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# Preparation of highly isotactic and syndiotactic poly(methyl methacrylate) macromonomers having the same chemical structure and their polymerization

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## SUMMARY

Highly isotactic living poly(methyl methacrylate) (PMMA) anion prepared with t-$C_4H_9MgBr$ in toluene at -78°C reacted quantitatively with p-bromomethylstyrene (p-BMST) in the presence of hexamethylphosphoramide or 1,8-diazabicyclo[5.4.0]-undec-7-ene to give the PMMA macromonomer with narrow molecular weight distribution. Highly syndiotactic PMMA macromonomer was also prepared by the reaction of p-BMST and the living PMMA anion formed by t-$C_4H_9Li$-(n-$C_4H_9)_3Al$ (Al/Li=3) initiation in the presence of tetramethylethylenediamine. Radical polymerization and copolymerization of these macromonomers were studied in some detail. The results showed the higher reactivity of the isotactic PMMA macromonomer than the syndiotactic one.

## INTRODUCTION

Preparation of graft copolymers of desired structure and molecular weight is the most interesting and important for pure and applied polymer chemistry. We have studied the controlled graft copolymerization of vinyl monomers on the copolymers of divinylbenzenes and 1,1-diphenylethylene by anionic mechanism, and the properties and practical applications of the resultant graft copolymers (1,2). Many papers have been published on the preparation of tailored graft copolymers using macromonomers. However, little attention has been paid on the synthesis of stereoregular macromonomers and their polymerization or copolymerization. Highly syndiotactic poly(methyl methacrylate) (PMMA) macromonomer was prepared using m-vinylbenzylmagnesium chloride in tetrahydrofuran (THF) at low temperatures (3). It was reported that o-vinylbenzylmagnesium chloride gave an isotactic and a syndiotactic PMMA macromonomer in toluene and in THF, respectively, and that the former macromonomer was a little more reactive than the latter in radical polymerization and copolymerization (4). The only problem in the syntheses of these stereoregular PMMA macromonomers was that the molecular weight and its distribution (MWD) of the macromonomer could not be fully controlled in the polymerizations of MMA with these vinylbenzylmagnesium chlorides.

Recently, we succeeded in preparing highly isotactic (5,6) and highly syndiotactic (7) PMMAs with narrow MWD by t-$C_4H_9MgBr$ and t-$C_4H_9Li$-$R_3Al$ systems, respectively, in toluene at low temperatures. Both the polymerization systems were living and the molecular weights of the polymers could be controlled by changing the ratio of monomer to initiator. It was the purpose of this work to prepare the highly isotactic and syndiotactic PMMA macromonomers having the same chemical structure using these living polymerization systems and to study the reactivity of these stereoregular PMMA macromonomers in the radical polymerization and copolymerization.

## EXPERIMENTAL

### Materials

MMA was distilled fractionally, dried over calcium dihydride, and then distilled under high vacuum before use.

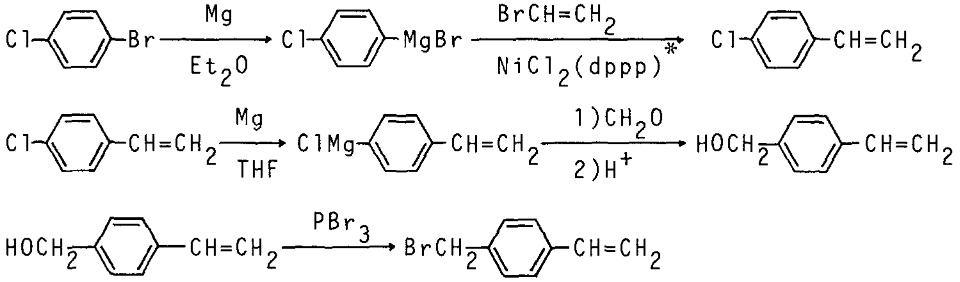
$t\text{-}C_4H_9MgBr$ was prepared from $t\text{-}C_4H_9Br$ and magnesium in dry diethyl ether.

$t\text{-}C_4H_9Li$ and $(n\text{-}C_4H_9)_3Al$ were obtained commercially.

