

# Formation of Poly(Methyl Methacrylate) with Novel Solubility Characters in the Photopolymerization with Bis(cyclopentadienyl)titanium Dichloride in a Water–Methanol Mixture

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**ABSTRACT:** Methyl methacrylate (MMA) was observed to be easily polymerized in the photopolymerization with bis(cyclopentadienyl)titanium dichloride ( $\text{Cp}_2\text{TiCl}_2$ ) in a water–methanol mixture under irradiation of a 15-W fluorescent room lamp. The polymerization proceeded heterogeneously. The rate ( $R_p$ ) of heterogeneous photopolymerization in a 1 : 1 (v/v) water–methanol mixture at 40°C was apparently given by  $R_p = k[\text{Cp}_2\text{TiCl}_2]^{0.2} [\text{MMA}]^{2.4}$ . The resulting poly(MMA) was found to contain a tetrahydrofuran (THF)-insoluble part. The separated THF-insoluble part differed significantly from the usual radical poly(MMA) in solubility characters. It is of great interest that the THF-insoluble poly(MMA) was soluble in benzene and toluene, but insoluble in polar solvents, such as ethyl acetate, acetone, methyl ethyl ketone, dimethylformamide, and dimethylsulfoxide. The copolymerization results of MMA and acrylonitrile revealed that the present photopolymerization initiated with  $\text{Cp}_2\text{TiCl}_2$  proceeds *via* a radical mechanism. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 525–531, 1998

**Key words:** photopolymerization; methyl methacrylate; solubility character; bis(cyclopentadienyl)titanium dichloride

## INTRODUCTION

Various metallocenes and their combinations with methylaluminumoxane have been intensively studied as catalysts for the polymerizations of olefins, most of which proceed through coordination mechanisms to give stereospecific polymers.<sup>1–9</sup>

On the other hand, 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.<sup>10–14</sup> Some

living polymerization characters were observed in the polymerization of methyl methacrylate (MMA) initiated with the binary system of cobaltocene and bis(ethyl acetoacetato)copper(II) in acetonitrile.<sup>15–17</sup>

In the preceding article, we found that bis(cyclopentadienyl)titanium dichloride ( $\text{Cp}_2\text{TiCl}_2$ ) serves as an effective initiator for the radical polymerization of MMA in a water–methanol ( $\text{H}_2\text{O}$ – $\text{MeOH}$ ) mixture, and it was of great interest that the resulting poly(MMA) contains a considerable fraction of novel solubility characters.<sup>18</sup>

Recently, we have found that the MMA polymerization with  $\text{Cp}_2\text{TiCl}_2$  is profoundly accelerated, even by irradiation of a 15-W fluorescent room lamp, although  $\text{Cp}_2\text{TiCl}_2$  was reported to act scarcely as a photoinitiator for MMA in bulk.<sup>19</sup>

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The present article describes the results obtained in the photopolymerization of MMA with  $\text{Cp}_2\text{TiCl}_2$  in a  $\text{H}_2\text{O}$ –MeOH mixture under irradiation of a 15-W fluorescent room lamp and presents a characterization of the resulting polymer.

## EXPERIMENTAL

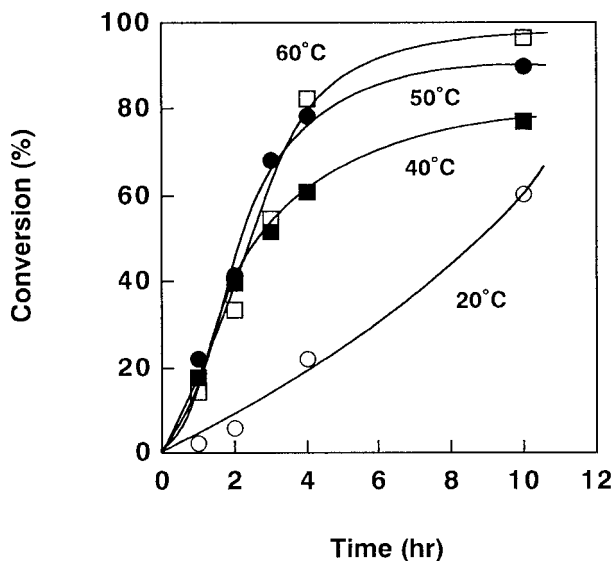
MMA was freed from inhibitor by treatment with a 5% NaOH aqueous solution, dried over anhydrous sodium sulfate, and distilled. Acrylonitrile (AN) and organic solvents were used after distillation. Ion-free water was used.  $\text{Cp}_2\text{TiCl}_2$  (supplied from Nichia Chemical Industries, Tokushima, Japan) was used without further purification.

