

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Polymerization of Methyl Methacrylate with Bis(Cyclopentadienyl)Titanium Dichloride in a Water-Methanol Mixture: Formation of Tetrahydrofuran-Insoluble Polymer

Tsuneyuki Sato^a; Tatsuo Umenoki^a; Makiko Seno^a; Hitoshi Tanaka^a

^a Department of Chemical Science and Technology Faculty of Engineering, Tokushima University, Tokushima, Japan

To cite this Article Sato, Tsuneyuki , Umenoki, Tatsuo , Seno, Makiko and Tanaka, Hitoshi(1995) 'Polymerization of Methyl Methacrylate with Bis(Cyclopentadienyl)Titanium Dichloride in a Water-Methanol Mixture: Formation of Tetrahydrofuran-Insoluble Polymer', *Journal of Macromolecular Science, Part A*, 32: 7, 1329 – 1340

To link to this Article: DOI: 10.1080/10601329508009359

URL: <http://dx.doi.org/10.1080/10601329508009359>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

POLYMERIZATION OF METHYL METHACRYLATE WITH BIS(CYCLOPENTADIENYL)TITANIUM DICHLORIDE IN A WATER-METHANOL MIXTURE: FORMATION OF TETRAHYDROFURAN-INSOLUBLE POLYMER

TSUNEYUKI SATO,* TATSUO UMENOKI, MAKIKO SENO, and HITOSHI TANAKA

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

ABSTRACT

Methyl methacrylate (MMA) was found to be effectively polymerized with bis(cyclopentadienyl)titanium dichloride (Cp_2TiCl_2) in a water-methanol mixture (1:1, v/v). The polymerization proceeded heterogeneously because the resulting poly(MMA) was insoluble in the system. The rate (R_p) of the heterogenous polymerization was apparently expressed by $R_p = k[\text{Cp}_2\text{TiCl}_2]^2[\text{MMA}]^{2.5}$ (at 40°C). The resulting poly(MMA) was observed to consist of tetrahydrofuran (THF)-soluble and insoluble parts. In contrast with the usual radical poly(MMA), the THF-insoluble part was soluble in benzene, toluene, and chloroform but insoluble in polar solvents such as ethyl acetate, acetone, acetonitrile, dimethylformamide, and dimethylsulfoxide. The polymerization was found to be profoundly accelerated by irradiation with a fluorescent room lamp (15 W). The results of copolymerization of MMA and acrylonitrile indicated that the present polymerization proceeds through a radical mechanism.

INTRODUCTION

Various metallocenes and their combinations with methylaluminoxane have been intensively studied as catalysts for olefin polymerizations, most of which proceed via coordination mechanisms to yield stereospecific polymers [1–5].

Some metallocenes such as ferrocene and cobaltocene have also been reported to initiate coordinated anionic polymerizations of electron-accepting vinyl monomers including methyl methacrylate (MMA) and acrylonitrile (AN) [6–8].

On the other hand, combined systems of metallocenes and organic halides or acid anhydrides have been observed to initiate radical polymerizations of vinyl monomers although the metallocenes alone have little activity [6, 9–12].

Recently we have found that bis(cyclopentadienyl)titanium dichloride ($\text{Cp}_2\text{-TiCl}_2$) effectively induces radical polymerization of MMA in a water–methanol mixture, and the resulting poly(MMA) contains a considerable fraction of tetrahydrofuran (THF)-insoluble part.

The present paper describes the results of polymerization of MMA with $\text{Cp}_2\text{-TiCl}_2$ in a water–methanol mixture and presents a characterization of the resultant polymer.

EXPERIMENTAL

Materials

Commercially available monomers [MMA, methyl acrylate (MA), diethyl itaconate (DEI), di-2-ethylhexyl itaconate (DEHI), AN, vinyl acetate (VAc) and styrene (St)] were freed from inhibitor by treatment with a 5% NaOH aqueous solution, dried over sodium sulfate, and distilled. Organic solvents were used after distillation. Ion-free water was used. Cp_2TiCl_2 (supplied from Nichia Chemical Industries) was used without further purification.

Polymerization

Polymerization and copolymerization were conducted in degassed and sealed glass tubes at a given temperature without shaking. The resulting polymers were isolated by pouring the polymerization mixtures into a large excess of methanol containing small amounts of 4-*tert*-butylcatechol as inhibitor and HCl. The polymers were filtered, dried under vacuum, and weighed. Poly(MMA) was further divided into soluble and insoluble parts in THF.