$\alpha,\alpha'$-Azobisisobutyronitrile (AIBN) was purified by recrystalization from ethanol.

Toluene, purified in a usual manner and stored over sodium metal, was mixed with a small amount of $n\text{-}C_4H_9Li$ and then vacuum-distilled.

p-Bromomethylstyrene (p-BMST) was prepared according to the following scheme; bp. 75°C/0.7 mmHg (100.5°C/4 mmHg (8)).



* dppp=1,3-bis(diphenylphosphino)propane

p-Chloromethylstyrene (p-CMST) was prepared according to the literature (9); bp. 58°C/0.4 mmHg (58-62°C/0.4 mmHg (9)).

Hexamethylphosphoramide (HMPA), 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU), and tetramethylethylenediamine (TMEDA) were purified by fractional distillation.

Nitrogen was dried by passing through the column packed with Molecular Sieves 4A cooled at -78°C.

### Preparation of highly isotactic PMMA macromonomer

The reaction was carried out in a separable flask equipped with mechanical stirrer and filled with dry nitrogen. The polymerization of MMA was initiated by adding $t\text{-}C_4H_9MgBr$ solution to the monomer solution in toluene cooled at -78°C. After 24 hr, a toluene solution of p-BMST was added to the reaction mixture. After 1 hr stirring, a toluene solution of HMPA or DBU was added. The mixture was allowed to stand for 12 hr at the same temperature, and then for further 12 hr at 0°C to complete the end-capping reaction. The reaction mixture was poured into a large amount of hexane. The precipitated polymer was collected by filtration and washed with hexane. The obtained macromonomer was dissolved in benzene and the solution was centrifuged to remove insoluble materials. After repeated reprecipitation, the obtained polymer was dried in vacuo at 30°C for 12 hr.

**Preparation of highly syndiotactic PMMA macromonomer**

To a toluene solution of $(n\text{-}C_4H_9)_3Al$ cooled at -78°C, $t\text{-}C_4H_9Li$ was added slowly. Polymerization was initiated by adding MMA slowly to the mixture. After the completion of the polymerization, p-BMST and TMEDA was added successively to the mixture at an interval of one hour. The mixture was allowed to stand for 12 hr at -78°C, and then for further 12 hr at 0°C. The reaction product was poured into a large amount of hexane. The precipitated polymer was purified in a similar manner to the isotactic PMMA macromonomer.

**Polymerization and copolymerization of PMMA macromonomers**

The reactions were carried out in a glass ampoule under nitrogen. The reaction products were precipitated in hexane. The unchanged macromonomer was removed from the reaction product by reprecipitation from toluene solution to methanol.

**Measurement**

$^1H$ NMR spectra were recorded on a JNM-FX 100 or a JNM-GX 500 spectrometer (JEOL) using nitrobenzene-$d_5$ and toluene-$d_8$ as solvent at 110 and 60°C, respectively.

Number average molecular weights ($\bar{M}n$'s) were measured on a Hitachi 117 vapor pressure osmometer (VPO) in toluene at 60.0°C. The Mn's of macromonomers were also determined from the relative intensities of the $^1H$ NMR signals due to the $t\text{-}C_4H_9$- and $CH_3O$- groups. Gel permeation chromatography (GPC) was performed on a JASCO FLC-A10 chromatograph equipped with Shodex GPC columns A-80M (50 cm x 2) using THF as an eluent. The chromatograms were calibrated against standard polystyrene samples.

Intrinsic viscosities ($[\eta]$'s) were measured in toluene at 30.0°C using an Ubbelohde viscometer.

Glass transition temperature (Tg) measurements were carried out using a Rigaku Denki DSC-8230 differential scanning calorimeter.

## RESULTS AND DISCUSSION

**Preparation of highly isotactic PMMA macromonomer**

$t\text{-}C_4H_9MgBr$ prepared in diethyl ether polymerizes MMA in toluene at -78°C to give highly isotactic and living PMMA with narrow MWD (5,6). End-capping reaction of this highly isotactic PMMA anion was attempted at first using p-CMST with or without additives such as THF, TMEDA, HMPA, tetrakis(triphenylphosphine)palladium(0), and $NiCl_2$(dppp). While most of the reactions did not give any polymer molecule having vinyl function, addition of HMPA brought about a slight incorporation of vinylbenzyl group into the PMMA chain. However, the yield was less than 5 %.