Polymerization and copolymerization of MMA were performed in degassed and sealed glass tubes 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*-butyl-catechol as inhibitor and HCl. The precipitated polymers were filtered, dried under vacuum, and weighed. Poly(MMA) was further divided into soluble and insoluble parts in tetrahydrofuran (THF).

$^1\text{H}$ -NMR spectra were obtained in deuteriochloroform with a Jeol GX-400 (400 MHz) spectrometer. Infrared spectra were recorded on a Perkin–Elmer 1600 FT-IR 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.  $\bar{M}_w$  of poly(MMA) was also viscometrically determined using eq. (1),<sup>20</sup> wherein the intrinsic viscosity ( $[\eta]$ ) was measured in benzene at 25°C with a Ubbelohde viscometer;

$$[\eta] = 5.5 \times 10^{-3} (\bar{M}_w)^{0.76} (\text{mL g}^{-1}) \quad (1)$$

Dynamic thermogravimetry (TG) of poly(MMA) was performed in a nitrogen atmosphere (flow rate: 20 mL min<sup>-1</sup>) on a Shimadzu TG-50 thermogravimeter at a heating rate of 10°C/min. A differential scanning calorimeter (DSC) (Shimadzu DSC-50) was used for thermal analysis of poly(MMA) (heating rate: 10°C min<sup>-1</sup>). Electron spin



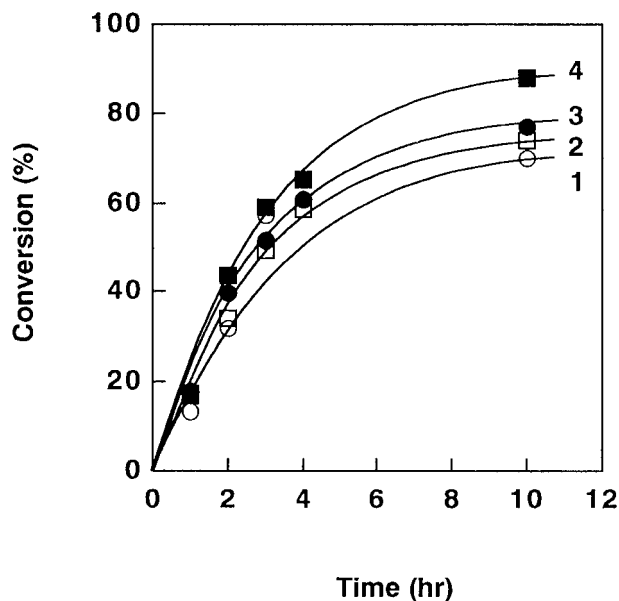
**Figure 1** Temperature effect on the photopolymerization of MMA with  $\text{Cp}_2\text{TiCl}_2$  in a  $\text{H}_2\text{O}$ –MeOH [1 : 1 (v/v)] mixture;  $[\text{MMA}] = 0.935 \text{ mol L}^{-1}$ ,  $[\text{Cp}_2\text{TiCl}_2] = 1.50 \times 10^{-3} \text{ mol L}^{-1}$ .

resonance (ESR) spectrum of the polymerization mixture in a degassed and sealed ESR tube was recorded with a Jeol-JES-FE2XG spectrometer operating at X-band (9.5 GHz) with a transverse electric field mode cavity.

