

Thermal Polymerization and Photopolymerization of Ethyl Methacrylate with Bis(cyclopentadienyl)titanium Dichloride in a Water–Methanol Mixture: Formation of a Polymer with Novel Solubility Characters

TSUNEYUKI SATO, TAKU KATAYOSE, MAKIKO SENO

Department of Chemical Science and Technology, Faculty of Engineering, Tokushima University, Minamijosanjima 2-1, Tokushima 770-8506, Japan

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ABSTRACT:: Methacrylate monomers such as methyl methacrylate, ethyl methacrylate (EMA), phenyl methacrylate, and benzyl methacrylate were found to be heterogeneously polymerized in high yields with bis(cyclopentadienyl)titanium dichloride (Cp_2TiCl_2) at 40°C in a 1:1 (v/v) water–methanol mixture under irradiation of a 15-W fluorescent room lamp. The polymerization of EMA with Cp_2TiCl_2 in a 1:1 (v/v) water–methanol mixture also proceeded at a moderate rate in the dark. The polymerization behavior of EMA with Cp_2TiCl_2 in a water–methanol mixture was examined under various conditions, both in the dark and under irradiation. The resulting poly(EMA) was observed to contain a considerable part that was acetone insoluble. In contrast to the usual radical poly(EMA), the fractionated acetone-insoluble part was insoluble in tetrahydrofuran, chloroform, ethyl acetate, methyl ethyl ketone, acetonitrile, dimethyl sulfoxide, and dimethylformamide, though it was soluble in aromatic solvents such as benzene and toluene. We prepared a bilayer film (48.7 μm) consisting of one acetone insoluble layer and one acetone-soluble layer. The film was observed to bend toward side of the acetone-insoluble layer in a 1:1 (v/v) water–acetone mixture. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 166–175, 2001

Key words: radical polymerization; bis(cyclopentadienyl)titanium dichloride; methacrylates; novel solubility character; solvent-sensitive film

INTRODUCTION

A variety of metallocenes and their combinations with methylaluminoxane have been widely investigated as catalysts for the polymerizations of olefins, most of which proceed through coordination mechanisms to yield stereospecific polymers.^{1–11}

On the other hand, combined systems of metallocenes and organic halides or acid anhydrides

were reported to initiate radical polymerization of vinyl monomers, although metallocenes alone show little initiating activity.^{12–16} Some living polymerization characters were observed in the polymerization of methacrylate monomers initiated with the binary system of cobaltocene and bis(ethyl acetoacetato)copper(II) in acetonitrile.^{16–18}

In earlier articles,^{20,21} we reported on our findings that bis(cyclopentadienyl)titanium dichloride (Cp_2TiCl_2) served as an effective initiator for the radical polymerization of methyl methacrylate (MMA) in a water–methanol (H_2O – MeOH) mixture. The polymerization is profoundly accel-

Correspondence to: T. Sato.

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erated by irradiation from a 15-W fluorescent room lamp, although it was reported that Cp_2TiCl_2 scarcely acted as a photoinitiator for MMA in bulk.²² It is worth noting that poly(MMA) formed in the polymerization with Cp_2TiCl_2 in a H_2O –MeOH mixture contains a considerable fraction of novel solubility characters.^{20,21}

Recently we have tried to extend the polymerization with Cp_2TiCl_2 in a H_2O –MeOH to those of other methacrylate monomers. This article describes the results observed in thermal and photopolymerizations of methacrylate monomers, especially ethyl methacrylate (EMA), initiated with Cp_2TiCl_2 in H_2O –MeOH and presents a characterization of resulting polymers.

EXPERIMENTAL

Methacrylate monomers were freed from the inhibitor by treatment with a 5% NaOH aqueous solution, dried over anhydrous sodium sulfate, and distilled. Acrylonitrile (AN) and organic solvents were used after distillation. Ion-free water was used. Dimethyl 2,2'-azobisisobutyrate (MAIB) was recrystallized from MeOH. Cp_2TiCl_2 (supplied from Nichia Chemical Industries, Tokushima, Japan) was used as received.

Polymerization and copolymerization of the methacrylates were performed in degassed and sealed glass tubes without shaking in the dark or under the irradiation of a 15-W fluorescent room lamp (Toshiba FL 15EX-N-H, Japan) from a distance of 60 cm. The resulting polymers were isolated by pouring the polymerization mixtures into a large excess of MeOH containing 4-tert-butylcatechol as inhibitor and HCl. The precipitated polymers were filtered, dried under vacuum, and weighed. Poly(EMA) was further divided into soluble and insoluble parts in acetone.

¹³C-NMR spectra were obtained in C_6D_6 with a Jeol GX-400 (100 MHz) spectrometer. Gel permeation chromatography (GPC) was performed with a Toso HLC-802H chromatograph at 38°C using tetrahydrofuran (THF) as eluent. The number-average (\bar{M}_n) and weight-average (\bar{M}_w) molecular weights were determined from the GPC results by calibration with polystyrene standards. The intrinsic viscosity ($[\eta]$) of poly(EMA) was measured in benzene at 25°C using a Ubbelohde viscometer. Dynamic thermogravimetry (TG) of poly(EMA) was performed in a nitrogen atmosphere (flow rate: 20 mL min⁻¹) with a Shimadzu TG-50 ther-

Table I Photopolymerization of Some Methacrylates with Cp_2TiCl_2 in a MeOH– H_2O [1 : 1 (v/v)] Mixture at 40°C for 10 h^a

Monomer	Conversion (%)
MMA	90
EMA	96
BMA	93
PMA	81
EGD	100

^a [MMA] = 0.935 mol L⁻¹, [EMA] = 0.4 mol L⁻¹, [BMA] = [PMA] = 0.15 mol L⁻¹, [EGD] = 0.5 mol L⁻¹, [Cp_2TiCl_2] = 1.5×10^{-3} mol L⁻¹.

mogravimeter at a heating rate of 10°C min⁻¹. A differential scanning calorimeter (DSC) (Shimadzu DSC-50) was used for thermal analysis of poly(EMA) (heating rate: 10°C min⁻¹).

