Syndiotactic-specific polymerization of methyl methacrylate with *tert*-butyllithium/trialkylaluminum in dichloromethane

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Abstract By using dichloromethane as a polymerization solvent, syndiotactic-specific polymerization of methyl methacrylate with *t*-BuLi in the presence of large excess of tributylaluminum at –78 °C proceeded more rapidly than in toluene and gave *st*-PMMA ($rr = 90\%$) with narrow molar mass distribution. This method allows us to prepare *st*-PMMA with molar mass up to 350×10^3 in 48 h.

Introduction

Poly(methyl methacrylate) (PMMA) with high syndiotacticity has attracted interest due to the fact that the glass transition temperature (T_g), an important materials property parameter, of PMMA rises with an increase in the syndiotacticity [1]. Intense research efforts have been directed at development of a polymerization system that can lead to the efficient production of highly syndiotactic (*st*-) PMMA [2–10]. Among them, anionic living polymerization of MMA with *tert*-butyllithium (*t*-BuLi) in combination with trialkylaluminum (R_3Al) in toluene is one of the earliest examples that proceed in a living manner to afford *st*-PMMA with *rr* content of *ca.* 90% [4]. While several coordination polymerization systems utilizing transition metal compounds have been also exploited as exemplified by a latest achievement by Chen et al. [10], which allows them to prepare *st*-PMMA with *rr* triad content up to 95% at 25 °C, *t*-BuLi/R_3Al is quite versatile since both the initiator components are readily available commercially. In this polymerization

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system, the added aluminum compound is assumed to stabilize the propagating anions so as to prevent possible side reactions, while it activates MMA monomer through coordination to the carbonyl group so as to compensate, to some extent, the lowered reactivity of the stabilized propagating anion. Due to the stabilization effect, the rate of the polymerization is relatively low and thus the preparation of high molar mass PMMA under typical conditions (MMA 10 mmol, toluene 10 mL, t-BuLi 0.2 mmol, $(n\text{-}C_4H_9)_3Al$ 0.6 mmol, at –78 °C) requires long polymerization time, i.e. the synthesis of st-PMMA with 5×10^3 M mass needs 24 h of polymerization time. The rate of polymerization can be enhanced by raising the polymerization temperature but only at the expense of decreased syndiotacticity of the polymer formed. This report provides a practically improved synthetic procedure for the synthesis of st-PMMA with the consideration of solvent effect, that allows us to prepare st-PMMA ($rr = 90\%$) with molar mass up to 350×10^3 in 48 h. Halogenated solvents such as dichloromethane or chloroform have scarcely been used as a solvent for anionic polymerization of methacrylates. Only a few studies have been reported using less basic initiators than alkyllithium such as Grignard reagents [11–14] or triphenylphosphine [15]. To the best of the authors' knowledge, this is the first example of polymerization of MMA with alkyllithium initiator using dichloromethane as a solvent, where the presence of $(n\text{-}C_4H_9)_3Al$ effectively suppresses the decomposition of t-BuLi through a reaction with dichloromethane.

Results and discussion

Polymerization of MMA with t-BuLi in the presence of 5-fold tributylaluminum $((n\text{-}C_4H_9)_3Al)$ was carried out in a series of mixed solvents consisting of toluene and dichloromethane at –78 °C for 24 h. The results are shown in Table 1. In this study, $(n\text{-}C_4H_9)_3Al$ was added first to the solvent containing dichloromethane, the mixture was cooled at −78 °C, and then t-BuLi was added to the solution. This addition order is indispensable for the successful polymerization. Under the conditions shown in the table, the polymerization in pure toluene did not reach complete conversion, while that in pure dichloromethane afforded st-PMMA in 100% yield. The yield decreased monotonically with increasing toluene content. Though the rr content of the obtained polymer slightly decreased when dichloromethane was used, the syndiotacticity of the PMMA is still kept at 90%. The value is high enough for st-PMMA to exhibit its specific properties such as gelation in toluene and other aromatic solvents [16, 17].