## RESULTS AND DISCUSSION

### Photopolymerization of MMA with $\text{Cp}_2\text{TiCl}_2$ in a $\text{H}_2\text{O}$ –MeOH Mixture

Polymerization of MMA with  $\text{Cp}_2\text{TiCl}_2$  in a  $\text{H}_2\text{O}$ –MeOH [1 : 1 (v/v)] was conducted at different temperatures under irradiation of a fluorescent lamp (15 W), wherein the concentrations of MMA and initiator were 0.935 and  $1.5 \times 10^{-3} \text{ mol L}^{-1}$ , respectively. The polymerization proceeded heterogeneously because the resulting poly(MMA) was insoluble in the medium. Figure 1 shows the results observed. In general, the temperature effect on the photopolymerization is small because the photoinitiation is almost insensitive to the temperature. A large accelerating effect by temperature was, however, observed in the range of 20–40°C in the present polymerization, although a further raise in temperature caused only a small effect.



**Figure 2** Effect of the  $\text{Cp}_2\text{TiCl}_2$  concentration on the photopolymerization of MMA with  $\text{Cp}_2\text{TiCl}_2$  in a  $\text{H}_2\text{O}$ -MeOH [1 : 1 (v/v)] mixture at  $40^\circ\text{C}$ ;  $[\text{MMA}] = 0.935 \text{ mol L}^{-1}$ .  $[\text{Cp}_2\text{TiCl}_2]$ : 1,  $0.50 \times 10^{-3}$ ; 2,  $1.00 \times 10^{-3}$ ; 3,  $1.50 \times 10^{-3}$ ; 4,  $2.00 \times 10^{-3} \text{ mol L}^{-1}$ .

Figure 2 illustrates the time-conversion curves observed in the photopolymerization of MMA with  $\text{Cp}_2\text{TiCl}_2$  at  $40^\circ\text{C}$  in a  $\text{H}_2\text{O}$ -MeOH [1 : 1 (v/v)] mixture when  $[\text{Cp}_2\text{TiCl}_2]$  was changed and  $[\text{MMA}]$  was fixed at  $0.935 \text{ mol L}^{-1}$ . The initial polymerization rate ( $R_p$ ) was found to be proportional to the 0.2 order of  $[\text{Cp}_2\text{TiCl}_2]$ .

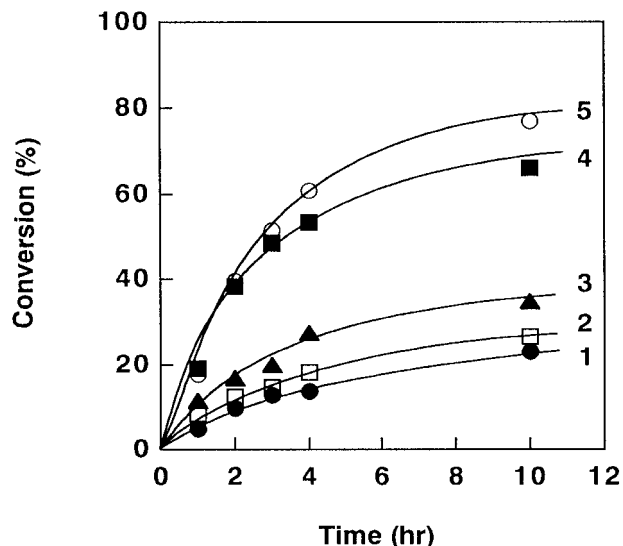
Figure 3 presents the time-conversion curves for the photopolymerization of MMA with  $\text{Cp}_2\text{TiCl}_2$  in a  $\text{H}_2\text{O}$ -MeOH [1 : 1 (v/v)] mixture when  $[\text{MMA}]$  was varied and  $[\text{Cp}_2\text{TiCl}_2]$  was kept constant at  $1.5 \times 10^{-3} \text{ mol L}^{-1}$ .  $R_p$  increased in proportion to the 2.4 order of  $[\text{MMA}]$ . Thus,  $R_p$  at  $40^\circ\text{C}$  was apparently expressed by eq. (2);

$$R_p = k[\text{Cp}_2\text{TiCl}_2]^{0.2} [\text{MMA}]^{2.4} \quad (2)$$

Figure 4 illustrates the time-conversion curves observed when the composition of polymerization medium was changed. The present polymerization was profoundly accelerated with increasing  $\text{H}_2\text{O}$  content.