RESULTS AND DISCUSSION

Photopolymerization of Some Methacrylates with Cp_2TiCl_2 in a H_2O –MeOH Mixture

As reported previously,²¹ Cp_2TiCl_2 serves as an effective photoinitiator for the polymerization of MMA in a H_2O –MeOH mixture. For a comparison, photopolymerization of some methacrylate monomers with Cp_2TiCl_2 was performed at 40°C for 10 h in a H_2O –MeOH mixture [1:1 (v/v)], with a fluorescent lamp (15-W) used as light source. The monomers used were MMA, EMA, benzyl methacrylate (BMA), phenyl methacrylate (PMA), and ethylene glycol dimethacrylate (EGD). Different monomer concentrations were taken, depending on the monomer used, because solubility in the polymerization medium was dependent on the monomers.

Table I presents the results obtained. All the methacrylates were found to produce a high polymer yield under the investigative polymerization conditions.

Thermal and Photopolymerizations of EMA with Cp_2TiCl_2 in a H_2O –MeOH Mixture

The thermal and photopolymerization behaviors of EMA with Cp_2TiCl_2 were examined in a H_2O –MeOH mixture. Although the initial polymerization system was homogeneous, the polymerization proceeded heterogeneously because the resulting poly(EMA) was insoluble in the medium.

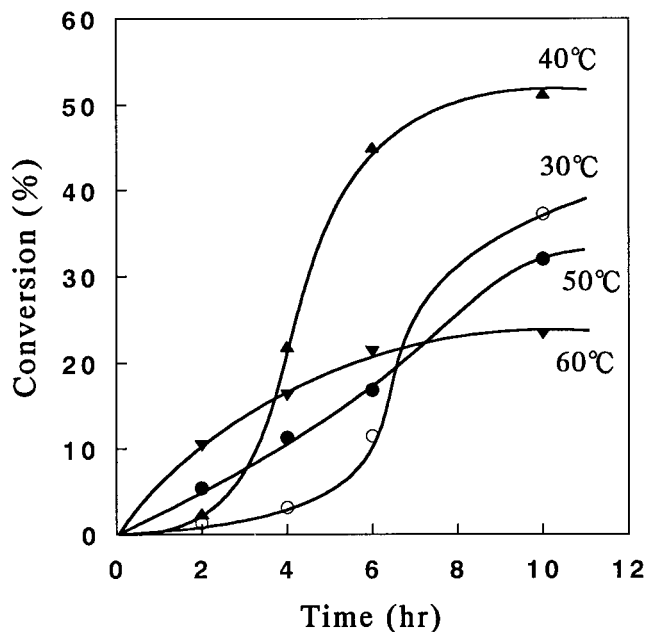


Figure 1 Figure 1 Temperature effect on polymerization of EMA with Cp_2TiCl_2 in a $\text{H}_2\text{O-MeOH}$ [1:1 (v/v)] mixture in the dark; $[\text{EMA}] = 0.40 \text{ mol L}^{-1}$, $[\text{Cp}_2\text{TiCl}_2] = 1.5 \times 10^{-3} \text{ mol L}^{-1}$.

Figure 1 shows time-conversion curves observed in the dark at different temperatures in a $\text{H}_2\text{O-MeOH}$ mixture [1:1 (v/v)], where the concentrations of EMA and Cp_2TiCl_2 were 0.40 and $1.5 \times 10^{-3} \text{ mol L}^{-1}$, respectively. An autoacceleration was observed at the lower temperatures, while a dead-end polymerization tendency²³ was observed at 60°C, though the initial polymerization rate increased with rising temperatures. The dead-end tendency at 60°C may come from more rapid consumption of the initiator at a higher temperature.

Figure 2 presents those polymerizations observed under irradiation from a 15-W fluorescent lamp. From a comparison with the results in the dark, the present polymerization was found to be highly accelerated by irradiation. EMA was almost quantitatively polymerized in 10 h at each temperature under irradiation. In contrast with polymerization in the dark, the photopolymerization at 60°C showed no dead-end tendency, though the polymerization rate was a fair bit lower than those at the lower temperatures. Comparison of the results at 60°C in the dark and under irradiation suggests that deactivated species derived from Cp_2TiCl_2 can be reactivated under irradiation, but the true mechanism is obscure.

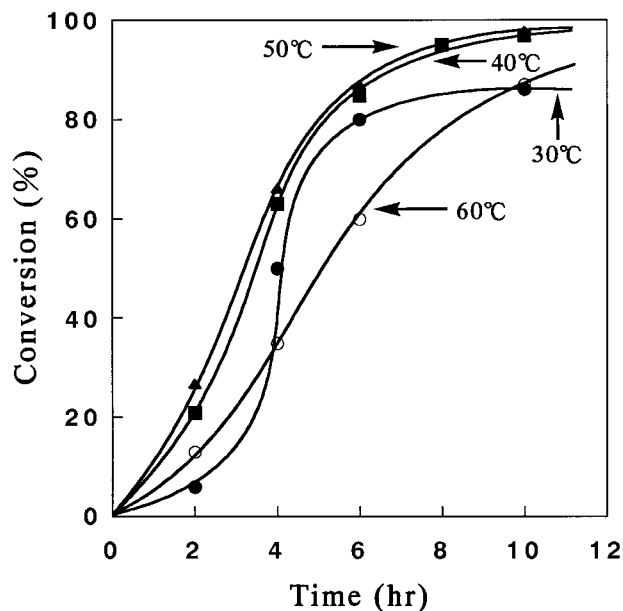


Figure 2 Temperature effect on photopolymerization of EMA with Cp_2TiCl_2 in a $\text{H}_2\text{O-MeOH}$ [1:1 (v/v)] mixture; $[\text{EMA}] = 0.40 \text{ mol L}^{-1}$, $[\text{Cp}_2\text{TiCl}_2] = 1.5 \times 10^{-3} \text{ mol L}^{-1}$.