Measurements

$^1\text{H-NMR}$ spectra were obtained in deuteriochloroform with a Jeol GX-400 (400 MHz) spectrometer. IR spectra were observed with a Perkin-Elmer 1600 FT-IR spectrometer. Gel permeation chromatograms (GPC) were recorded with a Toso HLC-802H chromatograph at 38°C using THF as eluent. The number-average (\overline{M}_n) and weight-average (\overline{M}_w) molecular weight were estimated from the GPC results, by standard procedures using poly(St) standards. \overline{M}_w of poly(MMA) was

also viscometrically determined using Eq. (1) [13], where the intrinsic viscosity ($[\eta]$) was measured in benzene at 25°C with a Ubbelohde viscometer;

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

Dynamic thermogravimetry (TG) of poly(MMA) was performed in an N₂ atmosphere (flow rate: 20 mL/min) 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).

RESULTS AND DISCUSSION

Polymerization of Some Vinyl Monomers with Cp₂TiCl₂ in a Water–Methanol Mixture

MMA was found to be effectively polymerized with Cp₂TiCl₂ at 40°C in a water–methanol mixture [1:1 (v/v)] when the polymerization was conducted in the dark without shaking. Polymerization results are presented in Table 1 together with those of other monomers which are soluble in the water–methanol mixture. Cp₂TiCl₂ showed little activity for monomers other than MMA under the present conditions, so the polymerization of MMA was investigated in detail. The polymerization of MMA proceeded heterogeneously because the resulting poly(MMA) was insoluble in the polymerization system.

Polymerization of MMA with Cp₂TiCl₂ in a Water–Methanol Mixture

Figure 1 shows the time–conversion curves observed for the polymerization in an H₂O–MeOH [1:1 (v/v)] mixture in the 20–60°C temperature range when the concentrations of Cp₂TiCl₂ and MMA were 1.5×10^{-3} and $0.935 \text{ mol} \cdot \text{L}^{-1}$, respectively. Lower conversions were observed at higher temperatures, 50 and 60°C, indicating that the initiator decomposes rapidly at higher temperatures and becomes inactive. It is to be noted that the polymerization at 20 and 30°C showed a profound autoacceleration, suggesting a strongly suppressed bimolecular termination.

TABLE 1. Polymerization of Some Vinyl Monomers with Cp₂TiCl₂ at 40°C in a Water–Methanol [1:1 (v/v)] Mixture^a

Monomer (M)	[M], mol·L ⁻¹	Time, h	Conversion, %
MMA	0.935	2	7.7
MMA	0.935	10	42.0
MMA	0.50	10	24.4
MA	0.50	10	1.4
AN	0.50	10	Trace
DEI	0.50	10	Trace
VAc	0.50	10	Trace

^a[Cp₂TiCl₂] = $1.50 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$.

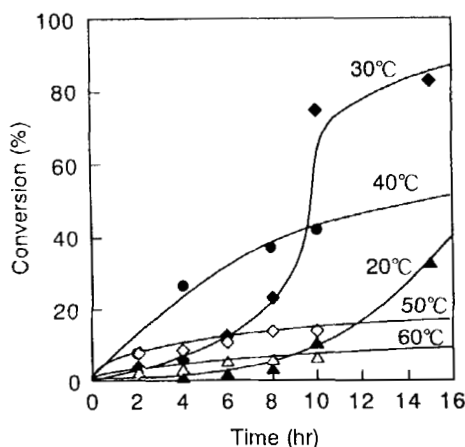


FIG. 1. Temperature effect on the polymerization of MMA with Cp_2TiCl_2 in an H_2O -MeOH (1:1, v/v) mixture. $[\text{MMA}] = 0.935 \text{ mol}\cdot\text{L}^{-1}$, $[\text{Cp}_2\text{TiCl}_2] = 1.50 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$.

Figure 2 presents the time-conversion curves for the polymerization of MMA with Cp_2TiCl_2 at 40°C in an H_2O -MeOH [1:1 (v/v)] mixture when $[\text{MMA}]$ was fixed at $0.935 \text{ mol}\cdot\text{L}^{-1}$ and $[\text{Cp}_2\text{TiCl}_2]$ was varied. Thus the initial polymerization rate (R_p) was proportional to the second order of $[\text{Cp}_2\text{TiCl}_2]$.