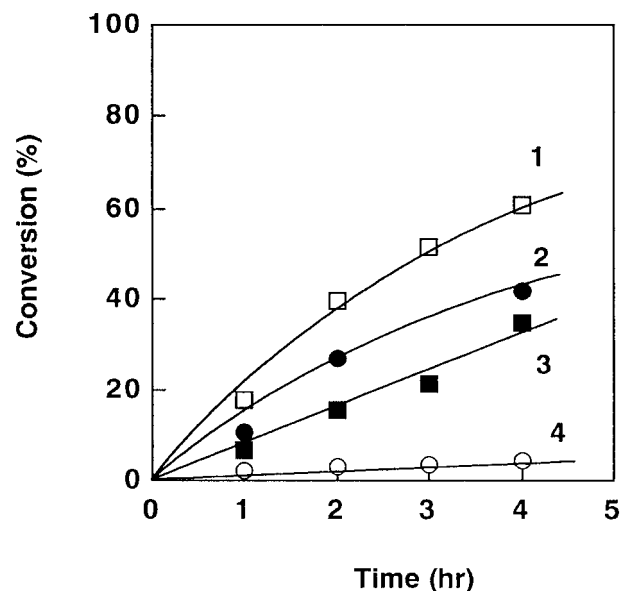
#### Photocopolymerization of MMA and AN with $\text{Cp}_2\text{TiCl}_2$ in a $\text{H}_2\text{O}$ -MeOH Mixture

To clarify the polymerization mechanism, the photocopolymerization of AN ( $M_1$ ) and MMA ( $M_2$ )

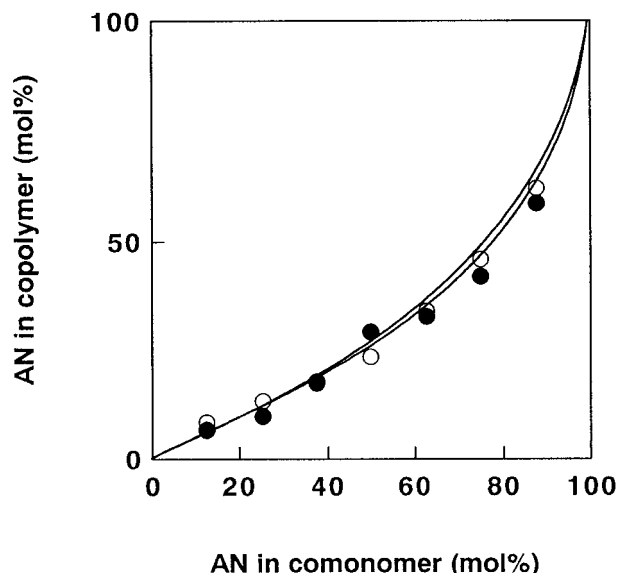


**Figure 3** Effect of the MMA concentration on the photopolymerization of MMA with  $\text{Cp}_2\text{TiCl}_2$  in a  $\text{H}_2\text{O}$ -MeOH [1 : 1 (v/v)] mixture at  $40^\circ\text{C}$ ;  $[\text{Cp}_2\text{TiCl}_2] = 1.50 \times 10^{-3}$ .  $[\text{MMA}]$ : 1, 0.30; 2, 0.50; 3, 0.60; 4, 0.80; 5,  $0.935 \text{ mol L}^{-1}$ .

with  $\text{Cp}_2\text{TiCl}_2$  was conducted in a  $\text{H}_2\text{O}$ -MeOH [1 : 1 (v/v)] mixture at  $40^\circ\text{C}$ . Figure 5 shows the copolymer composition curve obtained, together