Figures 3 and 4 show the effect of the initiator concentration on the polymerization of EMA with Cp_2TiCl_2 at 40°C in a $\text{H}_2\text{O-MeOH}$ mixture [1:1

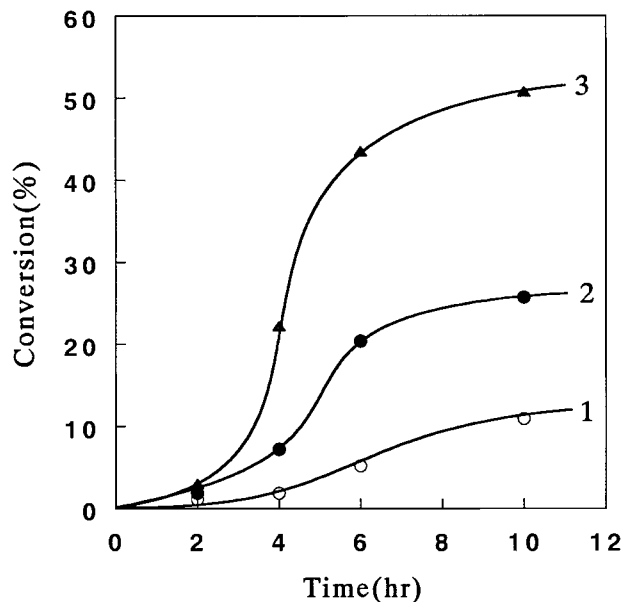


Figure 3 Effect of the initiator concentration on the polymerization of EMA with Cp_2TiCl_2 in a $\text{H}_2\text{O-MeOH}$ [1:1 (v/v)] mixture; $[\text{EMA}] = 0.40 \text{ mol L}^{-1}$, $[\text{Cp}_2\text{TiCl}_2] = 1, 0.5 \times 10^{-3} \text{ mol}$; 2, $1.0 \times 10^{-3} \text{ mol}$; 3, $1.5 \times 10^{-3} \text{ mol L}^{-1}$.

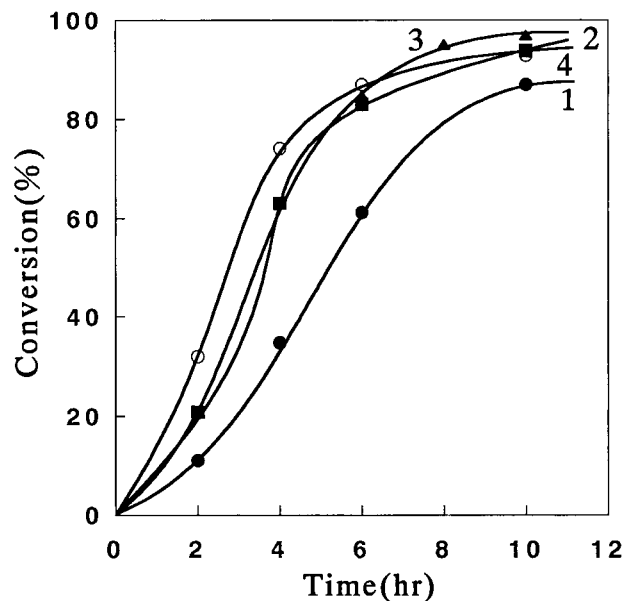


Figure 4 Effect of the initiator concentration on photopolymerization of EMA with Cp_2TiCl_2 in a H_2O -MeOH [1:1 (v/v)] mixture at 40°C ; $[\text{EMA}] = 0.40 \text{ mol L}^{-1}$, $[\text{Cp}_2\text{TiCl}_2] = 1, 0.5 \times 10^{-3}, 2, 1.0 \times 10^{-3}, 3, 1.5 \times 10^{-3}, 4, 2.0 \times 10^{-3} \text{ mol L}^{-1}$.

(v/v)] in the dark and under irradiation, where the EMA concentration was fixed at 0.4 mol L^{-1} . Thus, polymerization in the dark was highly accelerated by an increase in the initiator concentration. The rate of the photopolymerization also tended to increase with the initiator concentration, although its effect was rather small.

The effect of the monomer concentration on the polymerization was examined at 40°C in a H_2O -MeOH mixture [1:1 (v/v)], where the Cp_2TiCl_2 concentration was kept constant at $1.5 \times 10^{-3} \text{ mol L}^{-1}$. As shown in Figure 5, the polymer yield with in the dark polymerization increased with increasing monomer concentration in the early stage. However, the initially still homogeneous polymerization system at the highest monomer concentration (0.60 mol L^{-1}) used here showed a dead-end polymerization tendency²³ to give the lowest polymer yield in 10 h. Figure 6 shows the results observed under irradiation. Although the polymer yield increased with monomer concentration up to 0.4 mol L^{-1} , the use of a higher EMA concentration of 0.6 mol L^{-1} resulted rather in a pronounced retardation of polymerization. This unexpected result is not explicable at present.