Figure 3 shows the time-conversion curves for the polymerization of MMA with Cp_2TiCl_2 at 40°C in an H_2O -MeOH [1:1 (v/v)] mixture when $[\text{MMA}]$ was varied and $[\text{Cp}_2\text{TiCl}_2]$ was kept constant at $1.5 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$. R_p increased in proportion to the 2.5 power of $[\text{MMA}]$. R_p was apparently expressed by

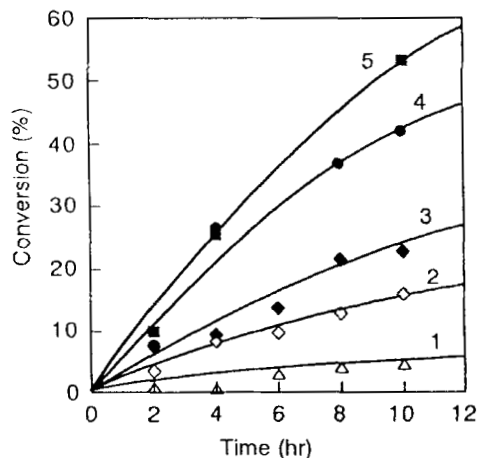


FIG. 2. Effect of the Cp_2TiCl_2 concentration on the polymerization of MMA with Cp_2TiCl_2 in an H_2O -MeOH (1:1, v/v) mixture at 40°C . $[\text{MMA}] = 0.935 \text{ mol}\cdot\text{L}^{-1}$. $[\text{Cp}_2\text{TiCl}_2] = 1, 0.5 \times 10^{-3}, 2, 1.00 \times 10^{-3}, 3, 1.25 \times 10^{-3}, 4, 1.50 \times 10^{-3}, 5, 2.00 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$.

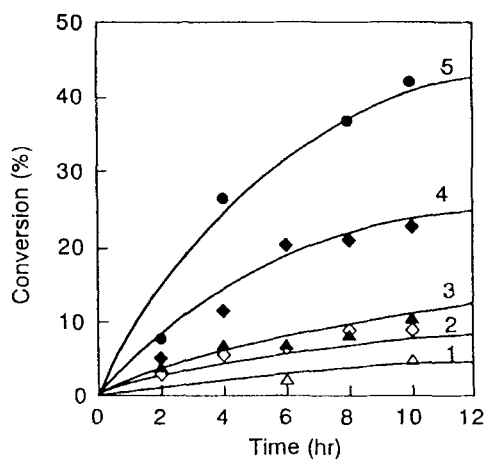


FIG. 3. Effect of the monomer concentration on the polymerization of MMA with Cp_2TiCl_2 in an H_2O -MeOH (1:1, v/v) mixture at 40°C . $[\text{Cp}_2\text{TiCl}_2] = 1.50 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$. $[\text{MMA}] = 1, 0.20; 2, 0.30; 3, 0.40; 4, 0.60; 5, 0.935 \text{ mol}\cdot\text{L}^{-1}$.

$$R_p = k[\text{Cp}_2\text{TiCl}_2]^2[\text{MMA}]^{2.5} \quad (2)$$

Figure 4 shows the results observed in the polymerization of MMA with Cp_2TiCl_2 at 40°C at various compositions of solvent, where the concentrations of Cp_2TiCl_2 and MMA were 1.5×10^{-3} and $0.935 \text{ mol}\cdot\text{L}^{-1}$. Thus R_p increased with an increasing content of H_2O in the polymerization medium.

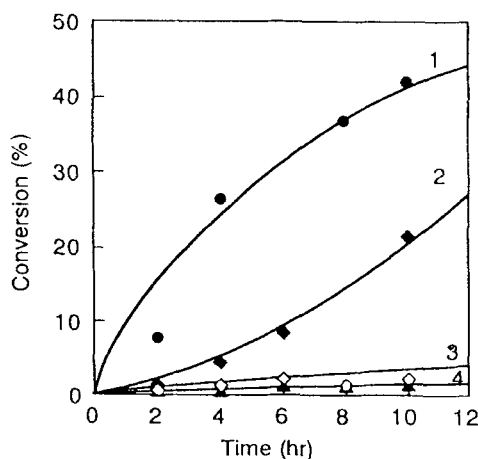


FIG. 4. Effect of the medium composition on the polymerization of MMA with Cp_2TiCl_2 in an H_2O -MeOH mixture at 40°C . $[\text{Cp}_2\text{TiCl}_2] = 1.50 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$, $[\text{MMA}] = 0.935 \text{ mol}\cdot\text{L}^{-1}$. Volume % of H_2O in the H_2O -MeOH mixture: 1, 50; 2, 40; 3, 30; 4, 10.