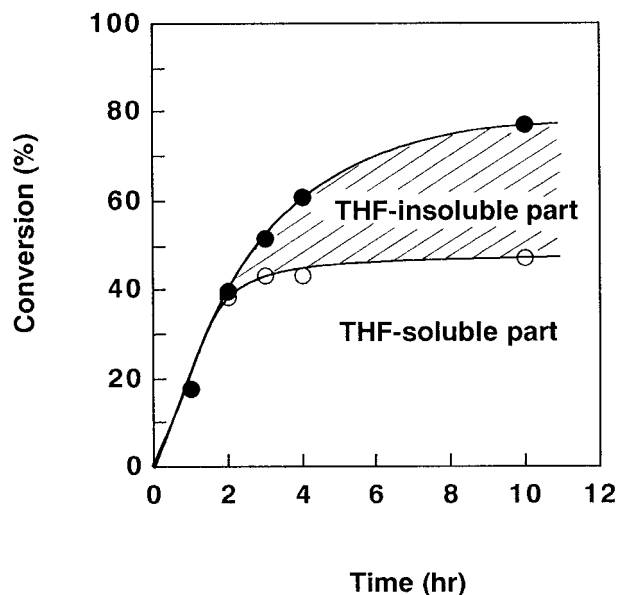


**Figure 4** Effect of medium composition on the photopolymerization of MMA with  $\text{Cp}_2\text{TiCl}_2$  in a  $\text{H}_2\text{O}$ -MeOH mixture at  $40^\circ\text{C}$ ;  $[\text{MMA}] = 0.935 \text{ mol L}^{-1}$ ,  $[\text{Cp}_2\text{TiCl}_2] = 1.50 \times 10^{-3} \text{ mol L}^{-1}$ . Vol % of  $\text{H}_2\text{O}$  in the  $\text{H}_2\text{O}$ -MeOH mixture: 1, 50; 2, 40; 3, 30; 4, 10.



**Figure 5** Copolymer composition curves for the photopolymerizations of AN and MMA with  $\text{Cp}_2\text{TiCl}_2$  (●) and with MAIB (○) at 40°C in a  $\text{H}_2\text{O}$ -MeOH [1 : 1 (v/v)] mixture.

with that observed in the photocopolymerization in the same medium initiated by dimethyl 2,2'-azobisisobutyrate (MAIB), a typical radical azo initiator. The copolymer composition was calculated from the nitrogen content by elemental analysis. The two composition curves are closely similar to each other, giving similar monomer reactivity ratios;  $r_1 = 0.12$ ,  $r_2 = 2.3$  for the photocopolymerization with  $\text{Cp}_2\text{TiCl}_2$  and  $r_1 = 0.16$ ,  $r_2 = 2.2$



**Figure 6** Time-profile for the total yield and the fractions of THF-soluble (white area) and THF-insoluble parts (shaded area) in the photocopolymerization of MMA with  $\text{Cp}_2\text{TiCl}_2$  at 40°C in a  $\text{H}_2\text{O}$ -MeOH [1 : 1 (v/v)] mixture;  $[\text{MMA}] = 0.935 \text{ mol L}^{-1}$ ,  $[\text{Cp}_2\text{TiCl}_2] = 1.50 \times 10^{-3} \text{ mol L}^{-1}$ .

for the photocopolymerization with MAIB. This finding reveals that the present photocopolymerization proceeds *via* a radical mechanism, as well as the polymerization with  $\text{Cp}_2\text{TiCl}_2$  in the dark.

#### Formation of Poly(MMA) with Novel Solubility

Poly(MMA) formed in the present photocopolymerization was found to contain a considerable frac-

**Table I** Solubilities of the THF-Soluble and THF-Insoluble Parts of Poly(MMA) Formed in the Photocopolymerization with  $\text{Cp}_2\text{TiCl}_2$  in a  $\text{H}_2\text{O}$ -MeOH [1 : 1 (v/v)] Mixture at 40°C<sup>a</sup>

Solvent	THF-Insoluble	THF-Soluble	Radical Poly(MMA) <sup>b</sup>
Benzene	Soluble	Soluble	Soluble
Toluene	Soluble	Soluble	Soluble
Chloroform	Soluble	Soluble	Soluble
THF	Insoluble	Soluble	Soluble
Ethyl acetate	Insoluble	Soluble	Soluble
Acetone	Insoluble	Soluble	Soluble
Methyl ethyl ketone	Insoluble	Soluble	Soluble
Acetonitrile	Insoluble	Insoluble	Soluble
DMF	Insoluble	Soluble	Soluble
DMSO	Insoluble	Soluble	Soluble

<sup>a</sup>  $[\text{MMA}] = 0.935 \text{ mol L}^{-1}$ ,  $[\text{Cp}_2\text{TiCl}_2] = 1.50 \times 10^{-3} \text{ mol L}^{-1}$ .

<sup>b</sup> Prepared by the polymerization with MAIB at 50°C in benzene.