Figures 7 and 8 show the effect of the medium composition on polymerization at 40°C in the

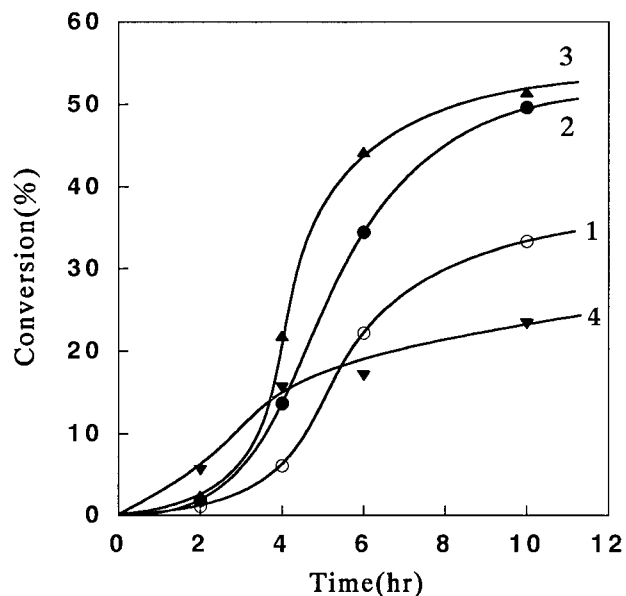


Figure 5 Effect of monomer concentration on polymerization of EMA with Cp_2TiCl_2 in a H_2O -MeOH [1:1 (v/v)] mixture at 40°C in the dark; $[\text{Cp}_2\text{TiCl}_2] = 1.5 \times 10^{-3} \text{ mol L}^{-1}$; $[\text{EMA}] = 1, 0.20; 2, 0.30; 3, 0.40; 4, 0.60 \text{ mol L}^{-1}$.

dark and under irradiation, where the concentrations of EMA and Cp_2TiCl_2 were 0.40 and $1.5 \times 10^{-3} \text{ mol L}^{-1}$, respectively. Thus, water was

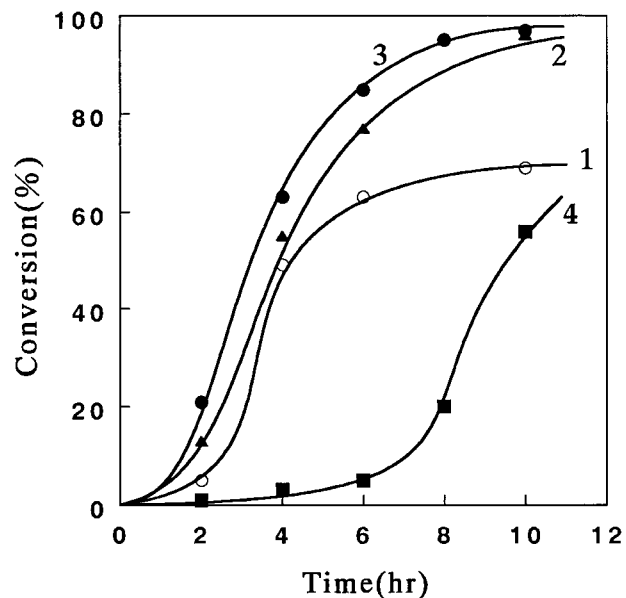


Figure 6 Effect of monomer concentration on photopolymerization of EMA with Cp_2TiCl_2 in a H_2O -MeOH [1:1 (v/v)] mixture at 40°C ; $[\text{Cp}_2\text{TiCl}_2] = 1.5 \times 10^{-3} \text{ mol L}^{-1}$; $[\text{EMA}] = 1, 0.20; 2, 0.30; 3, 0.40; 4, 0.60 \text{ mol L}^{-1}$.

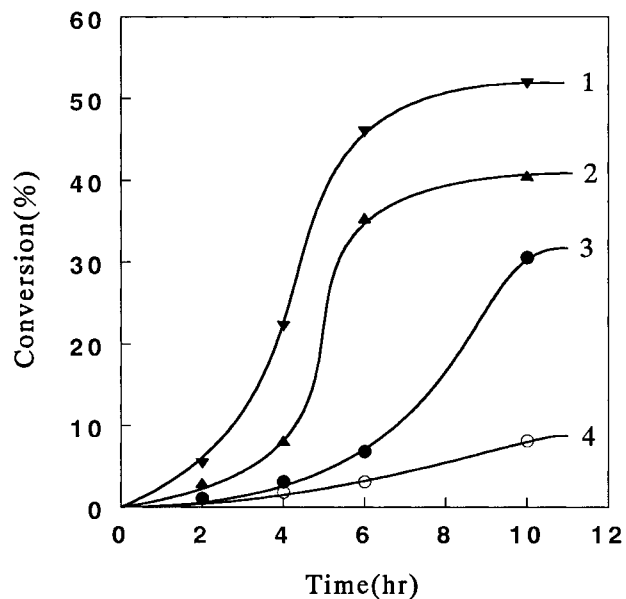


Figure 7 Effect of medium composition on polymerization of EMA with Cp_2TiCl_2 in a H_2O -MeOH mixture at 40°C in the dark; $[\text{EMA}] = 0.40 \text{ mol L}^{-1}$; $[\text{Cp}_2\text{TiCl}_2] = 1.5 \times 10^{-3} \text{ mol L}^{-1}$. Vol % of H_2O in H_2O -MeOH mixture: 1, 50; 2, 40; 3, 30; 4, 20.

found to exhibit a remarkable accelerating effect on polymerization, both in the dark and under irradiation. Photopolymerization for 10 h at a wa-