Large Acceleration of the Polymerization by Irradiation of a 15-W Fluorescent Room Lamp

The polymerization of MMA with Cp_2TiCl_2 in an H_2O -MeOH [1:1 (v/v)] mixture was found to be significantly accelerated by irradiation with a 15-W fluorescent room lamp (Toshiba FL 15EX-N-H). On the other hand, irradiation with a 400-W high-pressure Hg lamp seemed to cause rapid decomposition of Cp_2TiCl_2 , resulting in a low polymer yield. The results observed are shown in Fig. 5.

Copolymerization of MMA and AN with Cp_2TiCl_2 in a Water-Methanol Mixture

In order to confirm the polymerization mechanism, the copolymerization of MMA and AN with Cp_2TiCl_2 was performed in an H_2O -MeOH [1:1 (v/v)] mixture at 40°C. Figure 6 shows the copolymer composition curve obtained along with that for the copolymerization in the same medium initiated with dimethyl 2,2'-azobisisobutyrate (MAIB), a typical radical initiator. The copolymer composition was determined from the nitrogen content by elemental analysis.

The two composition curves are nearly the same, indicating that the present polymerization proceeds through a radical mechanism.

Characterization of the Resulting Poly(MMA)

Poly(MMA) formed in the present polymerization was observed to consist of THF-soluble and THF-insoluble parts. It is to be noted that the THF-insoluble part is not crosslinked because it is soluble in benzene and chloroform. Elemental analy-

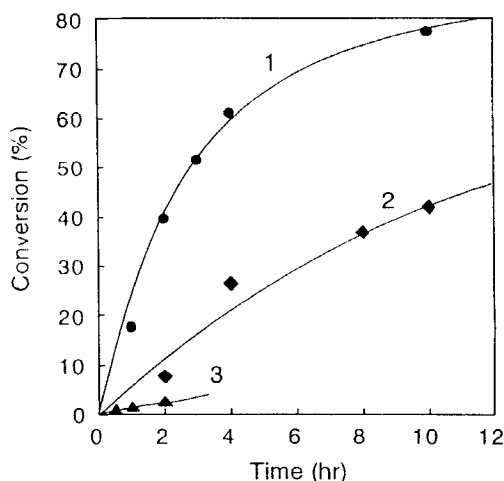


FIG. 5. Effect of photoirradiation on the polymerization of MMA with Cp_2TiCl_2 in an H_2O -MeOH (1:1, v/v) mixture. $[\text{Cp}_2\text{TiCl}_2] = 1.50 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, $[\text{MMA}] = 0.935 \text{ mol} \cdot \text{L}^{-1}$. 1: Irradiated at 40°C by a 15-W fluorescent room lamp. 2: At 40°C in the dark. 3: Irradiated at 25°C by a 400-W high-pressure Hg lamp.

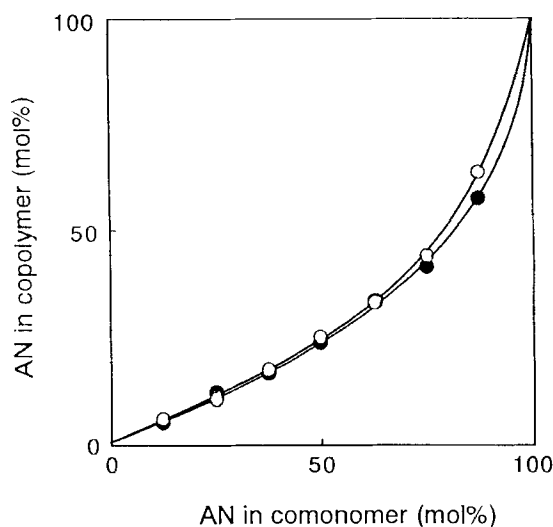


FIG. 6. Copolymer composition curves for the copolymerizations of AN and MMA with Cp_2TiCl_2 (●) and MAIB (○) at 40°C in an H_2O -MeOH (1:1, v/v) mixture.

sis of the soluble and insoluble parts revealed that neither part contained any inorganic residue.