**Table II Fractions of the THF-Soluble and THF-Insoluble Parts of Poly(MMA) Formed under Various Photopolymerization Conditions**

[Cp <sub>2</sub> TiCl <sub>2</sub> ] × 10 <sup>3</sup> (mol L <sup>-1</sup> )	[MMA] (mol L <sup>-1</sup> )	[H <sub>2</sub> O] (%) <sup>a</sup>	Temperature (°C)	Time (hr)	Total Yield (%)	Fraction (%)		THF-Soluble Part		
						THF- Soluble	THF- Insoluble	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$
1.50	0.935	50	20	10	60.2	60	40	5.1	15.0	2.9
1.50	0.935	50	30	10	93.1	64	36	6.0	15.9	2.7
1.50	0.935	50	40	10	77.2	61	39	6.3	15.2	2.4
1.50	0.935	50	50	10	90.1	45	55	6.2	16.3	2.6
1.50	0.935	50	60	10	96.6	44	56	6.4	16.1	2.5
0.50	0.935	50	40	10	70.2	69	31	12.1	22.5	1.9
1.00	0.935	50	40	10	74.0	64	36	9.2	18.4	2.0
2.00	0.935	50	40	10	87.9	74	26	5.4	17.3	3.2
5.00	0.935	50	40	10	66.2	94	6	3.8	14.4	3.8
10.0	0.935	50	40	10	45.4	98	2	1.9	13.4	7.2
1.50	0.30	50	40	10	23.0	100	0	1.4	6.1	4.2
1.50	0.50	50	40	10	26.4	98	2	2.7	9.4	3.5
1.50	0.60	50	40	10	34.7	92	8	4.2	12.8	3.1
1.50	0.80	50	40	10	65.7	68	32	5.3	14.9	2.8
1.50	0.935	10	40	10	23.2	100	0	2.6	9.3	3.6
1.50	0.935	20	40	10	63.7	100	0	4.2	15.1	3.6
1.50	0.935	30	40	10	66.0	100	0	4.8	15.4	3.2
1.50	0.935	40	40	10	74.1	94	0	4.9	15.5	3.2

<sup>a</sup> Vol % of H<sub>2</sub>O in the H<sub>2</sub>O–MeOH mixture.

tion of THF-insoluble parts. Elemental analysis of the THF-soluble and THF-insoluble parts established that neither part contained any inorganic residue.

The THF-insoluble poly(MMA) was observed to show novel solubility characters. It was soluble in benzene and toluene, but insoluble in polar solvents, such as acetone, dimethylformamide (DMF), and dimethylsulfoxide (DMSO). Table I compares the solubilities in various solvents of the THF-soluble part, the THF-insoluble part, and poly(MMA) separately prepared by the MAIB-initiated polymerization. Thus, the THF-insoluble poly(MMA) formed in the radical photopolymerization initiated with Cp<sub>2</sub>TiCl<sub>2</sub> in a H<sub>2</sub>O–MeOH mixture is quite different in solubility from the usual radical poly(MMA).

Figure 6 shows a time profile for the total yield and the fractions of THF-soluble and insoluble parts in the photopolymerization of MMA (0.935 mol L<sup>-1</sup>) with Cp<sub>2</sub>TiCl<sub>2</sub> (1.50 × 10<sup>-3</sup> mol L<sup>-1</sup>) in a H<sub>2</sub>O–MeOH mixture [1 : 1 (v/v)]. An induction period of about 2 h was observed for formation of the THF-insoluble part. The polymer formed after

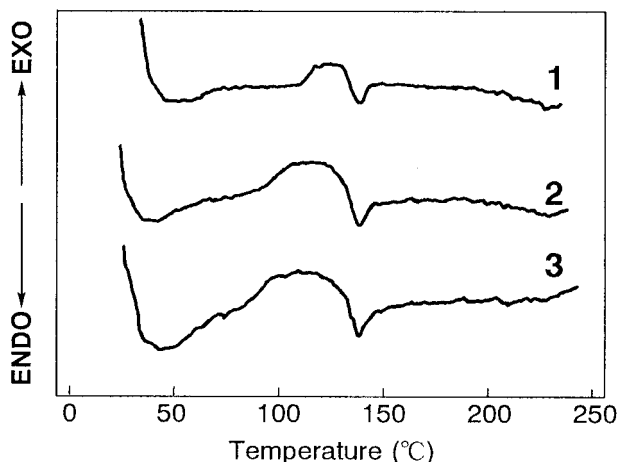
the induction period was THF-insoluble for the most part.