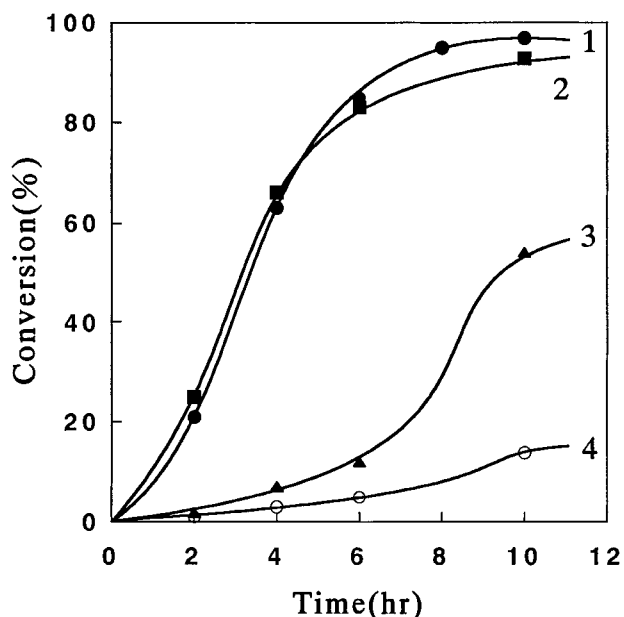


Figure 8 Effect of medium composition on photopolymerization of EMA with Cp_2TiCl_2 in a H_2O -MeOH [1:1 (v/v)] mixture at 40°C ; $[\text{EMA}] = 0.40 \text{ mol L}^{-1}$; $[\text{Cp}_2\text{TiCl}_2] = 1.5 \times 10^{-3} \text{ mol L}^{-1}$. Vol % of H_2O in H_2O -MeOH mixture: 1, 50; 2, 40; 3, 30; 4, 20.

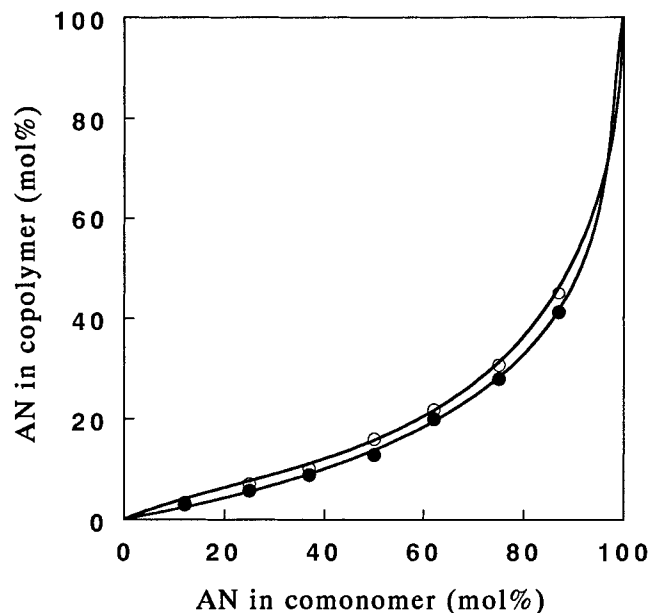


Figure 9 Copolymer composition curves for photocopolymerizations of AN and EMA with Cp_2TiCl_2 (●) and MAIB (○) in a H_2O -MeOH [1:1 (v/v)] mixture at 40°C .

ter content higher than 40 vol % produced an almost quantitative polymer yield.

Photocopolymerization of Acrylonitrile and EMA with Cp_2TiCl_2 in a H_2O -MeOH Mixture

In order to examine the polymerization mechanism, the copolymerization of acrylonitrile (AN) and EMA with Cp_2TiCl_2 was performed at 40°C in a H_2O -MeOH mixture [1:1 (v/v)] under irradiation. The copolymer yields were controlled so as to be less than 10%. The copolymer composition was estimated from nitrogen content by elemental analysis.

Figure 9 compares the results observed in photocopolymerization with Cp_2TiCl_2 and in photocopolymerization with dimethyl 2,2'-azobisisobutyrate (MAIB), a typical radical azo-initiator, in the same medium. Thus, closely similar composition curves were obtained in both copolymerization systems, indicating that photocopolymerization of EMA with Cp_2TiCl_2 in a H_2O -MeOH mixture proceeds through a radical mechanism.

Characterization of the Resulting Poly(EMA)

Interestingly, in addition to the acetone-soluble part, a considerable fraction of the acetone-insoluble part was observed to be contained in poly-

Table II Solubilities^a of Acetone-Soluble and Acetone-Insoluble Parts of Poly(EMA) Formed in Photopolymerization with Cp_2TiCl_2 in a $\text{MeOH-H}_2\text{O}$ [1 : 1 (v/v)] Mixture at 40°C^b

Solvent	Radical Poly(EMA) ^c	Acetone-Insoluble	Acetone-Soluble
Benzene	○	○	○
Toluene	○	○	○
Chloroform	○	×	○
THF	○	×	○
Ethyl acetate	○	×	○
Acetone	○	×	○
MEK	○	×	○
Acetonitrile	○	×	×
DMF	○	×	○
DMSO	○	×	○

^a ○: soluble, ×: insoluble.

^b $[\text{EMA}] = 0.40 \text{ mol L}^{-1}$, $[\text{Cp}_2\text{TiCl}_2] = 1.50 \times 10^{-3} \text{ mol L}^{-1}$.

^c Prepared by polymerization with MAIB at 40°C in benzene for 10 h.

(EMA)s formed in both polymerizations with Cp_2TiCl_2 in the dark and under irradiation. Elemental analysis of the acetone-soluble and acetone-insoluble parts revealed that neither part contained any inorganic residue.

The acetone-insoluble part of poly(EMA) was found to show novel solubility characters. It was soluble in benzene and toluene but insoluble in THF, chloroform, ethyl acetate, methyl ethyl ketone (MEK), acetonitrile, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). Thus, the insoluble character of the acetone-insoluble part does not stem from crosslinking because it was soluble in some aromatic solvents.

Table II compares the solubilities in various solvents of the acetone-soluble part, the acetone insoluble part, and poly(EMA) separately prepared by MAIB-initiated polymerization. As can be seen from the table, the acetone-insoluble poly(EMA) formed in the radical polymerization with Cp_2TiCl_2 in a $\text{H}_2\text{O-MeOH}$ mixture is distinguishably different in solubility from conventional radical poly(EMA).

