

STEREOREGULARITY OF POLY (METHYL METHACRYLATE) OBTAINED WITH CHIRAL ANIONIC COMPLEX INITIATOR*

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ABSTRACT

The stereoregular polymerization of methyl methacrylate (MMA) have been investigated with chiral anionic complex initiator $[\text{F}(\text{Li}(-)\text{SP})]$ in toluene, THF and toluene/THF $[1/1(\text{v/v})]$.

The tacticities of PMMAs obtained in the three solvents have been found to be mainly a syndiotactic triads (s-PMMA) with content of 72.3, 67.7 and 71.4%, respectively.

INTRODUCTION

The stereospecific polymerization of methyl methacrylate (MMA) have been extensively studied by Fox^[1], Glusker^[2], Yuki^[3], Hatada^[4] and Yasuda^[5]. The tacticities of PMMA obtained at low temperature in polar or nonpolar solvent with anionic initiators have been characterized by using $^1\text{H-NMR}$ ^[3], IR^[6] techniques etc. Generally speaking, the influence of polymerization solvent are very important in anionic polymerization. For example, an isotactic and a syndiotactic PMMA are mainly formed in a nonpolar (toluene) and polar (THF) solvent with $n\text{-BuLi}$ ^[3] or 9-fluorenyllithium ($\text{F}(\text{Li})$)⁷, respectively. Recently we found that the PMMAs obtained in toluene, THF and toluene/THF $[1/1(\text{v/v})]$ mixture at -78°C with chiral anionic complex initiator $[\text{F}(\text{Li}(-)\text{SP})]$ (Scheme 1) possessed syndiotacticities (s-PMMA) mainly. The characterization of properties and microstructures of s-PMMA has been carried out with $^1\text{H-NMR}$, IR and WAXS.

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EXPERIMENTAL

Materials

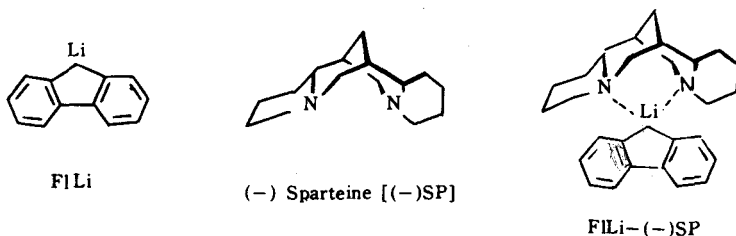
Solvents: Toluene was purified in the usual manner. It was refluxed and distilled with sodium wire before use. THF was refluxed and distilled over sodium wire under nitrogen atmosphere.

Monomer: Methyl methacrylate from commercial product was treated with calcium hydride and redistilled over calcium hydride.

Initiator: *n*-BuLi was synthesized in hexane by our laboratory. Fluorene (F1) (Aldrich Chem. Co) was commercially available. Chiral ligand (-) Sparteine [(-)SP] (Sigma Co.) was dried over calcium hydride and distilled under reduced pressure and the fraction of 102°C/133.3Pa was collected.

Fluorene and *n*-BuLi (1/1 mole/mole) were mixed in toluene at room temperature to form a FLiLi solution as anionic initiator and (-) sparteine (1:2 mole/l mole to [Li]) was added into the above mentioned solution to produce a chiral anionic complex initiator [FLi-(-)SP] solution.

Scheme 1



Polymerization

The polymerization was carried out in a dried glass ampule under nitrogen. The ampule was evacuated on a vacuum line and flushed with dry nitrogen. After this procedure was repeated three times the monomer (MMA) and solvent (toluene or THF) were added with a hypodermic syringe. It was cooled to the temperature of polymerization (-78°C) and initiator solution was then added with a syringe into the monomer solution in the ampule. The reaction was terminated by the addition of a few drops of methanol. The polymer was precipitated in a large amount of petroleum ether ($30-60^{\circ}\text{C}$) and separated by centrifugation.

