Syndiotactic Poly(Methyl Methacrylate)
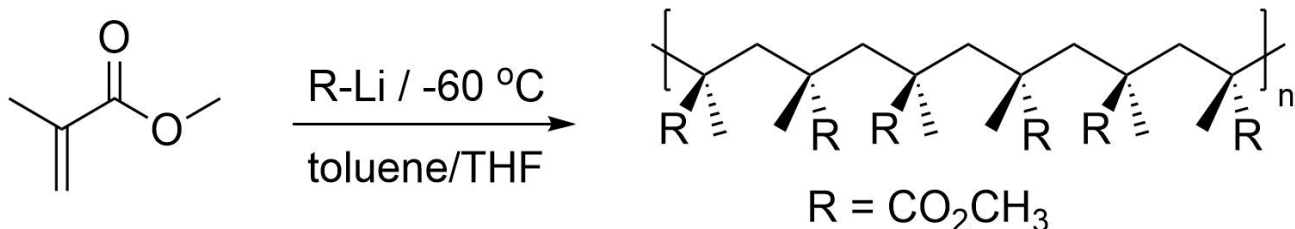
Submitted by: R. A. Galluccio and D. L. Glusker[1]
Checked by: Y. Okamoto and H. Yuki[2]

R-Li / -60 °C
toluene/THF

R = CO$_2$CH$_3$

1. Procedure (Note 1)

A 500 mL, three-necked, round-bottomed flask is equipped through the use of Y-tubes with a mechanical stirrer, gas inlet and outlet, thermometer (Note 2), and a rubber serum cap. The gas outlet is connected with gum rubber tubing to a large bubbler filled with mineral oil. After thorough flaming of the apparatus in a stream of helium, 260 mL of toluene (Note 3) is added through the serum cap with a syringe equipped with a stopcock and needle. This is followed by 22.7 mL of THF (Note 4) and 7.26 mL of 0.207N 9-fluorenyllithium solution (1.5 mmol) in THF (Note 5), added in the same fashion. The solution is then cooled with a dry ice-acetone bath to -60° with care being taken to provide sufficient helium flow during the cooling period to prevent air being sucked into the apparatus. The reaction is started by injecting 10 mL (94 mmol) of methyl methacrylate (Note 6) as rapidly as possible. The overall reaction mixture contains 10% of THF by volume, and the monomer to initiator mole ratio is 62.7. Except for an initial temperature rise to -58° when the monomer is added, the reaction temperature is kept at -60 ± 0.5° for 1 h (Note 7). The reaction is then terminated by the addition of 10 mL of methanol. After warming to room temperature, the reaction mixture is slowly poured into 1.5 L of hot n-hexane. The precipitated polymer is dissolved in 75-100 mL of reagent acetone and reprecipitated from 1.5 L of hot n-hexane. The recovered polymer is then dried to constant weight at ca 75° in vacuo. The yield is 8-9 g (85-95%).

2. Characterization

a. Determination of Molecular Weight

The UV spectrum of typical fluorenyllithium-initiated poly(methyl methacrylate) is remarkably similar to that of the parent hydrocarbon, fluorene. Published data[3] show that number-average molecular weights of fluorenyllithium-initiated PMMA can be accurately determined by measurement of the UV absorption spectrum of the purified polymer. This determination depends on the presence of one fluorenyl group per chain having a molar extinction coefficient equal to that of the parent hydrocarbon.

The absorption band at 304 nm of the fluorenyl group on the polymer chain is used for quantitative measurements. The molar extinction coefficient of the fluorenyl group on the polymer

is taken to be equal to that of fluorene, 8800 cm^2/mol. The number average molecular weight of the polymer is 16,000. M_n can be calculated from the following relation: $\log I_o/I = 8800 IC/M_n$, where C is the concentration of polymer solution in CHCl$_3$ in grams per liter, I is the cell length in centimeters, and $\log I_o/I$ is the absorbance at 304 nm.