Figures 10 and 11 present a time profile for the total yield and the fractions of the acetone-soluble and acetone-insoluble parts in the polymerization of EMA (0.40 mol L^{-1}) with Cp_2TiCl_2 at 40°C in a $\text{H}_2\text{O-MeOH}$ mixture [1:1 (v/v)] in the dark ($\text{Cp}_2\text{TiCl}_2 = 1.5 \times 10^{-3} \text{ mol L}^{-1}$) and under irradiation ($\text{Cp}_2\text{TiCl}_2 = 5.0 \times 10^{-4} \text{ mol L}^{-1}$), respectively. An induction period of about 4 h was observed for the formation of the acetone-insoluble

part in both polymerization systems. The polymer produced after the induction period was acetone-insoluble for the most part in the photopolymerization. Consequently, the fraction of the insoluble part increased with increasing total yield.

Table III summarizes the results of fractionation of poly(EMA)s formed in the dark for 10 h under different conditions. Thus, the fraction of the acetone-insoluble part tended to increase with decreasing temperature and increasing water content. The acetone-insoluble fraction seemed to show a maximum on varying the monomer concentration, while it was almost independent of the initiator concentration. As shown in Figure 10, the insoluble fraction showed a tendency to increase with increasing total yield. The lower fraction at a high EMA concentration of 0.6 mol L^{-1} (No. 4) may come from the lower total yield. On the other hand, polymerization at a low initiator concentration ($5.0 \times 10^{-4} \text{ mol L}^{-1}$) also produced a similar insoluble fraction despite a low total yield (No. 5). These results led us to carry out polymerization at a low temperature (25°C), at a low initiator concentration ($50 \times 10^{-4} \text{ mol L}^{-1}$), and a moderate monomer concentration (0.4 mol L^{-1}) at a high water content (50 vol %) for a long time (72 h), so that a high total yield could be

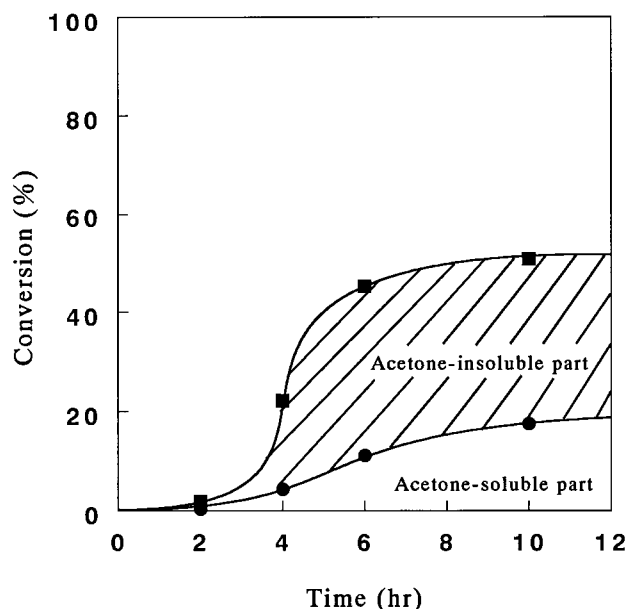


Figure 10 Time profile for total yield and fractions of acetone-soluble (white area) and acetone-insoluble (shaded area) parts in the polymerization of EMA with Cp_2TiCl_2 in a $\text{H}_2\text{O-MeOH}$ [1:1 (v/v)] mixture at 40°C in the dark; $[\text{EMA}] = 0.40 \text{ mol L}^{-1}$, $[\text{Cp}_2\text{TiCl}_2] = 1.5 \times 10^{-3} \text{ mol L}^{-1}$.

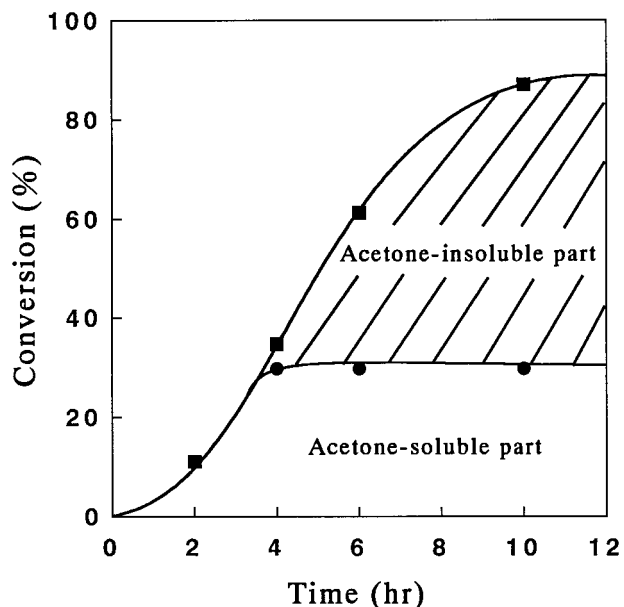


Figure 11 Time profile for total yield and fractions of acetone-soluble (white area) and acetone-insoluble parts (shaded area) in the photopolymerization of EMA with Cp_2TiCl_2 in a H_2O -MeOH [1:1 (v/v)] mixture at 40°C ; $[\text{EMA}] = 0.40 \text{ mol L}^{-1}$; $[\text{Cp}_2\text{TiCl}_2] = 0.50 \times 10^{-3} \text{ mol L}^{-1}$.

obtained. As a result, a high total yield (93%) and a high insoluble fraction (60%) were achieved.

Table IV presents the results of poly(EMA)s formed in photopolymerization for 10 h under

various conditions. The fraction of the acetone-insoluble part was observed to decrease with rising temperature and decreasing water content. It showed a maximum on varying the monomer concentration or the initiator concentration. The photopolymerization of EMA (0.40 mol L^{-1}) with Cp_2TiCl_2 ($5.0 \times 10^{-4} \text{ mol L}^{-1}$), which was conducted separately at 30°C for 24 h, produced an almost quantitative total yield (95%) and an acetone-insoluble fraction as high as 70%.