Measurement

^1H -NMR spectrum was taken on FX100 (100MHz) instrument. FT-IR spectrum was recorded on BRUKER-IFS-113v IR spectrometer. X-ray diffraction patterns (WAXS) were obtained on Rigaku D/max-3B diffractometer with 0.154nm of wave length of CuK α radiation.

RESULTS AND DISCUSSION

Table 1 showed the results of the polymerization of MMA with various initiators.

From the tacticity triads data of PMMAs which were prepared with radical, anionic and chiral anionic complex initiator under various conditions it was showed that the polymerization by *n*-BuLi and FILi gave mainly isotactic PMMA in toluene and syndiotactic product in THF. But only syndiotactic PMMA were chiefly obtained by chiral anionic initiator [FILi(-)SP] in toluene, THF and toluene/THF [1/1 (v/v)]. The PMMAs obtained have been characterized by using various techniques.

Table 1 Stereoregularity of poly(methyl methacrylate) (PMMA) obtained from various initiators and solvents^a

Initiators	Solvent	Temperature (°C)	Tacticities (%) ^b			<i>l</i> (mm or rr) ^c
			mm	mr	rr	
AIBN ^d	Toluene	60	6	36	58	4.22
<i>n</i> -BuLi ^d	Toluene	-78	72	17	11	9.47
<i>n</i> -BuLi	Toluene	-78	72	18	10	9.00
<i>n</i> -BuLi ^d	THF	-78	6	38	56	3.95
<i>n</i> -BuLi	THF	-78	19.5	23.7	56.8	5.79
FILi ^e	Toluene	-60	mainly isotacticity			
FILi	Toluene	-78	86.0	6.0	8.0	29.6
FILi ^e	THF	-60	mainly syndiotacticity			
FILi(-)SP	Toluene	-78	5.5	22.2	72.3	7.51
FILi(-)SP	THF	-78	8.1	24.2	67.7	6.59
FILi(-)SP	Toluene/THF [1/1 (v/v)]	-78	6.5	22.1	71.4	7.46

a Polymerization conditions: [MMA]/[Li] (mol) = 20, solvent/monomer = 20 (ml/g)

b mm, mr and rr represent Isotactic, heterotactic and syndiotactic triad, respectively

c *l* is the mean sequence length. $l(\text{mm or rr}) = [2(\text{mm or mr}) + \text{rr}] / \text{mr}$

d Data from Ref. 3

e Data from Ref. 6

$^1\text{H-NMR}$ spectrum is an efficient method to measure the tacticity of PMMA^[8,9]. The chemical shift of the protons of $\alpha\text{-CH}_3$ group are 1.20, 1.04 and 0.91ppm corresponding to isotactic(i or mm), heterotactic(h or mr) and syndiotactic(s or rr) triad of PMMA. The chemical shift differences among these three peaks are sufficiently large and the intensity measurement can be done accurately.

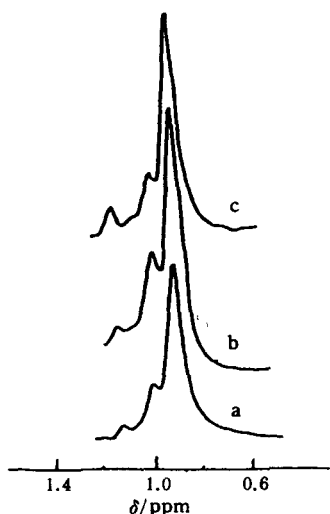


Fig. 1 The chemical shifts of $\alpha\text{-CH}_3$ group in $^1\text{H-NMR}$ spectra of PMMA obtained by chiral initiator in the solvents.

a) Toluene; b) Toluene/THF; c) THF

$\text{CH}_2\text{—}$), 966 ($\alpha\text{-CH}_3$) and 749cm^{-1} ($\text{—CH}_2\text{—}$ coupled with skeletal stretching) — stereoregularity sensitive frequency of s-PMMA. In general, the difference in IR spectrum is very small based on their relative content of i- and s-PMMA.