Anderson et al. reported the successful end-capping of polymethacrylate anion with lithium counter ion by p-BMST in THF (10). Higher electrophilicity of the bromide than the chloride appeared to overcome reduced reactivity of the PMMA anion caused by the ester function. Accordingly, p-BMST was employed as an end-capping reagent for the living isotactic PMMA anion formed by $t\text{-}C_4H_9MgBr$ initiation. The results are shown in Table 1. In contrast to the Anderson's case, p-BMST alone did not react with the isotactic PMMA anion. In order to increase the reactivity of the anion, HMPA was added to the polymerization mixture containing p-BMST. Further details are described in the experimental section. Figure 1 shows the $^1H$ NMR spectrum of the resultant macromonomer. The signals due to vinyl methylene and methine protons at 5.02-5.56 and 6.52-6.57 ppm, respectively, as well as those for phenyl protons at 6.99-7.22 ppm are clearly observed. The benzyl methylene protons resonate at 2.51-2.94 ppm. The peak at 0.81 ppm was assigned to $t\text{-}C_4H_9$- group originated from the initiator. It was ascertained, by quantitative NMR analysis in combination with deuterated monomer method, that the $t\text{-}C_4H_9$- group

Table 1
Preparation of Isotactic PMMA Macromonomer with Narrow MWD

| Preparation of living PMMA[a] | | | Coupling reaction[b] | | | | |
|---|---|---|---|---|---|---|---|
| MMA (mmol) | Toluene (ml) | $\frac{[MMA]}{[t\text{-}C_4H_9MgBr]}$ | Deactivator | (mmol) | Additive | (mmol) | $CH_2=CH$- per chain[c] |
| 10 | 5 | 20 | p-CMST | 2.5 | HMPA | 1 | < 0.05 |
| 10 | 5 | 20 | p-BMST | 2.5 | none | - | 0 |
| 150 | 70 | 20 | p-BMST | 38 | HMPA | 23 | 0.97 |
| 100 | 100 | 23 | p-BMST | 22 | DBU | 13 | 0.96 |

a) Temp. -78°C, time 24 hr. b) Reaction time: 12 hr at -78°C and further 12 hr at 0°C. c) Number of vinyl group per chain determined by $^1H$ NMR.