Table II summarizes the results of fractionation of poly(MMA)s produced in the photopolymerization at 40°C for 10 h under various conditions. The fraction of THF-insoluble part tended

**Table III Photopolymerization of MMA with Cp<sub>2</sub>TiCl<sub>2</sub> in H<sub>2</sub>O–Various Solvent [1 : 1 (v/v)] Mixtures at 40°C for 10 h<sup>a</sup>**

Solvent	Polymer Yield (%)	Fraction of THF-Insoluble Part (%)
Methanol	27.4	18.7
Ethanol	32.4	Trace
<i>n</i> -Propanol	10.9	0.0
Isopropanol	11.1	0.0
THF	1.1	0.0
DMF	59.4	0.0
DMSO	9.9	0.0
Acetone	2.8	0.0
Acetic acid	13.3	0.0

<sup>a</sup> [MMA] = 0.60 mol L<sup>-1</sup>, [Cp<sub>2</sub>TiCl<sub>2</sub>] = 1.50 × 10<sup>-3</sup> mol L<sup>-1</sup>.



**Figure 7** DSC curves of the THF-soluble (1) and THF-insoluble (2) parts and poly(MMA) formed with MAIB (3).

to increase with rising temperature, increasing MMA concentration, and increasing H<sub>2</sub>O content. On the other hand, the THF-insoluble fraction showed a maximum on varying the Cp<sub>2</sub>TiCl<sub>2</sub> concentration.

The molecular weights of the THF-soluble parts are also listed in Table II. The  $\bar{M}_n$  value was in the range of  $1.4\text{--}12.1 \times 10^5$ . The molecular weight increased with decreasing initiator concentration, increasing monomer concentration, and increasing H<sub>2</sub>O content. The polydispersity ( $\bar{M}_w/\bar{M}_n$ ) in turn decreased with increasing Cp<sub>2</sub>TiCl<sub>2</sub> concentration, decreasing MMA concentration, and decreasing H<sub>2</sub>O content. Temperature showed little effect on the molecular weight and polydispersity of the THF-soluble part.

The photopolymerization of MMA with Cp<sub>2</sub>TiCl<sub>2</sub> was examined using other H<sub>2</sub>O-miscible organic solvents in place of MeOH, whereas the concentrations of monomer and initiator were 0.60 and  $1.50 \times 10^{-3}$  mol L<sup>-1</sup>, respectively. The results obtained are presented in Table III. Although a much higher polymer yield was observed in DMF, the resulting poly(MMA) contained no THF-insoluble part. A little THF-insoluble part was also obtained in other solvents used.

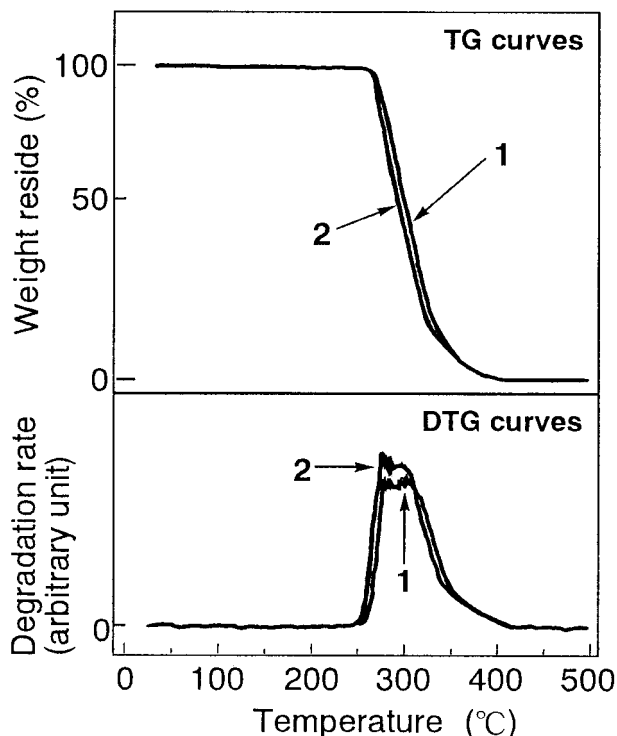
The molecular weight of the THF-insoluble part was viscometrically determined in benzene and compared with that of the THF-soluble part, of which the original poly(MMA) was prepared in the photopolymerization of MMA ( $0.935$  mol L<sup>-1</sup>) with Cp<sub>2</sub>TiCl<sub>2</sub> ( $1.50 \times 10^{-3}$  mol L<sup>-1</sup>) at 40°C for 10 h in a H<sub>2</sub>O–MeOH [1 : 1 (v/v)] mixture:  $\bar{M}_w$