X-ray diffraction patterns of powder samples i- and s-PMMA have been shown in Fig. 3. From Fig. 3(a) the i-PMMA with high crystallinity gave the most intense diffraction peak $2\theta = 8.8, 14.5$ and 17.2 degree. The i-PMMA sample obtained by n-BuLi in toluene, precipitated from petroleum ether ($30\text{—}60^\circ\text{C}$) and dried in vacuum at 50°C for 24h has lower crystallinity and seems a completely amorphous i-PMMA [Fig. 3(b)]^[11]. The s-PMMA sample obtained by FLi(-)SP in toluene gave X-ray diffraction pattern with

Infrared spectrum was used by Baumann et al.^[10] to measure the tacticities of PMMA. The IR spectra of i-(mm-) and s-(rr-) PMMA were discussed in detail by Nagai^[6]. Fig. 2. explained that FT-IR spectrum of isotactic PMMA (i-PMMA) [Fig. 2(a)] and syndiotactic PMMA (s-PMMA) [Fig. 2(b)] were mainly obtained in toluene with FLi and FLi(-)SP initiators, respectively.

In Fig. 2(a) characteristic frequencies of i-PMMA were shown to be 1263 (C—C—O , coupled with C—O), 989 (C—O—C coupled with $\text{CH}_3\text{—O}$) and 759cm^{-1} (skeletal stretching coupled with $\text{—CH}_2\text{—}$) — stereoregularity sensitive frequency of i-PMMA. In Fig. 2(b) s-PMMA with characteristic frequencies 1450 ($\text{—CH}_2\text{—}$), 966 ($\alpha\text{-CH}_3$) and 749cm^{-1} ($\text{—CH}_2\text{—}$ coupled with skeletal stretching) — stereoregularity sensitive frequency of s-PMMA. In general,

very low crystallinity with weak diffraction peaks $2\theta=13.5$ and 18.9 degree [Fig. 3(e)] which is comparable with the result reported by Spevacek^[12] [Fig. 3(d)] (weak diffraction peaks $2\theta=13.5$ and 18.9 degrees).

According to anionic polymerization theory^[13,14], in general, organic alkali metals easily produce association ion pairs in a nonpolar solvent as well as free ions in a polar one as solvation. Therefore, the solvent has an important effect on anionic polymerization. The PMMA obtained by chiral anionic initiator [FILi-(-)SP] almost are not effected by the solvent as polar, nonpolar and their mixture are used in polymerization. It seems that the chiral anionic initiator complexes should play a special role to control the conformation during polymerization of MMA. The coordination of chiral ligand (-)SP with chair conformation with FILi could form an asymmetrically chiral cavity — chiral active center^[15,16]. The monomer should enter into the active center laid to the chiral cavity to be initiated, propagated by regular manner to produce the PMMA with syndiotactic conformation.

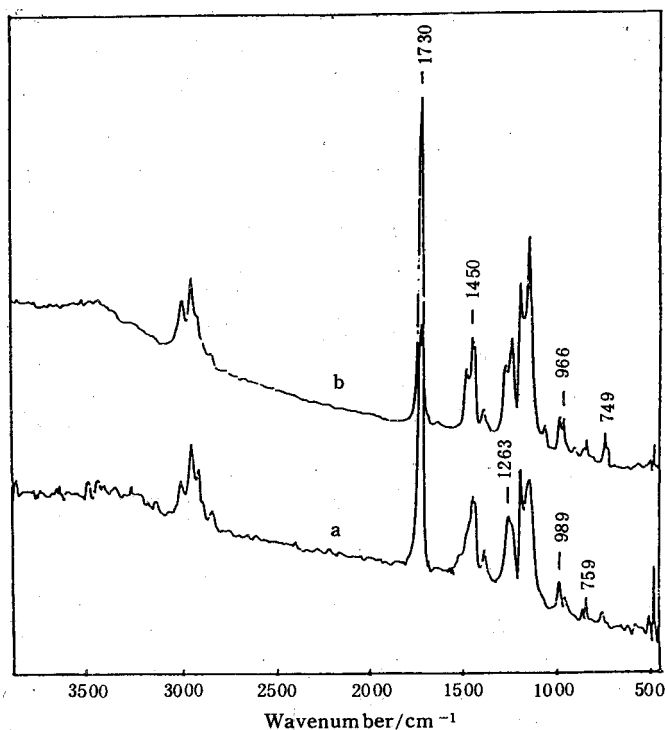


Fig. 2 FT-IR spectra of mainly isotactic and mainly syndiotactic PMMA.
 (a) by FILi in toluene at -78°C
 (b) by FILi-(-)SP in toluene at -78°C