Table IV also lists the molecular weights (\bar{M}_n and \bar{M}_w) and polydispersity (\bar{M}_w/\bar{M}_n) of the acetone-soluble part of some poly(EMA)s formed during photopolymerization. The \bar{M}_n value was quite high, in the range of 3.7 – 15.2×10^5 . The molecular weight tended to increase with increasing monomer concentration, increasing initiator concentration, and increasing water content, while it was almost independent of temperature. The polydispersity was not so broad ($\bar{M}_w/\bar{M}_n = 1.9$ – 2.8), in spite of the heterogeneous polymerization, up to high polymer yields.

In order to get any information on the molecular weight of the acetone-insoluble part, intrinsic viscosity ($[\eta]$) was measured at 25°C in benzene and compared with that of the soluble one, of which the original poly(EMA) was prepared in photopolymerization (No. 16 in Table IV). The $[\eta]$ value was determined to be 2.6 for the acetone-soluble part ($\bar{M}_n = 9.2 \times 10^5$ by GPC) and 3.3 for

Table III Fractions of Acetone-Soluble and Acetone-Insoluble Parts of Poly(EMA) Formed under Various Dark Polymerization Conditions^a

No.	[EMA] (mol L^{-1})	$[\text{Cp}_2\text{TiCl}_2]$ $\times 10^3$ (mol L^{-1})	Temperature ($^\circ\text{C}$)	$[\text{H}_2\text{O}]$ (%) ^b	Total Yield (%)	Fraction (%)	
						Acetone- Soluble	Acetone- Insoluble
1	0.2	1.5	40	50	33	85	15
2	0.3	1.5	40	50	49	69	31
3	0.4	1.5	40	50	51	66	34
4	0.6	1.5	40	50	23	92	8
5	0.4	0.5	40	50	10	64	36
6	0.4	1.0	40	50	25	65	35
7	0.4	2.0	40	50	23	58	42
8	0.4	1.5	30	50	38	52	48
9	0.4	1.5	50	50	33	80	20
10	0.4	1.5	60	50	23	82	18
11	0.4	1.5	40	40	40	74	26
12	0.4	1.5	40	30	30	95	5
13	0.4	1.5	40	20	5	100	0

^a Polymerized for 10 h.

^b Vol % of H_2O in H_2O -MeOH mixture.

Table IV Fractions of Acetone-Soluble and Acetone-Insoluble Parts of Poly(EMA) Formed under Various Photopolymerization Conditions^a

No.	[EMA] (mol L ⁻¹)	[Cp ₂ TiCl ₂] × 10 ³ (mol L ⁻¹)	Temperature (°C)	[H ₂ O] (%) ^b	Total Yield (%)	Fraction (%)		$\bar{M}_n \times 10^{-5}$	$\bar{M}_w \times 10^{-5}$	\bar{M}_w/\bar{M}_n
						Acetone-Soluble	Acetone-Insoluble			
14	0.2	1.5	40	50	69	93	7	3.7	9.7	2.7
15	0.3	1.5	40	50	96	46	54	—	—	—
16	0.4	1.5	40	50	97	63	37	9.2	20.2	2.2
17	0.5	1.5	40	50	94	61	39	—	—	—
18	0.6	1.5	40	50	56	91	9	11.5	23.6	2.1
19	0.8	1.5	40	50	29	100	0	13.7	26.9	2.0
20	0.4	0.1	40	50	1	—	—	—	—	—
21	0.4	0.2	40	50	13	100	0	—	—	—
22	0.4	0.3	40	50	52	52	48	—	—	—
23	0.4	0.4	40	50	53	49	51	—	—	—
24	0.4	0.5	40	50	87	35	65	7.0	19.1	2.8
25	0.4	1.0	40	50	94	46	54	9.2	23.0	2.5
26	0.4	2.0	40	50	93	86	14	13.8	25.6	2.0
27	0.4	1.5	20	50	62	44	56	—	—	—
28	0.4	1.5	30	50	87	51	49	15.2	30.1	2.0
29	0.4	1.5	50	50	90	66	34	14.1	29.0	2.1
30	0.4	1.5	60	50	87	62	38	15.2	29.3	1.9
31	0.4	1.5	40	40	93	87	13	9.8	23.2	2.3
32	0.4	1.5	40	30	54	100	0	6.3	15.3	2.4
33	0.4	1.5	40	20	14	100	0	4.0	11.1	2.7

^a Polymerized for 10 h.^b Vol % of H₂O in H₂O—MeOH mixture.

the insoluble part, respectively. Thus, no significant difference was observed in their molecular weights.

The tacticities of the acetone-soluble and acetone-insoluble parts obtained from photopolymerization (No. 16 in Table IV) were also examined by ¹³C-NMR spectroscopy. The results obtained for both parts were compared with those of poly(EMA) prepared separately by polymerization with MAIB at 50°C in benzene [soluble part: *mm* = 3.5, *mr* = 31.4, *rr* = 65.1; insoluble part: *mm* = 3.4, *mr* = 32.6, *rr* = 64.0; radical poly(EMA): *mm* = 3.4, *mr* = 35.2, *rr* = 61.4]. No significant difference was observed among them, although the syndiotacticity of poly(EMA)s formed with Cp₂TiCl₂ was somewhat higher than that of the polymer formed with MAIB.

Figure 12 illustrates DSC curves of the acetone-soluble and acetone-insoluble parts, together with that of radical poly(EMA). Little difference was found between the soluble and insoluble parts. However, the poly(EMA)s produced with Cp₂TiCl₂ showed a considerably higher glass-transition temperature than did the radical poly(EMA).