Time dependence of the polymerization in dichloromethane was also examined as shown in Table 2. The polymerization for 1 h produced st-PMMA in 91% yield. First-order plots of the monomer consumption gave an apparent rate coefficient of polymerization of 3.5×10^{-2} L mol^{-1} s^{-1}, which is almost one order larger than that reported for the polymerization in toluene, 3.4×10^{-3} L mol^{-1} s^{-1} [4].

To confirm the living nature of the polymerization, the monomer-addition experiment was performed and the SEC traces of the pre-formed and final PMMAs are shown in Fig. 1, which demonstrates clear shift of the SEC peak without any

Table 1 Polymerization of MMA with $t\text{-}C_4H_9Li/(n\text{-}C_4H_9)_3Al$ (1/5) in toluene/CH_2Cl_2 at $-78\ °C$ for 2 h

Toluene/$CH_2Cl_2^a$	Yield (%)	M_n			M_w/M_n^b	Tacticity (%)^c			Initiator efficiency^d
		SEC	NMR	Calcd		mm	mr	rr	
0/10	100	5730	5870	5060	1.06	1	9	90	0.88
1/9	93.8	5710	5100	4750	1.07	0	10	90	0.83
5/5	72.9	5130	4770	3710	1.08	0	9	91	0.72
9/1	66.5	4250	3980	3330	1.08	0	8	92	0.78
10/0	59.3	4100	3680	3030	1.09	0	8	92	0.74

MMA 10 mmol, $t\text{-}C_4H_9Li$ 0.20 mmol, CH_2Cl_2 10 mL

[a] Mixed solvent (mL/mL)

[b] Determined by SEC (PMMA standards)

[c] Determined by ^1H NMR

[d] Calculated from the amount of $t\text{-}C_4H_9Li$ used and of the polymer molecule formed which was determined from the polymer yield and the M_n value

Table 2 Polymerization of MMA with $t\text{-}C_4H_9Li/(n\text{-}C_4H_9)_3Al$ (1/5) in CH_2Cl_2 at $-78\ °C$ for different polymerization time

Time (min)	Yield (%)	M_n			M_w/M_n^a	Tacticity (%)^b			Initiator efficiency^c
		SEC	NMR	Calcd		mm	mr	rr	
5	24	1640	1470	1270	1.12	1	9	90	0.77
10	34	2280	2190	1770	1.09	0	10	90	0.78
15	59	3430	3290	3010	1.07	1	9	90	0.88
30	74	4400	4270	3760	1.07	1	9	90	0.85
60	91	5440	5330	4610	1.06	0	10	90	0.85

MMA 10 mmol, $t\text{-}C_4H_9Li$ 0.20 mmol, CH_2Cl_2 10 mL

[a] Determined by SEC (PMMA standards)

[b] Determined by ^1H NMR

[c] Calculated from the amount of $t\text{-}C_4H_9Li$ used and of the polymer molecule formed which was determined from the polymer yield and the M_n value

tailing, confirming the living nature of the polymerization in dichloromethane, through the initiator efficiency is less than unity.

Based on these findings, preparation of high molar mass st-PMMA was attempted at varying monomer-to-initiator ratios (Table 3). In order to further enhance the rate of polymerization, the initial monomer concentration was set higher than those in the previous polymerizations (Tables 1, 2); the ratio of MMA and dichloromethane was 1–5 in volume. In all the cases examined, st-PMMAs with rr content of 90% and narrow molar mass distribution were obtained, though the M_n values are larger than those expected from the initial monomer-to-initiator ratio and the polymer yield. While st-PMMA with M_n of 32 K was obtained quantitatively within 24 h, the polymerizations at the initial monomer-to-initiator ratios of 500 and 2500 did not complete at 24 h. However, extension of the polymerization time to 48 h