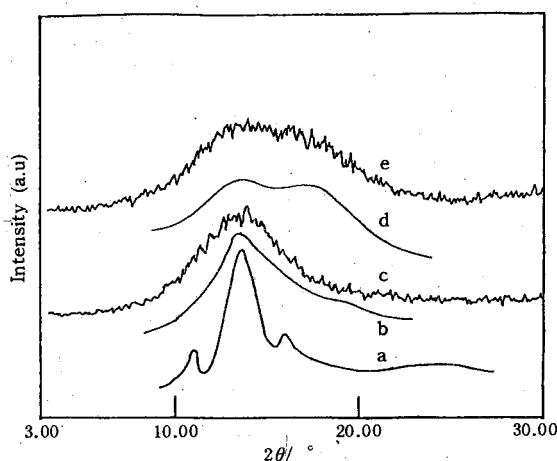


Fig. 3 X-ray powder pattern of poly(methyl methacrylate)s with stereoregularity.
 (a) Crystalline i-PMMA from Ref[11]; (b) Non-crystalline i-PMMA from Ref. [11];
 (c) Non-crystalline i-PMMA from FILi, toluene; (d) Amorphous s-PMMA from Ref[12];
 (e) Amorphous s-PMMA from FILi-(-)SP

Keyword:

PMMA; Stereoregulatory; Syndiotactic triad; Chiral anionic initiator

REFERENCES

- [1] Fox, T. G.; Goode, W. E.; Gratch, S., et al., *J. Polym. Sci.*, **1958**, 31, 173.
- [2] Glusker, D. J. and Evans, R. A. *J. Am. Chem. Soc.*, **1964**, 86, 187.
- [3] Yuki, H.; Hatada, K.; Ohta, K., et al., *Macromol. Sci. Chem.*, **1975**, A9 (6), 983.
- [4] Kitayama, T.; Shinozaki, T.; Masuda, E., et al., *Polym. Bull.*, **1988**, 20, 505.
- [5] Yasuda, H.; Yamamoto, H.; Yokata, K., et al., *J. Am. Chem. Soc.*, **1992**, 114 (12), 4908.
- [6] Nagai, H., *J. Appl. Polym. Sci.*, **1963**, 7, 1697.
- [7] Goode, W. E.; Owens, F. H.; Fellmann, R. P., et al., *J. Polym. Sci.*, **1960**, 46, 317.
- [8] Bovey, F. A. and Tiers, G. V. D., *J. Polym. Sci.*, **1960**, 44, 173.
- [9] Johnsen, U., *Kolloid und Polymer*, **1966**, 168, 160.
- [10] Baumann, U.; Schreiber, H. and Tessmar, H., *Makromol. Chem.*, **1960**, 36, 81.
- [11] Kusy, R. P., *J. Polym. Sci. Polym. Chem. Ed.*, **1976**, 14, 1527.
- [12] Spevacek, J.; Schusider, B.; Dybal, J., et al., *J. Polym. Sci., Polym. Phys. Ed.*, **1984**, 22, 617.
- [13] West, P. and Waack, R., *J. Am. Chem. Soc.*, **1967**, 89, 4395.
- [14] Szwarc, M., "Living Polymers and Mechanism of Anionic Polymerization" Berlin, Springer-Verlag, **1983** (Advances in Polymer Science, 49).
- [15] Okamoto, Y.; Suzuki, K.; Kitayama, T., et al., *J. Am. Chem. Soc.*, **1982**, 104, 4618.
- [16] Yu, B.; Lin, X. C.; Ding, M. X., et al., *Science Bulletin* (in Chinese) **1992**, 37 (22), 2051.