Table 2 summarizes the solubility of the fractionated parts in various solvents. For comparison, the data of poly(MMA) separately obtained in the MAIB-initiated polymerization in benzene are also presented in the table. It is of great interest that

TABLE 2. Solubility of the THF-Soluble and Insoluble Parts of Poly(MMA) Formed in the Polymerization with Cp_2TiCl_2 in a Water-Methanol Mixture at 40°C for 10 Hours^a

Solvent	THF-insoluble	THF-soluble	Radical poly(MMA) ^b
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
Dimethylformamide	Insoluble	Soluble	Soluble
Dimethylsulfoxide	Insoluble	Soluble	Soluble

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

^bPrepared by polymerization with dimethyl 2,2'-azobisisobutyrate at 60°C in benzene.

the THF-insoluble poly(MMA) formed in the radical polymerization initiated with Cp_2TiCl_2 in a water-methanol mixture is quite different in solubility from the usual radical poly(MMA). However, it is obscure at present why the polymerization with Cp_2TiCl_2 in a water-methanol mixture yields poly(MMA) with such a unique solubility character. Figure 7 shows a time profile for the yields of THF-soluble and insoluble parts. An induction period of about 2 hours was observed for the formation of the insoluble part. The polymer formed after the induction period was THF-insoluble for the most part.

Table 3 presents the results of fractionation of poly(MMA) produced under various polymerization conditions. Higher fractions of the THF-insoluble part tended to be obtained at higher total polymer yields.

Table 4 summarizes the molecular weights of the THF-soluble part of poly(MMA) formed under different polymerization conditions. The molecular weights were very high ($\bar{M}_n = \text{ca. } 10^6$) although their distributions were fairly broad. The molecular weight of the insoluble part was viscometrically determined and compared with that of the soluble part, of which the original poly(MMA) was obtained in the polymerization at 40°C for 10 hours in $\text{H}_2\text{O-MeOH}$ [1:1 (v/v)]: $\bar{M}_w = 1.1 \times 10^6$ (insoluble part) and 4.4×10^6 (soluble part). The insoluble part was found to have a rather lower molecular weight.

$^1\text{H-NMR}$ -determined tacticities of THF-soluble and insoluble parts were closely similar to that of the usual radical poly(MMA) as follows: soluble part, $rr = 69.2$, $mr = 27.6$, $mm = 3.1$; insoluble part, $rr = 70.1$, $mr = 26.0$, $mm = 3.9$. The IR spectra of both parts were also nearly the same.

As shown in Fig. 8, the soluble and insoluble parts and radically formed poly(MMA) gave similar DSC curves, showing nearly the same T_g . However, different TG and different differential thermogravimetric (DTG) curves were observed

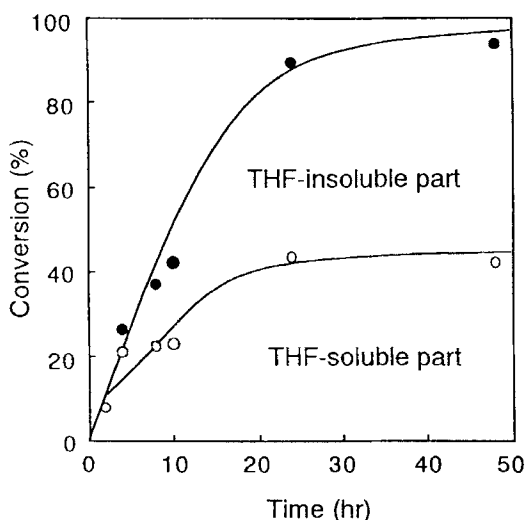


FIG. 7. Time profile for the yields of THF-soluble and insoluble parts in the polymerization of MMA with Cp_2TiCl_2 in an $\text{H}_2\text{O-MeOH}$ (1:1, v/v) mixture at 40°C . $[\text{Cp}_2\text{TiCl}_2] = 1.50 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$, $[\text{MMA}] = 0.935 \text{ mol}\cdot\text{L}^{-1}$.