Viscosity-average molecular weights[4] are calculated from intrinsic viscosities determined in benzene at 30°, using the following equations based on unpublished results from this laboratory:

$$[\eta] = 5.2 \times 10^{-5} M_v^{0.76} \text{ for } M_v \text{ greater than } 34,000$$

$$[\eta] = 1.95 \times 10^{-3} M_v^{0.41} \text{ for } M_v \text{ less than } 34,000$$

The M_v of this preparation was 33,900.

b. Tacticity Determination by NMR

Nuclear magnetic resonance spectra are determined using 10% solutions of polymer in chloroform. Spectra are measured at room temperature with tetramethylsilane as an internal standard. Instrumental conditions are chosen such that peak area ratios for the OCH$_3$, α-CH$_3$, and CH$_2$ protons are the appropriate 3:2:1. The three incompletely resolved peaks of the α-methyl groups are separated by constructing a symmetrical peak shape for the largest peak and then determining the areas of the subsidiary peaks by analytical subtraction. The sums of the peak areas thus separated correspond to the total area under the original peak to within ± 3%. Peaks for isotactic, heterotactic, and syndiotactic triads (α-methyl group configurations in three adjacent monomer units) are assigned following Bovey and Tiers.[5] The peak at the lowest field is assigned to isotactic, that at intermediate to heterotactic, and that at the highest field to syndiotactic placements. The ratio of syndiotactic to heterotactic to isotactic for the preparation is 83:9:8 (Note 8).

3. Methods of Preparation

Although the specific preparation described here leads to a predominantly syndiotactic polymer, analogous reactions with lower concentrations of THF can be used to prepare stereoblock polymers and even predominantly isotactic polymers.[6] If diethyl ether is substituted for THF, both in the preparation of fluorenyllithium and in the polymerization of methyl methacrylate, an even more highly isotactic polymer is obtained. Synthesis of highly syndiotactic polymer with narrow molecular weight distribution was repeated.[7]

4. Notes

1. The techniques described in this preparation, if carefully followed, allow the precise, quantitatively reproducible, preparation of stereoregular polymers of methyl methacrylate without recourse to high vacuum techniques. We consider the following points to be the most important aspects of correct experimental procedure:
    a. Calcium hydride is the preferred drying agent. According to A. S. Brown and co-workers[8], one day of drying over calcium hydride reduces the water content of benzene to lower levels than does refluxing for six months with sodium.
    b. Helium is used as the inert atmosphere for this preparation. It is further purified by passage through copper turnings at 500° (furnace, vertical, tube, gas-purifying, Sargent No. S-36517; furnace tube, oxygen-removing, copper-filled, Sargent No. S-36518) and then through a 4-ft spiral trap packed with Linde 5A Molecular Sieves and cooled with liquid nitrogen. The gas

is delivered to the reaction flask through a copper and glass manifold and does not contact rubber tubing at any point. There is no quantitative evidence to suggest that prepurified grade nitrogen is unsatisfactory for this preparation. However, when *n*-butyl lithium is prepared via the procedure described here, it gives a clear colorless solution with helium as the inert atmosphere and a faintly yellow one with nitrogen. Likewise, 9-fluorenyllithium is a somewhat darker orange when prepared under nitrogen than under helium.

c. Solutions and liquid reagents are deoxygenated by bubbling helium through them for at least 15 min with stirring. Polargraphic determination of oxygen content indicates that this period of bubbling reduces the oxygen content to levels equivalent to those achieved by four freeze-thaw cycles under high vacuum.

d. The standard rubber serum cap is leak tight only before it is punctured for the first time. Therefore storage vessels closed only be serum caps allow slow contamination by air of the reagents therein unless kept under substantial excess pressure of inert gas. The organometallic reagents used in this preparation, especially 9-fluorenyllithium, are extremely sensitive to minute amounts of oxygen and water. We have found it convenient to utilize storage vessels incorporating a high vacuum stopcock between the solution and the serum cap. When aliquots are removed from the flask, the space between the stopcock and the serum cap is flushed with helium by insertion of a pair of hypodermic needles, one of which is connected to a helium supply. Aliquots are withdrawn with hypodermic syringes fitted with metal stopcocks and 12-in, 18 gauge needles. The needle is forced through the serum cap, then through the vacuum stopcock into the solution. Excess helium pressure can be developed in the flask by closing the outlet needle with a finger, and this pressure forces the solution into the syringe. The syringe stopcock is then closed forming a closed vessel of the syringe, and the entire aliquot is transferred without loss or contamination.