Fig. 1 SEC curves of *st*-PMMAs obtained with *t*-C₄H₉Li/(*n*-C₄H₉)₃Al (1/5) in CH₂Cl₂ at −78 °C **a** before and **b** after second monomer addition (eluent THF, flow rate 0.8 mL min⁻¹, 40 °C). Polymerization conditions; MMA 10 mmol, *t*-C₄H₉Li 0.20 mmol, CH₂Cl₂ 10 mL, Second portion of MMA; 10 mmol
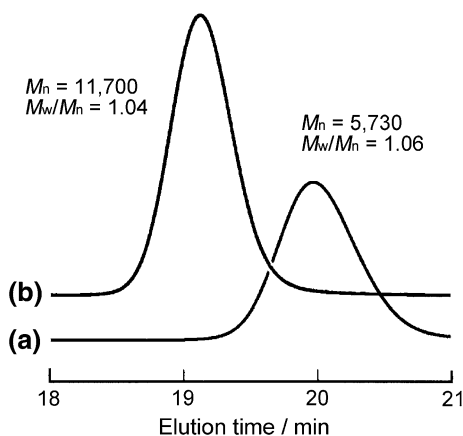
Table 3 Polymerization of high molar mass *st*-PMMA with *t*-C₄H₉Li/(*n*-C₄H₉)₃Al in CH₂Cl₂ at −78 °C for 24 h

$[M]_0/[I]_0^a$	Yield (%)	M_n		M_w/M_n^b	Tacticity (%)[c]			T_g (°C)
		Obsd[b]	Calcd		*mm*	*mr*	*rr*	
200[d]	100	32400	20100	1.03	0	10	90	–
500	89	69200	44600	1.03	0	10	90	129.7
2500[e]	63	270600[f]	157700	1.03[f]	1	9	90	131.7
2500[g]	100	345500[f]	250400	1.03[f]	0	10	90	132.4

MMA 50 mmol, CH₂Cl₂/[M]₀ = 5/1 (vol/vol)

[a] The initial ratio of monomer to initiator

[b] Determined by SEC (PMMA standards)

[c] Determined by ¹H NMR

[d] MMA 20 mmol

[e] (*n*-C₄H₉)₃Al 1.25 mmol

[f] Due to the existence of higher molar mass fraction over the exclusion limits of SEC in the sample, the M_n and M_w/M_n values are shown as approximate values
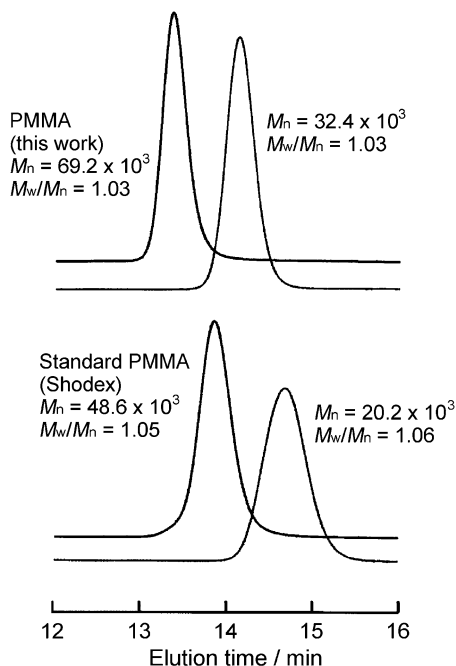
[g] (*n*-C₄H₉)₃Al 1.25 mmol, polymerization for 48 h

resulted in a quantitative yield and *st*-PMMA with M_n of 345 K was successfully synthesized by the present polymerization system. The narrow molar mass distribution of these *st*-PMMAs are well demonstrated by comparing their SEC curves with those of the commercial PMMA standard samples (Fig. 2).