=  $3.4 \times 10^5$  (insoluble part) and  $2.5 \times 10^6$  (soluble part). It is of interest that the THF-insoluble part had a fairly lower molecular weight than the THF-soluble part.

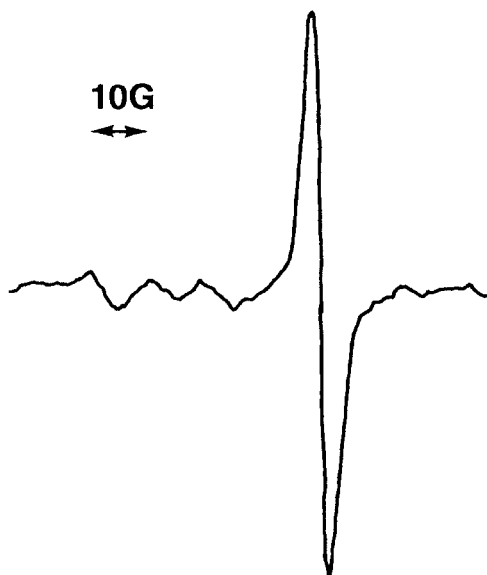
It has been known that isotactic poly(MMA) and syndiotactic poly(MMA) associate to form a crystalline complex in certain solvents, such as toluene, DMF, and acetone.<sup>21</sup> So, we have examined the tacticities of THF-soluble and THF-insoluble parts. However, <sup>1</sup>H-NMR-determined tacticities of both parts were closely similar to that of the usual radical poly(MMA) as follows: soluble part— $rr = 62.5$ ,  $mr = 33.7$ ,  $mm = 3.8$ ; insoluble part— $rr = 62.4$ ,  $mr = 33.8$ ,  $mm = 3.8$ ; and radical poly(MMA)— $rr = 61.8$ ,  $mr = 34.5$ ,  $mm = 3.7$ .

The infrared and Raman spectra of the THF-soluble and THF-insoluble parts were also nearly the same as those of radical poly(MMA) separately prepared.

Figure 7 shows DSC curves of the THF-soluble and THF-insoluble parts, together with that of radical poly(MMA). Little difference was observed between these DSC curves. As shown in Figure 8, both of the THF-soluble and THF-insol-



**Figure 8** TG and differential thermogravimetric (DTG) curves of the THF-soluble (1) and THF-insoluble (2) parts.



**Figure 9** ESR spectrum observed in the photopolymerization of MMA with  $\text{Cp}_2\text{TiCl}_2$  in a  $\text{H}_2\text{O}-\text{MeOH}$  [1 : 1 (v/v)] at  $40^\circ\text{C}$  for 2.5 h.

uble parts gave similar TG and differential thermogravimetric curves.

#### ESR Study on the Polymerization System

Figure 9 presents ESR spectrum observed in the photopolymerization of MMA with  $\text{Cp}_2\text{TiCl}_2$  in a  $\text{H}_2\text{O}-\text{MeOH}$  [1 : 1 (v/v)]. A large absorption observed is due to  $\text{Ti}^{3+}$ . Photolysis of  $\text{Cp}_2\text{TiCl}_2$  was reported to yield a  $\text{Ti}^{3+}$  species.<sup>22</sup> The  $\text{Ti}^{3+}$  species is suggested to play an important role in the present photopolymerization though the true initiation mechanism is obscure at present.

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