e. Standard hypodermic syringes equipped with stopcocks (Becton, Dickinson & Co., No. MS09) form excellent leakproof transfer vessels, as described, only if they are filled by use of excess helium pressure to force reagents into them. If the more usual practice of manually extracting the plunger to create a vacuum is followed, there is some leakage of air along the space between barrel and plunger, leading to contamination of solutions.

2. It is necessary for the mechanical stirrer seal to be vapor tight. Ace Glass Tru-Bore stirrer shafts and bearings were found to be satisfactory if kept well lubricated with mineral oil.

Pentane-filled thermometers supplied by Arthur H. Thomas Co. (catalog No. 9587) were found to be satisfactory for this work. The thermometer was fitted to the reaction vessel with a 24/40 T_s Teflon thermometer gland (stirring rod gland, Matheson Scientific, Cat. No. 60260-05).

All T joints and stopcocks were lubricated with the minimum quantity of Dow-Coring High Vacuum Silicone Grease, and stopcocks and joints were held in place with spring retainers.

3. Toluene (Baker and Adamson, reagent grade) is refluxed with sodium for 8 h, then distilled in a stream of helium into a flask containing calcium hydride, from which it is distilled after standing for 24 h into a reservoir where it is stored under helium. This second distillation is carried out just before each polymerization.

4. Tetrahydrofuran (duPont) is dried over calcium hydride for a minimum of 24 h, then transferred to a flask containing lithium aluminum hydride where it is stored under helium for a least three days. Tetrahydrofuran is then distilled from the lithium aluminum hydride in a packed column under helium to remove peroxides completely. The distillate is passed through Woelm neutral alumina, to remove residual hydroquinone. It is stored over calcium hydride under helium after vacuum degassing.

5. 9-Fluorrenyllithium is prepared by the exchange reaction between fluorene and *n*-butyllithium in solution in THF. Reagent grade fluorene, mp 115.5-115.6° uncorr., (4.13 g, 25 mmol) is added to a clean, dry, 500 mL round-bottomed flask. The flask is then closed with a high vacuum stopcock having a male 24/40 T joint at one end and a female joint at the other end. The opening

at the female end is sealed with a rubber serum cap. About 100 mL of purified THF (Note 4) is transferred via a syringe equipped with a stopcock and a 12 in needle. The solution of fluorene is then deoxygenated by passage of helium through a long syringe needle which is inserted through the serum cap and stopcock bore into the solution; a second short needle is inserted into the serum cap to relieve pressure. After thorough deoxygenation, 18.3 mL of 1.31N butyllithium (Note 9) dissolved in *n*-hexane (24 mmol) is injected into the solution of fluorene at room temperature. The formation of fluorenyllithium is very rapid under these conditions, leading to a clear, red-orange-colored solution (in diethyl ether, fluorenyllithium forms light yellow solutions). If trace impurities are allowed to contaminate the solution, it immediately turns murky brown. This appears to be a very sensitive indication of purity, and discolored solutions should be discarded.

The concentration of fluorenyllithium in THF is determined by adding an aliquot of the solution to excess water and titrating the liberated LiOH with standardized HCl. This preparation resulted in a 0.207N solution.

6. Freshly distilled, uninhibited methyl methacrylate is dried over calcium hydride and deoxygenated by bubbling helium through it for 1 h prior to its use. A convenient method for removing the inhibitors from commercial grades of methyl methacrylate is to pass the monomer through a column of an equal weight of Woelm neutral alumina, activity grade 1. The monomer is collected over calcium hydride, and stored under helium at -20° until used. Deoxygenation with helium is carried out immediately prior to use.