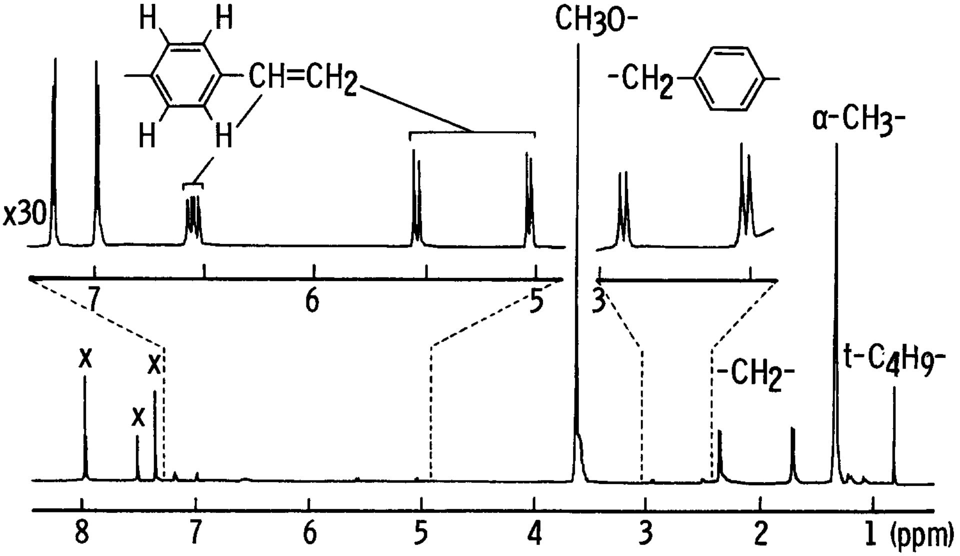


Figure 1. $^1H$ NMR spectrum of isotactic PMMA macromonomer prepared through the end-capping reaction of living PMMA with p-BMST (500 MHz, $C_6D_5NO_2$, 110°C, HMDS). Signals labelled X are due to the solvent.
Preparation of living PMMA: MMA 150 mmol, toluene 70 ml, $t\text{-}C_4H_9MgBr$ 7.5 mmol, temp. -78°C, time 24 hr. Coupling reaction: p-BMST 38 mmol, HMPA 23 mmol, reaction time 12 hr at -78°C and further 12 hr at 0°C.

attached to the α-end of the PMMA chain amounted unity per chain (6). The M̄n of the PMMA, estimated from the relative intensities of the $^1H$ NMR signals due to t-$C_4H_9$- and $CH_3O$-groups, agreed well with that determined by VPO (Table 2). Therefore, the number of styrene group introduced at the ω-end was determined from the intensity measurement of the $^1H$ NMR signals due to the t-$C_4H_9$- group and the vinyl group. The measurements indicated that most of the macromonomer molecules contained one styrene group at the ω-end (Table 1). DBU was also found to be an effective additive for the end-capping reaction of the PMMA anion with p-BMST.

## Preparation of highly syndiotactic PMMA macromonomer

In the course of searching the syndiotactic PMMA having the same chemical structure as the isotactic PMMA obtained by t-$C_4H_9MgBr$, we found that t-$C_4H_9Li$-$R_3Al$ system (Al/Li≥3) gave highly syndiotactic and living PMMA with narrow MWD in toluene at low temperatures. The polymer molecules were found to contain one t-$C_4H_9$- group at the α-end and one methine proton at the ω-end and no alkyl group originated from $R_3Al$ in the chain (7).

The coupling reaction of the syndiotactic living PMMA with p-BMST was examined similarly to the case of the isotactic PMMA macromonomer. In the presence of TMEDA, the end-capping reaction proceeded quantitatively and a highly

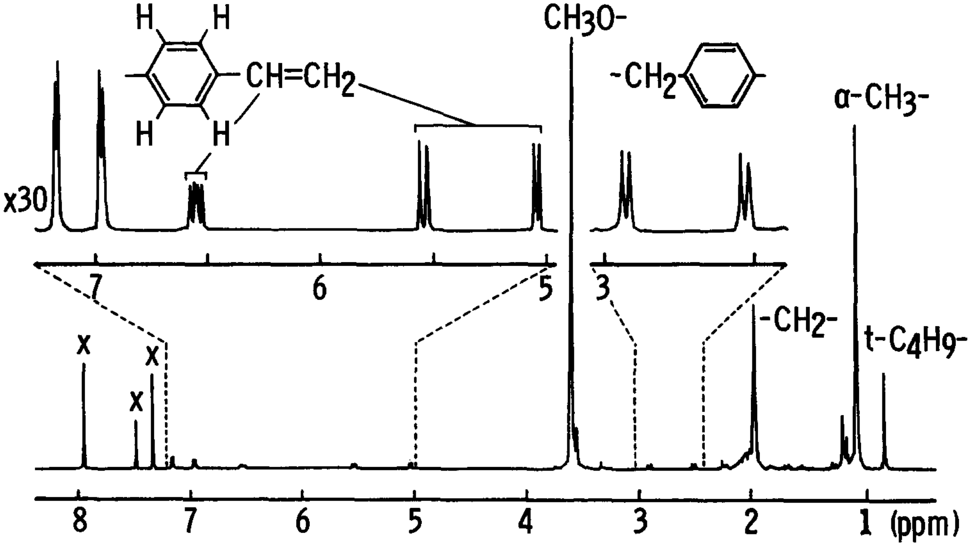
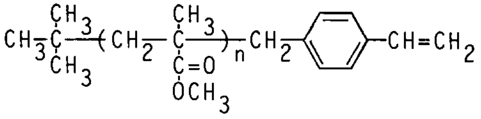


