

Tacticity of Poly(methyl methacrylate) Obtained by Slow-Growth Polymerization Using *n*-BuLi Catalyst

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About twenty five years ago Schildknecht and his coworkers studied a "polyphase" or "proliferous" polymerization of vinyl ether. There the catalyst $\text{BF}_3 \cdot \text{OEt}_2$ was present as a separate liquid phase and the polymer slowly grew as a solid phase around the catalyst. The polymer obtained has a high degree of chain regularity, which was recognized later as isotacticity, and crystallinity.¹

In this work we studied the anionic polymerization of methyl methacrylate in a similar manner and obtained a polymer having a higher isotacticity than that of the polymer prepared by ordinary methods.

The polymerizations were carried out as follows.

Procedure A: In a 30-ml glass ampoule filled with dry nitrogen was placed a solution of 1 g of methyl methacrylate in 10 ml of toluene. The solution was cooled to -78°C in a Dry Ice—acetone bath and 0.5 mmol of *n*-BuLi in 1 ml of *n*-heptane was added slowly so as to be present on the monomer solution as a separate liquid phase. Then the ampoule was sealed off and allowed to stand at -78°C . The polymer slowly grew downwards from the interface between the solutions of the *n*-BuLi and the monomer. After 18 days, when the front edge of the polymer mass reached the bottom, the reaction mixture was cooled to the temperature of liquid nitrogen and the ampoule was carefully broken. The cooled reaction mass thus obtained was quickly cut into four pieces, which were specified I, II, III, and IV from top to

bottom, and each portion was transferred to a home blender containing a large amount of methanol. The blender was turned to high speed for about 30 sec and the mixture was allowed to stand overnight at room temperature. The precipitated polymer was collected by filtration, washed with methanol, and dried *in vacuo* at about 50°C . The filtrate and the washings were combined and the combined solution was concentrated to dryness under reduced nitrogen pressure. The oligomeric product of methyl methacrylate thus obtained was redissolved in benzene and was freeze-dried. *Procedure B:* The *n*-BuLi catalyst was added to the monomer solution cooled at -78°C with stirring under nitrogen pressure. Then the ampoule was sealed off and was allowed to stand at -78°C . After 24 hr the reaction mixture was quickly transferred to the blender containing a large amount of methanol, and the mixture was treated in the same way as in procedure A.

The PMR spectra of the polymer and the oligomer of methyl methacrylate were taken on the 10-w/v % CDCl_3 solution at 55°C using a JEOL 100 MHz spectrometer (JNM-MH-100).

The results of the polymerization are summarized in Table I. The isotacticity and the molecular weight of the polymer prepared by the slow-growth procedure (A) were considerably higher than those of the polymer obtained by the ordinary procedure (B). The molecular weights of the polymer A increased in order of the portions: $\text{I} < \text{II} < \text{III} < \text{IV}$.

Table I. Polymerization of methyl methacrylate in toluene at -78°C by *n*-BuLi^a

| Polymer | | Yield, % | Tacticity, % | | | $\bar{M}_v \times 10^{-5b}$ |
|----------------|-----|----------|--------------|------|------|-----------------------------|
| Procedure | | | I | H | S | |
| A | I | 11.6 | 84.1 | 11.5 | 4.4 | 3.1 |
| | II | 21.3 | 83.5 | 10.9 | 5.6 | 14.6 |
| | III | 26.7 | 81.2 | 12.4 | 6.4 | 17.6 |
| | IV | 21.9 | 84.4 | 9.9 | 5.7 | 18.1 |
| B ^c | | 65.3 | 68.0 | 19.2 | 12.8 | 1.9 |
| Oligomer | | Yield, % | Tacticity, % | | | \bar{M}_n^d |
| Procedure | | | I | H | S | |
| A | I | 3.7 | 71.5 | 16.4 | 12.1 | 960 |
| | II | 3.1 | 70.9 | 14.7 | 14.4 | 889 |
| | III | 1.0 | 69.3 | 15.8 | 14.9 | 667 |
| | IV | 7.2 | 70.2 | 17.0 | 12.8 | 897 |
| B ^c | | 33.8 | 63.8 | 22.6 | 13.6 | 1329 |

^a MMA, 10 mmol; toluene, 10 ml; *n*-BuLi, 0.5 mmol in 1 ml of *n*-heptane; time, 429 hr.

^b Calculated according to $[\eta] = 7.0 \times 10^{-5} \bar{M}_v^{0.71}$. The intrinsic viscosity was measured on the toluene solution at $30.0 \pm 0.03^{\circ}\text{C}$.

^c Time, 24 hr.

^d Determined by using a vapor pressure osmometer (Mechrolab Model 301 A).

Each portion contained an oligomer as shown in Table I, although their total amount was smaller than that of the oligomer obtained by procedure B. The structure of each oligomer was found to be very similar by ¹H- and ¹³C-NMR spectroscopy to that of the corresponding methanol-insoluble high polymer.² The isotacticity of the oligomers A was higher than that of oligomer B.

Polymerizations were similarly carried out in tetrahydrofuran at -78°C by *n*-BuLi. In this case the reaction mass produced by the slow-growth polymerization (C) was cut into two portions. The results are given in Table II. In tetrahydrofuran the polymer obtained by the usual method (D) has a predominantly syndiotactic structure. In procedure C the isotacticity of the polymer increased in association with the decrease in the syndiotacticity, and, consequent-

Table II. Polymerization of methyl methacrylate in tetrahydrofuran at -78°C by *n*-BuLi^a

| Polymer | | Yield, % | Tacticity, % | | | $\bar{M}_v \times 10^{-5}$ |
|----------------|----|----------|--------------|------|------|----------------------------|
| Procedure | | | I | H | S | |
| C | I | 34.3 | 20.3 | 46.2 | 33.5 | 1.12 |
| | II | 15.7 | 18.4 | 51.2 | 30.4 | 0.75 |
| D ^b | | 77.6 | 9.3 | 38.2 | 52.2 | 1.65 |
| Oligomer | | Yield, % | Tacticity, % | | | \bar{M}_n |
| Procedure | | | I | H | S | |
| C | I | 5.4 | 35.6 | 35.5 | 28.9 | 787 |
| | II | 8.0 | 32.3 | 33.8 | 33.9 | 742 |
| D ^b | | 17.3 | 12.7 | 38.4 | 48.9 | 935 |

^a MMA, 10 mmol; THF, 10 ml; *n*-BuLi 0.5 mmol in 1 ml of *n*-heptane; time, 600 hr.

^b Time, 24 hr.

ly, a poly(methyl methacrylate) having a nearly random configuration, where the proportion of I:H:S was close to 1:2:1, was obtained. Only a few studies have been reported on poly(methyl methacrylate) having a random configuration.^{3,4}

Polymers having higher isotacticity were also obtained by the slow-growth polymerizations of methyl α -ethylacrylate and methyl α -phenylacrylate in toluene at -78°C . For the anionic polymerization of methacrylate by *n*-BuLi in a nonpolar solvent it is postulated that the growing chain is in a helical conformation, which results in the formation of an isotactic polymer chain.^{5,6} The increased occurrence of isotactic placement in the slow-growth polymerization may be due partly to the slow growth of the polymer mass, which would favor the helical growth of the propagating chain. It must be noted however that the reaction conditions, such as the local concentrations of the active polymer chain and the monomer, were different from those in an ordinary homogeneous reaction mixture. The complete explanation should be found after further research.

Tacticity of PMMA Obtained by Slow-Growth Polymn.

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