7. A dry-ice acetone bath lowers the temperature of the apparatus and solution to -60°. As long as it is kept well stocked with dry ice, the reaction stays at this temperature, with out use of elaborate thermoregulators.

8. The checkers following the procedure obtained an s:h:i ratio of 72:16:12 using a JNM-MH-60 spectophotomerter. Using a JNM-MH-100 instrument, with its greater accuracy and precision, the checkers found a somewhat lower content of syndiotactic sequences, 65:23:12. Samples of the submitter's polymers, made at a time when 100 mHz NMR was not in use, were not kept, and redetermination of their tacticity could not be performed.

9. *n*-Butyllithium is prepared from *n*-butyl chloride and lithium wire in hexane. A three way stopcock is attached to a 500 mL three-necked round-bottomed flask so that helium can enter all parts of the synthesis apparatus. A fritted glass filtration apparatus is attached to one neck and an addition funnel is attached to another. After allowing the inert gas to flow through the apparatus for ca 15 min, the helium lines and the flask are flamed. The three-way stopcock is then turned to isolate the reaction vessel from the filtration apparatus attached to one of the necks. Distilled *n*-hexane (300 mL) is poured into the three-necked, 500 mL round-bottomed flask. Degreased lithium wire (10.0 g, 1.44 mol) is cut into short lengths and added to the flask. Butyl chloride (48 mL, 0.47 mol) is charged into the pressure-equalized addition funnel and heating of the hexane is begun. When refluxing begins, dropwise addition of butyl chloride into the reaction vessel is begun. After addition of butyl chloride is complete, refluxing is continued for 5 h. The reaction mixture is then cooled to room temperature and allowed to settle overnight under a very slight flow of helium.

The filtration section of the apparatus is isolated from the reaction vessel by turning the stopcock. This section of the apparatus is then evacuated and filled with helium several times through the lower gas connector, and finally left in the evacuated state. The Y-tube and associated apparatus on the reaction vessel are removed and as rapidly as possible replaced with a connecting tube with a stopcock that is connected to a helium supply. The three-way stopcock is turned to connect the reaction vessel with the filtration apparatus, and the solution if forced under helium pressure into the filter flask. The 500 mL receiver is immersed in liquid nitrogen to prevent excessive evaporation of hexane. Filtration results in a clear, colorless, sediment-free solution of *n*-butyllithium in *n*-hexane. The receiving flask and associated stopcock are removed from the apparatus, and a serum cap is affixed to the open end. The area between the serum cap and

stopcock is flushed with helium as previously described. Solutions prepared in this way can be stored at -20° for a long time without deterioration.

The concentration of butyllithium in hexane is determined by addition of 2 mL of the solution to 150 mL of water followed by titration with standardized HCl. The preparation described results in a 1.313N solution of the reagent.

4. References

1. *Research Laboratories, Rohm and Haas Company, Spring House, PA 19477.*
2. *Nagoya University, Department of Applied Chemistry, Faculty of Engineering, Furo-chu, Chikusa-ku, Nagoya, 464 Japan.*
3. Glusker, D. L.; Stiles, E.; Yoncoskie, B. *J. Polym. Sci.*, **1961**, *49*, 297.
4. Glusker, D. L.; Lysloff, I.; Stiles, B. *J. Polym. Sci.*, **1961**, *49*, 315.
5. Bovey, F. A.; Tiers, G. V. D. *J. Polym. Sci.*, **1960**, *44*, 173.
6. Glusker, D. L.; Galluccio, R. A.; Evans, R. A. *J. Am. Chem. Soc.*, **1964**, *86*, 187.
7. Kitayama, T.; Shinozaki, T. Sakamota, T.; Yamamoto, M.; Hatoda, K. *Macromolecules*, **1989**, *15*, 167, and references cited therein.
8. Brown, A. S.; Levin, P. M.; Abrahamson, E. W. *J. Chem. Phys.*, **1951**, *19*, 1226.