TABLE 3. Fractions of the THF-Soluble and Insoluble Parts of Poly(MMA) Formed under Various Polymerization Conditions

[Cp ₂ TiCl ₂] × 10 ³ mol·L ⁻¹	[MMA], mol·L ⁻¹	[H ₂ O], % ^a	Temp., °C	Time, h	Total yield, %	Fraction, %	
						THF- soluble	THF- insoluble
1.50	0.935	50	20	6	1.8	100	0
1.50	0.935	50	20	10	10.3	61	39
1.50	0.935	50	20	15	32.7	59	41
1.50	0.935	50	30	10	74.5	64	36
1.50	0.935	50	40	10	42.0	55	45
1.50	0.935	50	40	24	89.4	49	51
1.50	0.935	50	50	10	13.9	80	20
1.50	0.935	50	60	10	6.4	90	10
0.50	0.935	50	40	10	2.5	100	0
1.00	0.935	50	40	10	16.0	94	6
1.25	0.935	50	40	10	22.7	89	11
1.50	0.935	50	40	10	42.0	55	45
2.00	0.935	50	40	10	53.3	53	47
2.00	0.935	50	40	24	76.1	36	64
1.50	0.20	50	40	10	4.9	100	0
1.50	0.30	50	40	10	8.8	100	0
1.50	0.40	50	40	10	10.5	100	0
1.50	0.60	50	40	10	22.7	56	44
1.50	0.935	10	40	10	3.5	100	0
1.50	0.935	30	40	10	2.3	100	0
1.50	0.935	40	40	10	21.5	82	18

^aVol% of H₂O in the H₂O-MeOH mixture.

for each part (Fig. 9). Thus, the insoluble part was thermally more stable than the soluble part.

It was reported that the degradation of radically polymerized poly(MMA) occurs in three stages which are attributable to different modes of initiation of depolymerization: the scission of head-head linkages formed through recombination termination of two polymer radicals (180°C), the scission of the bond β to a terminal double bond formed through disproportionation termination (300°C), and the random scission of the polymer main chain (380°C) [14, 15]. The DTG curves in Fig. 9 suggest that the initiation of degradation of the soluble part comes from scission of the bond β to a terminal double bond and the random scission of the polymer main chain, and that of the insoluble part results mainly from random polymer chain scission. The insoluble part may be formed by a chain transfer reaction involving no monomer.

Investigation of the formation mechanism and characterization of the THF-insoluble poly(MMA) is now in progress.

TABLE 4. Molecular Weights and Polydispersities of the THF-Soluble Part of Poly(MMA) Formed under Various Polymerization Conditions

$[\text{Cp}_2\text{TiCl}_2] \times 10^3 \text{ mol} \cdot \text{L}^{-1}$	$[\text{MMA}], \text{ mol} \cdot \text{L}^{-1}$	$[\text{H}_2\text{O}], \text{ \%}^a$	Temp., °C	Time, h	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w \times 10^{-5}$	\bar{M}_w/\bar{M}_n
1.50	0.935	50	20	6	5.3	20.2	3.8
1.50	0.935	50	20	10	10.6	23.7	2.2
1.50	0.935	50	20	15	14.2	33.8	2.4
1.50	0.935	50	30	6	7.7	28.1	3.7
1.50	0.935	50	30	10	9.3	20.6	2.2
1.50	0.935	50	40	10	13.1	26.3	2.0
1.50	0.935	50	50	10	4.8	17.9	3.7
1.50	0.935	50	60	10	9.0	23.7	2.6
0.50	0.935	50	40	10	9.1	18.7	2.1
1.00	0.935	50	40	10	13.1	27.7	2.1
1.25	0.935	50	40	10	16.3	29.3	1.8
2.00	0.935	50	40	10	8.0	20.4	2.5
1.50	0.20	50	40	10	2.2	6.3	2.9
1.50	0.30	50	40	10	2.8	8.7	3.1
1.50	0.40	50	40	10	3.9	12.5	3.2
1.50	0.60	50	40	10	5.2	16.0	3.1
1.50	0.935	10	40	10	4.1	13.9	3.4
1.50	0.935	30	40	10	4.5	16.1	3.6
1.50	0.935	40	40	10	7.1	22.4	3.2

^aVol% of H₂O in the water-methanol mixture.

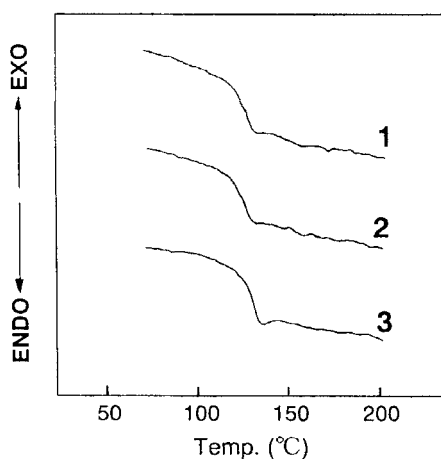


FIG. 8. DSC curves of the THF-soluble (1) and insoluble (2) parts and poly(MMA) (3) formed with MAIB in benzene at 50°C.