Figure 2. $^1H$ NMR spectrum of syndiotactic PMMA macromonomer prepared through the end-capping reaction of living PMMA with p-BMST (500 MHz, $C_6D_5NO_2$, 110°C, HMDS). Signals labelled X are due to the solvent. Preparation of living PMMA: MMA 100 mmol, toluene 100 ml, t-$C_4H_9Li$ 5 mmol, $(n\text{-}C_4H_9)_3Al$ 15 mmol, temp. -78°C, time 24 hr. Coupling reaction: p-BMST 15 mmol, TMEDA 15 mmol, reaction time 12 hr at -78°C and further 12 hr at 0°C.

syndiotactic PMMA macromonomer was obtained. The $^1H$ NMR spectrum of this macromonomer is shown in Figure 2.

Both the isotactic and the syndiotactic PMMA macromonomers thus obtained have the same chemical structure as shown below.



## Radical polymerization and copolymerization of highly isotactic and syndiotactic PMMA macromonomers having the same chemical structure

The results of characterization of the PMMA macromonomers used in the following experiments are summarized in Table 2.

Polymerization of isotactic ($\bar{M}n$=2900) or syndiotactic ($\bar{M}n$=2600) PMMA macromonomer with AIBN in toluene-$d_8$ at 60°C was monitored in an NMR sample tube by using $^1H$ NMR spectroscopy. The conversion of the macromonomer was determined from the relative intensity of vinyl methylene proton signals to $t$-$C_4H_9$- signal.

The plots of $-\ln([M]/[M]_0)$ versus polymerization time clearly indicate that the reactivity of the isotactic PMMA macromonomer is slightly but meaningfully higher than that of the syndiotactic PMMA macromonomer (Figure 3). Higher reactivity of the isotactic PMMA macromonomer may be caused by the higher segmental mobility of isotactic PMMA chain than that of syndiotactic one, which was evidenced from $^{13}C$-$T_1$ measurement (11).

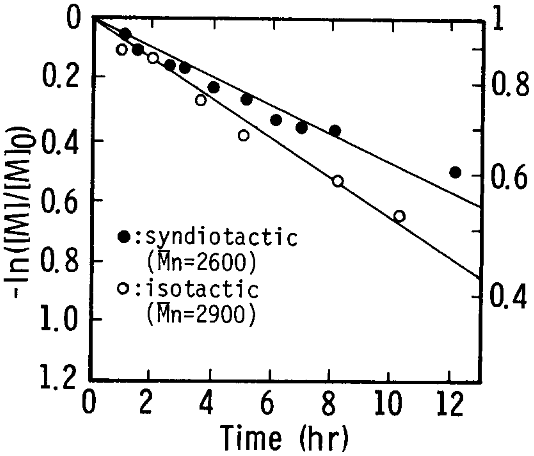


Figure 3. Effect of tacticity on the polymerization of PMMA macromonomer with AIBN in toluene-$d_8$ at 60°C. $[M]_0$=0.05 mol/l, $[M]_0/[I]_0$=20 mol/mol.

The isotactic ($\bar{M}n$=2580) and syndiotactic ($\bar{M}n$=2600) macromonomers were

Table 2
Characterization of Highly Isotactic and Syndiotactic PMMA Macromonomers Having the Same Chemical Structure

| Tacticity (%) | | | $\bar{M}n$ | | $\bar{M}w/\bar{M}n^a$ | $CH_2$=CH- per chain$^b$ |
|---|---|---|---|---|---|---|
| mm | mr | rr | NMR | VPO | | |
| 95 | 4 | 1 | 2580 | 2520 | 1.11 | 0.97 |
| 95 | 4 | 1 | 2900 | 2860 | 1.12 | 0.96 |
| 1 | 11 | 88 | 2600 | 2600 | 1.10 | 0.96 |

a) Determined by GPC. b) Determined by $^1H$ NMR.