As seen in Table 3, the glass transition temperature (T_g) of the *st*-PMMAs increased with increasing molar mass as expected from the well-known equation proposed by Fox and Flory [18];

$$T_g = T_{g\infty} - K/Mn \quad (T_{g\infty} : Tg \text{ for infinite molar mass polymer}).$$

Though the number of sample is limited, the $T_{g\infty}$ for *st*-PMMA with *rr* content of 90% was estimated to be 133.2 °C and the *K* value of 2.9×10^{-5} °C.

Fig. 2 SEC curves of *st*-PMMAs obtained in this work (see Table 3), and those of standard PMMA samples from Shodex (eluent THF, flow rate 0.8 mL min^{-1}, 40 °C)

PMMA (this work)
M_n = 69.2 x 10^3
M_w/M_n = 1.03

M_n = 32.4 x 10^3
M_w/M_n = 1.03

Standard PMMA (Shodex)
M_n = 48.6 x 10^3
M_w/M_n = 1.05

M_n = 20.2 x 10^3
M_w/M_n = 1.06

12   13   14   15   16
Elution time / min

In conclusion, use of dichloromethane as a solvent for anionic polymerization of MMA with t-C$_4$H$_9$Li/(n-C$_4$H$_9$)$_3$Al effectively enhances the rate of polymerization about ten times in comparison with the originally reported toluene medium probably due to the higher dielectric constant (9.1) than that of toluene (2.4), which facilitates the ionic reaction process, while maintaining high syndiotactic specificity of the polymerization. Thus, the present method provides a facile means to prepare relatively high molar mass *st*-PMMA from practically accessible sources.

Experimental

Materials

Dichloromethane (Nacalai Tesque) was distilled under nitrogen, stored over calcium dihydride (CaH$_2$), and vacuum distilled just before use. Toluene (Aldrich Co. Ltd., anhydrous grade) were mixed with a small amount of butyllithium and distilled under high vacuum just before use. MMA (Nacalai Tesque) was fractionally distilled and stored over CaH$_2$. The monomer was distilled over CaH$_2$ under reduced nitrogen pressure just before use. t-BuLi in pentane (Aldrich Co. Ltd.) was used as a heptane solution by replacing the solvent under high vacuum. The concentration was determined by titration with butan-2-ol and with o-phenanthroline as an indicator [19]. Tributylaluminum [(n-C$_4$H$_9$)$_3$Al, Kishida Chemical] was used for polymerization as a toluene solution.

Polymerizations

Polymerizations were carried out in glass ampoules, filled with dried nitrogen passed through Molecular Sieves 4A, cooled at –78 °C. In a typical polymerization experiment, $(n\text{-}C_4H_9)_3Al$ in toluene (1.0 mmol) was added to 10 mL of dichloromethane and the mixture was cooled at -78 °C. The initiator (t-BuLi 0.20 mmol) solution was added at the polymerization temperature, and the reaction was initiated by adding MMA (10 mmol) to the initiator solution and terminated by adding a small amount of methanol containing aqueous HCl at the polymerization temperature. The reaction mixture was poured into a large amount of hexane and the precipitate was collected by filtration, washed with hexane, dilute HCl (aq), and hexane, successively, and dried in vacuo at 40 °C.

Instruments

^{1}H NMR spectra were recorded in chloroform-d on a Varian Unity Inova 500 spectrometer. Chemical shifts in ^{1}H NMR spectra were referred to the signal due to CHCl$_3$ in the solvent (at 7.24 ppm). Molar mass and its distributions of the polymers were determined by size exclusion chromatography (SEC) using a Jasco model GPC-900 chromatograph equipped with two Polymer Laboratories SEC columns [PL-gel, Mixed C (300 mm × 7.5 mm)], using THF as an eluent at a flow rate of 0.8 mL min^{-1} and at a column temperature of 40 °C, and calibrated against standard PMMA samples (Shodex, MW: 1577100, 744900, 174100, 20200, 5700, 1850). T_g was determined on a SEIKO Instruments EXSTAR 6000 apparatus under nitrogen flow (100 mL min^{-1}) at a heating rate of 10 °C min^{-1}.

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