Macromolecular Syntheses

C. G. OVERBERGER

Volume 1

Macromolecular Syntheses

A Periodic Publication

of Methods for the Preparation

of Macromolecules

VOLUME ONE

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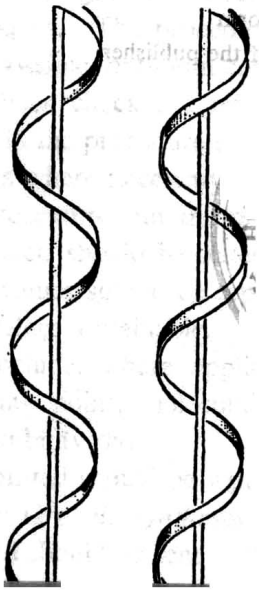
C. G. OVERBERGER, Editor



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Submission of Preparations

Chemists are invited to submit for publication in *MACROMOLECULAR SYNTHESES* procedures for the preparation of polymers which are of general interest or which illustrate useful preparative techniques. The procedures submitted should represent, as nearly as possible, optimum conditions for the preparations and should have been checked carefully by the submitter. Full details of all steps in the procedure should be included, with elaboration in the Notes where necessary. The method of preparation or source of the reactants and the criteria for the purity of the reactants and products should be stated. The range of yields and polymer property values should be reported rather than the maximum yield and values obtainable. The characterization of the polymer should include, where applicable, such information as softening or melting point, molecular weight values, functional group analyses, solubility data.

Procedures submitted should be written in the style employed in the latest volume of *Organic Syntheses*. Two copies of procedures which are submitted should be sent to the Secretary:

Dr. Norman G. Gaylord
Gaylord Associates Inc.
20 Mt. Pleasant Avenue
Newark 4, New Jersey

Preface

The science of polymer chemistry—our knowledge and understanding of macromolecules—is relatively recent. Initial pioneering work in this area was carried out between 1920 and 1930. However, the preparation and characterization of large macromolecules did not become a part of organic chemistry until the 1930's. A major reason for this was ignorance of the chemical nature of macromolecules, as well as the inapplicability of standard methods for their characterization.

Soon the enormous industrial interest in the properties of these large molecules gave a strong impetus to research in this area and helped to elucidate their preparation and characterization, although even now many organic chemists have the strong archaic bias that non-crystalline products cannot be of interest because they cannot be characterized in conventional fashion.

Since about 1950, however, new and improved methods have been developed and it could be demonstrated that it is quite possible to prepare and characterize a mixture of large molecules by other than conventional techniques. A number of chemists working in the organic polymer area in academic institutions and in industrial research laboratories were therefore convinced that the time was appropriate for the beginning of a series on macromolecular syntheses containing detailed directions for polymerization and characterization. At the same time, it was felt that these procedural methods should be checked in a rigorous way following the successful pattern of *Organic Syntheses,* so that they might be easily repeated by a student or a research worker.

One intent in this series is to provide trustworthy examples of polymer preparations for organic laboratory courses at the graduate and undergraduate levels since there are few such examples in the usual organic laboratory textbook. In addition, it is well recognized that, unless an industrial laboratory has a staff with a background of working with macromolecules, it is sometimes difficult to obtain sufficiently detailed information for the preparation of polymers from the patent literature. Thus we hope that this series will provide help to industrial concerns wishing to enter the field, by aiding the chemists in these organizations who have had no previous experience in the synthesis and characterization of macromolecules.

The projected series has been aided greatly by the recent publication of a book entitled *Preparative Methods of Polymer Chemistry* by Wayne Sorenson and Tod W. Campbell. In particular, we refer the readers to Chapter 2, "Preparation, Fabrication, and Characterization of Polymers." This excellent book with a chapter which clearly describes methods of characterization which are used in many of the preparations greatly helps and strengthens our series.

While the first volume contains preparations submitted largely by members of the Editorial Board, we now encourage contributions from the scientific community at large. The preparation of monomers and polymers of all types will be included. Thus it is intended to include also macromolecules of biochemical origin, such as polypeptides, polysaccharides, and nucleic acids. In the preparation of the first volume it has been necessary to do most of the checking at the Polytechnic Institute of Brooklyn for the sake of expediency. Some of the preparations represent older, some newer, procedures. As the series proceeds, the older preparations will be mixed with the new, the main "driving force" being an attempt to represent all types of monomers and polymers. All useful methods of preparation will be represented, with the further goals that the procedures can be easily repeated, and that appropriate methods of characterization of these polymers are clearly described.

C. G. OVERBERGER

Brooklyn, New York
June, 1963

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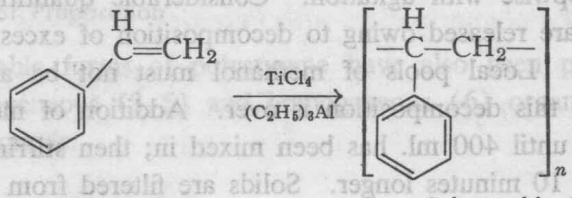
Crystalline Polystyrene



Submitted by R. J. Kern (1)

Checked by C. G. Overberger and E. Davidson (2)

1. Procedure

Caution! Triethylaluminum is highly incendiary.

