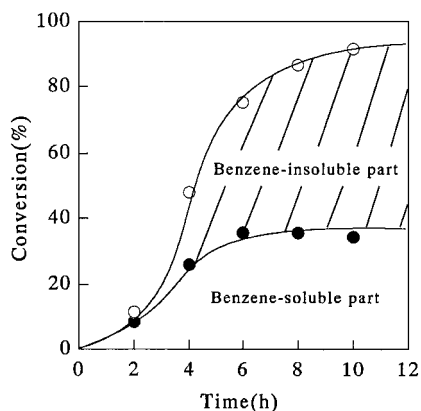


Figure 6 Time-profiles for the yields of benzene-soluble and -insoluble parts in the photopolymerization of EMA with the $\text{Cp}_2\text{TiCl}_2/\text{Spr}$ system in a $\text{MeOH-H}_2\text{O}$ [1 : 1 (v/v)] mixture at 40°C ; $[\text{EMA}] = 0.4 \text{ mol/L}$, $[\text{Cp}_2\text{TiCl}_2] = 0.5 \times 10^{-3} \text{ mol/L}$, $[\text{Spr}] = 0.5 \times 10^{-4} \text{ mol/L}$.

Cp_2TiCl_2 ($0.5 \times 10^{-3} \text{ mol/L}$) at 40°C for 10 h in an $\text{H}_2\text{O-MeOH}$ [1 : 1 (v/v)] mixture in the presence of Spr, of which concentration was varied from null to $2.0 \times 10^{-3} \text{ mol/L}$. The total polymer yield decreased with increasing Spr concentration. Only a 0.3% polymer yield was observed at $[\text{Spr}] = 2.0 \times 10^{-3} \text{ mol/L}$.

As reported previously,¹² the photopolymerization of EMA with Cp_2TiCl_2 in an $\text{H}_2\text{O-MeOH}$ mixture gives a significant fraction of the acetone-insoluble part, which is, however, soluble in benzene. On the other hand, poly(EMA), produced in the photopolymerization in the presence of Spr, was found to contain a benzene-insoluble part, similar to the

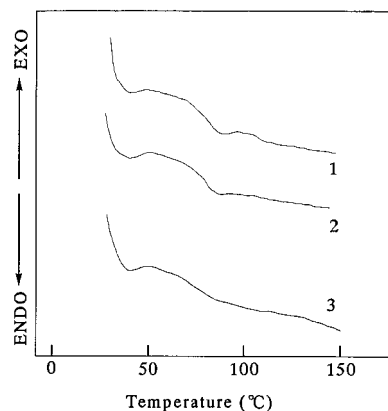


Figure 7 DSC curves of (1) benzene-soluble and (2) -insoluble parts of poly(EMA) formed in the photopolymerization of EMA with the $\text{Cp}_2\text{TiCl}_2/\text{Spr}$ system in a $\text{MeOH-H}_2\text{O}$ [1 : 1 (v/v)] mixture at 40°C , and (3) poly(EMA) formed in the MAIB-initiated polymerization in benzene at 40°C .

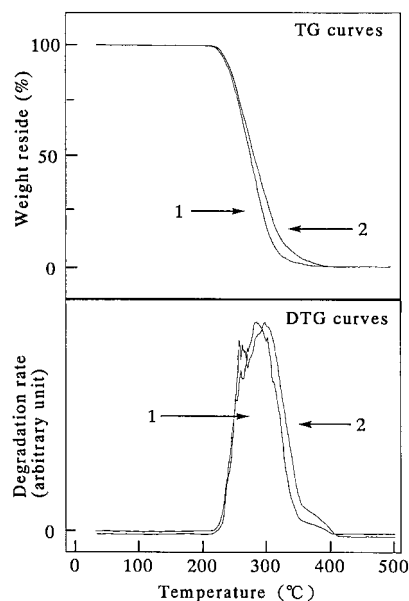


Figure 8 TG and DTG curves of (1) benzene-soluble and (2) -insoluble parts of poly(EMA) formed in the photopolymerization of EMA with the $\text{Cp}_2\text{TiCl}_2/\text{Spr}$ system in a $\text{MeOH-H}_2\text{O}$ [1 : 1 (v/v)] mixture at 40°C .

photopolymerization of MMA. The benzene-insoluble part of poly(EMA) formed in the presence of Spr was fractionated. The results of fractionation are also shown in Table VI. It is of interest that a small amount of Spr ($0.05 \times 10^{-3} \text{ mol/L}$) caused formation of a large fraction (69%) of the insoluble part. The fraction of insoluble part tended to decrease with the Spr concentration. The \bar{M}_n values of soluble part were $5.1\text{--}6.3 \times 10^5$, almost independently of the Spr concentration. The \bar{M}_w/\bar{M}_n values (2.1–2.9) were also similar.

The benzene-insoluble part was insoluble in usual organic solvents (toluene, chloroform, THF, ethyl acetate, acetone, MEK, acetonitrile, DMF, and DMSO), while the soluble part was soluble in such solvents except for acetonitrile and DMSO. These solubility behaviors are similar to those of the benzene-soluble and -insoluble parts of poly(MMA) formed in the photopolymerization in the presence of Spr as described above.

Figure 6 illustrates time profiles for the total yield and the benzene-soluble and -insoluble parts observed in the photopolymerization of EMA (0.4 mol/L) with Cp_2TiCl_2 ($0.50 \times 10^{-3} \text{ mol/L}$) at 40°C in the presence of Spr ($0.50 \times 10^{-4} \text{ mol/L}$). In this case, any increase in the yield of soluble part was found to be almost stopped in about 4 h. Thus, the insoluble poly(EMA) only was observed to be formed in the later stage of the photopolymerization.

Almost the same IR spectra were observed for the benzene-soluble and -insoluble parts.

Figure 7 shows the DSC curves for the benzene-soluble and -insoluble parts obtained in the photopolymerization at 40°C, where the concentrations of EMA, Cp₂TiCl₂, and Spr were 0.4, 0.50 × 10⁻³, and 0.80 × 10⁻³ mol/L, respectively. Thus, the two curves were closely similar to each other, and also similar to that of poly(EMA) formed in the MAIB-initiated polymerization.

Figure 8 shows TG and DTG curves of the soluble and insoluble parts (the same samples as used for Fig. 7). The insoluble part seemed to be thermally somewhat stable than the soluble one.

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