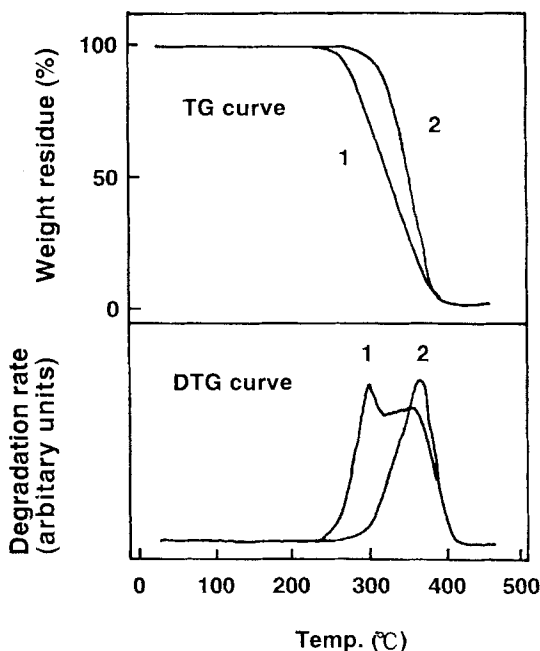


FIG. 9. TG and DTG curves of the THF-soluble (1) and insoluble (2) parts.

CONCLUSIONS

The polymerization of MMA was effectively induced with Cp_2TiCl_2 in a water-methanol [1:1 (v/v)] mixture. The polymerization rate (R_p) was given by $R_p = k[\text{Cp}_2\text{TiCl}_2]^2[\text{MMA}]^{2.5}$. The resulting poly(MMA) contains a considerable fraction (up to 64%) of the THF-insoluble part. The insoluble part is soluble in benzene, toluene, and chloroform but insoluble in polar solvents such as ethyl acetate, acetone, acetonitrile, dimethylformamide, and dimethylsulfoxide. The polymerization was strongly accelerated by irradiation from a 15-W fluorescent room lamp. Copolymerization results of MMA and AN indicate that the polymerization of MMA with Cp_2TiCl_2 in a water-methanol mixture proceeds via a radical mechanism.

REFERENCES

- [1] J. C. W. Chien and He, *J. Polym. Sci., Polym. Chem. Ed.*, **29**, 1585 (1991).
- [2] R. L. Halterman, *Chem. Rev.*, **92**, 965 (1992).
- [3] J. Okada, *Angew. Chem. Int. Ed. Engl.*, **31**, 47 (1992).
- [4] C. Sishta, R. M. Hathorn, and T. J. Mark, *J. Am. Chem. Soc.*, **114**, 1112 (1992).
- [5] G. W. Coates and R. M. Waymouth, *Ibid.*, **115**, 91 (1993).
- [6] K. Kaeriyama, *Polymer*, **12**, 422 (1971).
- [7] S. Kubota and T. Otsu, *Kobunshi Ronbunshu*, **33**, 201 (1976).
- [8] T. Otsu and Y. Mun, *J. Macromol. Sci. - Chem.*, **A11**, 1783 (1977).

- [9] C. H. Bamford, *J. Polym. Sci., Part C*, **4**, 1571 (1964).
- [10] S. Kubota and T. Otsu, *Kobunshi Ronbunshu*, **31**, 759 (1974).
- [11] T. Ouchi, H. Taguchi, and M. Imoto, *J. Macromol. Sci.—Chem.*, **A12**, 719 (1978).
- [12] Y. Mun and T. Otsu, *Polym. Bull.*, **11**, 109 (1984).
- [13] H.-J. Cantow and G. V. Schulz, *Z. Phys. Chem. (Frankfurt)*, **2**, 117 (1954).
- [14] I. J. Popovic, L. Katsikas, U. Müller, J. S. Velickovic, and H. Weller, *Macromol. Chem. Phys.*, **195**, 889 (1994).
- [15] T. Kashiwagi, A. Inaba, J. E. Brown, K. Hatada, T. Kitayama, and E. Masuda, *Macromolecules*, **19**, 2160 (1986).

Received July 15, 1994

Revision received December 10, 1994