A 1-l. four-necked flask is fitted with a mechanical stirrer, a thermometer, and a nitrogen sweep system. The stirring shaft operates through a vacuum-tight bearing and has a blade of stainless steel or 1.125-inch Teflon sheet cut to wipe the flask bottom closely. The assembly is baked for 1 hour at 120°C. and then swept with purified nitrogen (Note 1) for 30 minutes while cooling (Note 2). Titanium tetrachloride (0.9 ml., 1.55 g., 8 mmoles) is added by means of a hypodermic syringe. The flask bottom is cooled externally to about 0°C. Because of the extremely hazardous nature of the reaction between triethylaluminum and water, a Dry Ice-dimethoxyethane cooling bath is used. A solution of triethylaluminum (3.3 ml., 2.7 g., 24 mmoles) in

5 ml. of hexane is added dropwise, by means of a small pressure-equilibrated addition funnel, over a period of 20 minutes with slow (40–60 r.p.m.) agitation. After addition is complete, the cooling bath is removed and stirring is continued for 30 minutes at room temperature. Four hundred milliliters of styrene (Note 3) is added from a pressure-equilibrated addition funnel. The temperature is then raised to 50°C. and agitation increased to about 120 r.p.m. Granulation of the black mixture soon occurs, becoming steadily more viscous (and mushy). Polymerization is allowed to proceed until a granular gel is obtained without apparent free-flowing liquid (Note 4). This requires 2–4 hours.

After removal of the heating unit, methanol is cautiously added dropwise with agitation. Considerable quantities of gas and heat are released owing to decomposition of excess triethylaluminum. Local pools of methanol must not be allowed to form until this decomposition is over. Addition of methanol is continued until 400 ml. has been mixed in; then stirring is continued for 10 minutes longer. Solids are filtered from the black liquors, washed on a Büchner funnel with 400 ml. of acetone containing 2 ml. of concentrated 36% hydrochloric acid, and then reslurried in 400 ml. of acetone (Note 5). Solids are filtered and sucked nearly dry on a filter funnel and then stirred in refluxing freshly distilled methyl ethyl ketone for 2 hours. The produce is filtered, rinsed with acetone and then with distilled water and dried (Note 6). Yield 30–50 g. of product, m.p. 233–236°C.

2. Notes

1. Prepurified or lamp grade nitrogen containing not more than 10 p.p.m. of oxygen or water should be used.

2. Repeated evacuation with vacuum release by nitrogen is preferred.

3. Styrene containing no more than 10 p.p.m. of water should be used; it may be obtained by distillation (50°C./14 mm.) after a fore-run equal to one-third the charge has been discarded.

Styrene should be distilled directly into a previously baked addition funnel.

4. The degree to which polymerization is allowed to proceed is arbitrary. As higher conversions are attained, the mass becomes stiffer and less tractable in subsequent work-up operations. Reaction mixtures containing 8–12 wt. % solids are about the maximum which can be conveniently handled in conventional laboratory glassware.

5. It is recommended that at this point the solids be whipped in the acetone in a Waring Blendor.

6. Drying temperatures up to 140°C. in air may be used.

3. Methods of Preparation

Crystallizable forms of polystyrene have also been prepared using heterogeneous (3–5) and homogeneous (6) organo-alkali metal compounds.

4. References

1. Monsanto Chemical Company, Dayton 7, Ohio.
2. Polytechnic Institute of Brooklyn, Brooklyn 1, N.Y.
3. Williams, Vandenberge, Dunham and, Dulmage, *J. Am. Chem. Soc.*, 79, 1716 (1957).
4. Williams, Laakso, and Dulmage, *J. Org. Chem.*, 23, 638 (1958).
5. Smith, *J. Polymer Sci.*, 38, 259 (1959).
6. Kern, *Nature*, 187, 410 (1960).

Atactic Polystyrene

A. Bulk Polymerization with Peroxide Catalysis

$$C_6H_5CH{=}CH_2 \xrightarrow{[(C_6H_5CO_2)_2]} \left[\begin{array}{l}-CH_2-CH- \\ \qquad\quad | \\ \qquad\quad C_6H_5\end{array}\right]_n$$

Submitted by C. G. Overberger (1)

Checked by H. Friedman (1)

1. Procedure

A glass polymerization tube (Note 1) is charged with 25.00 ml. (22.68 g.) of freshly distilled styrene (Note 2) and 0.50 g. of benzoyl peroxide. The tube is connected to a three-way stopcock, the other two inlets of the stopcock being connected to a vacuum pump and a balloon containing nitrogen, respectively. The contents of the polymerization tube are then degassed and sealed under vacuum (Note 3).