copolymerized with styrene in toluene at 60°C using AIBN as an initiator. Both the starting macromonomers were soluble in methanol and could be easily removed from the reaction mixtures by reprecipitation from toluene solution into methanol. The GPC curves of the resulting copolymer measured with RI and UV detectors were very similar to each other, indicating that the products were actually graft copolymers and not mixtures of polystyrene and poly(PMMA macromonomer). From the intensity measurements of the $^1$H NMR signals due to the t-$C_4H_9$- group in the macromonomer unit and the phenyl groups, the compositions of the copolymers could be accurately determined over a wide range of copolymer composition. Figure 4 shows the copolymer composition curves and monomer reactivity ratios. These results indicate that the isotactic macromonomer is more reactive than the syndiotactic one as in the case of their homopolymerizations.

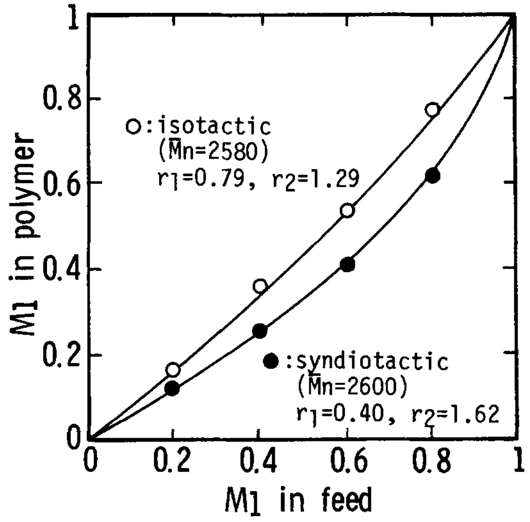


Figure 4. Copolymer composition curves for radical copolymerization of PMMA macromonomer ($M_1$) with styrene ($M_2$) by AIBN in toluene at 60°C.
$[M_1]_0$=0.07 mol/l,
$[M_1+M_2]_0/[I]_0$=100 mol/mol.

**Characteristics of the poly(PMMA macromonomer)**

Table 3 shows the [η]'s and Tg's of the isotactic and syndiotactic PMMA macromonomers, the poly(PMMA macromonomer)s

Table 3
Characteristics of Isotactic (iso-) and Syndiotactic (syn-) PMMAs with Various Structures

| | PMMA | $\bar{M}n$ VPO | $\bar{M}n$ GPC | $\bar{M}w/\bar{M}n^a$ | $[\eta]^b$ (dl/g) | $k'^c$ | Tg (°C) |
|---|---|---|---|---|---|---|---|
| | Macromonomer | 2520 | 2350 | 1.11 | 0.005 | - | 21 |
| iso- | Polymacromonomer | 75000 | 43700 | 1.45 | 0.090 | 1.70 | 44 |
| | PMMA$^d$ | 56500 | 61600 | 1.24 | 0.393 | 0.43 | 50 |
| | Macromonomer | 2600 | 2120 | 1.10 | 0.005 | - | 94 |
| syn- | Polymacromonomer | 61100 | 31100 | 1.26 | 0.074 | 1.48 | 114 |
| | PMMA$^e$ | 53900 | 59600 | 1.19 | 0.260 | 0.59 | 124 |

a) Determined by GPC. b) Measured in toluene at 30.0°C. c) Huggins' constant. d) Tacticity (%) mm:mr:rr=97:3:0. e) Tacticity (%) mm:mr:rr=0:8:92.

derived therefrom, and isotactic and syndiotactic PMMAs with similar molecular weights to the corresponding poly(PMMA macromonomer)s. The Tg's of the poly(PMMA macromonomer)s lay between those of the starting PMMA macromonomers and the linear PMMAs. The [η]'s of the polymacromonomers were lower than those of the corresponding linear PMMAs with the similar molecular weight, and the Huggins' constants were larger than those of the linear PMMAs. Although the conformity does not exist in the literature as regards the influence of branching on the viscosity, most results indicate that the increased value of Huggins' constant is obtained with a higher degree of branching (12). So the results obtained here indicate that the polymacromonomers obtained are actually the comblike polymer and the molecules have smaller volume in solution than the linear PMMA.

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