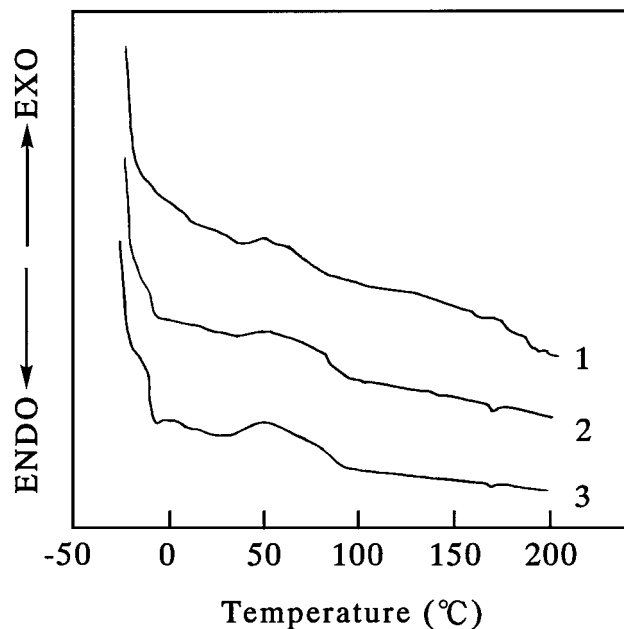


Figure 12 DSC curves of (1) poly(EMA) prepared with MAIB, (2) the acetone-soluble part, and (3) acetone-insoluble part.

Figure 13 compares *TG* and differential *TG* (*DTG*) curves of the acetone-soluble and acetone-insoluble parts. The insoluble part seemed to degrade by one step, while the soluble part did so by two steps.

Preparation of Bilayer Film from Acetone-Soluble and Acetone-Insoluble Poly(EMA)s

A bilayer thin film was prepared from acetone-soluble and acetone-insoluble poly(EMA)s. First, a film was prepared by casting a benzene solution of acetone-insoluble poly(EMA) on a glass plate. Then an acetone solution of soluble poly(EMA) was cast on the film obtained from insoluble poly(EMA). The resulting bilayer film, 48.7 μm thick, consisted of a layer of acetone-soluble poly(EMA) and a layer of acetone-insoluble poly(EMA). Figure 14 shows the deformation behavior of the bilayer film (23 mm \times 3 mm) in a H_2O -acetone [1:1 (v/v)] mixture. Thus, the film was observed to

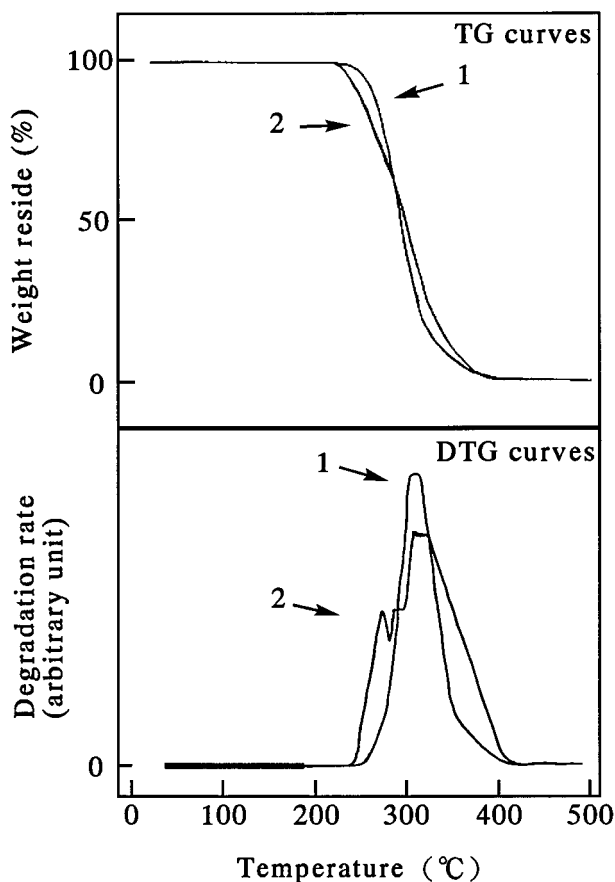


Figure 13 *TG* and differential thermogravimetric (*DTG*) curves of (1) acetone-insoluble part and (2) acetone-soluble part.

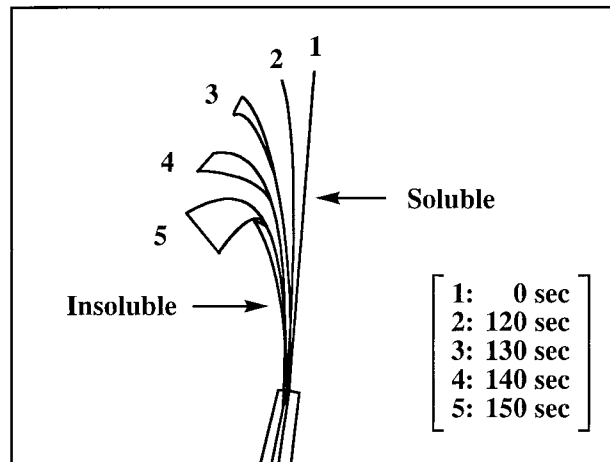


Figure 14 Deformation behavior of a bilayer film consisting of an acetone-soluble poly(EMA) layer and an acetone-insoluble poly(EMA) layer in a H_2O -acetone [1:1 (v/v)] mixture.

bend to the insoluble polymer side with time. This is because only the acetone-soluble layer could be swollen in the H_2O -acetone mixture. This phenomenon adds support to the contention that the solubility behavior of acetone-insoluble poly(EMA) is quite different from its acetone-soluble counterpart.

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