The monomer is polymerized by heating the sealed tube at 55–60°C. for 66 hours (2.75 days).

At the end of the reaction period the plug of polymer is obtained by tapping the glass tube with a hammer (Note 4) and separating the broken glass from the plug.

The polymer is dissolved in 300 ml. of benzene at room temperature with stirring, and the solution (Note 5) is then added dropwise to 3 l. of methanol (Note 6) with vigorous stirring in order to precipitate the polymer. The polystyrene is collected by

filtering through a coarse, sintered glass funnel. The polymer is further purified by redissolving in benzene and reprecipitating from methanol.

After drying overnight in a vacuum oven at 60°C., the polymer weighed 22.5 g., η_{inh} = 0.37–0.38 at 29.4°C. in a 0.5% benzene solution.

2. Notes

1. The polymerization tube has a bulb 12 cm. in length and 2.5 cm. in diameter. A constricted neck, 15 cm. long, is connected to the bulb.

2. It is necessary to distill the styrene under reduced pressure in order to free the monomer of inhibitor and other impurities. The first 5% of styrene distilled is discarded, the middle fraction being saved. An alternative procedure is to wash the styrene with a 5% aqueous sodium hydroxide solution and dry over anhydrous calcium sulfate.

3. The tube with its contents is frozen in a Dry Ice-acetone bath and evacuated. After nitrogen is introduced, the monomer is thawed, refrozen, and evacuated again. This procedure is repeated several times. Before the tube is sealed the monomer is refrozen and the tube re-evacuated.

4. The tube should be wrapped in a towel in order to prevent glass from flying as the result of an implosion or an explosion.

5. The solution may be freed of dust particles by filtering through a coarse sintered glass funnel.

6. The non-solvent is used in a volume ten times that of the solvent in order to ensure complete precipitation of the polymer.

B. Solution Polymerization with Cationic Catalysis

$$C_6H_5CH{=}CH_2 \xrightarrow{SnCl_4} \left[-CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}- \right]_n$$

Submitted by C. G. Overberger (1)

Checked by H. Friedman (1)

1. Procedure

The Catalyst. Into a dried 2-oz. screw-cap bottle (Note 1) which has been thoroughly dried in an oven is pipetted 20 ml. of C.P. reagent grade carbon tetrachloride (Note 2). The bottle and its contents are then accurately weighed.

Stannic chloride catalyst, 0.6 ml. (1.32 g.) (Note 3), is withdrawn with a 5-ml. medicinal hypodermic syringe and immediately injected into the 2-oz. bottle without unscrewing the cap. The bottle is then accurately reweighed to determine the exact amount of catalyst transferred. Sufficient carbon tetrachloride is added to the bottle to bring the solution to a concentration of 2.14 wt. % in catalyst. The cap of the bottle is closed tightly, and the catalyst solution is immersed in a beaker of chopped ice until ready for further use (Note 4).

The Monomer. Freshly distilled styrene, 6.5 ml. (Note 2, Part A), is pipetted into a thoroughly dried 4-oz. screw-cap bottle (Note 5). From a pipet, 20 ml. of carbon tetrachloride and 25.5 ml. of nitrobenzene (Note 6) are added to the monomer. The cap of the 4-oz. bottle is closed tightly, and the bottle is shaken briefly. The bottle is then placed in the same ice bath with the catalyst solution.

After about 10 minutes has been allowed for the contents of both bottles to cool to 0°C., 4 ml. (6.5 g.) of the catalyst solution is withdrawn with a hypodermic syringe. The contents of the syringe are injected into the 4-oz. bottle of monomer solution (Note 7). After standing for a period of 5 hours in an ice bath, the solution is added to 500 ml. of methanol (Note 7, Part A) with vigorous stirring to precipitate the polymer. The polystyrene is collected by filtering through a fine, sintered glass funnel. The polymer is further purified by redissolving in 50 ml. of ethyl methyl ketone and reprecipitating from 500 ml. of methanol. This purification process is repeated twice.

After drying overnight in a vacuum desiccator (Notes 8, 9) the polymer weighed 5 g., η_{inh} = 0.19–0.20 at 29.2°C. in a 0.5% benzene solution.

2. Notes

1. The cap of the bottle should be perforated and fitted with two rubber gaskets. The lower gasket, exposed to the contents of the bottle, consists of vulcanized rubber (chemically inert to the solvents), and the upper gasket is a puncture-sealing rubber material.

2. The carbon tetrachloride should be stored over anhydrous calcium chloride if not used immediately.

3. The main supply of stannic chloride catalyst should be stored in a screw-top bottle, fitted at the cap as described in Note 1 with two rubber gaskets. In the event that the main supply of catalyst becomes contaminated, it may be purified by heating under reflux over phosphorous pentoxide for 1–2 hours and then distilling under reduced pressure.

4. A more elaborate procedure than that described above for preparing the catalyst in such polymerization reactions is reported in the literature (2).

5. The 4-oz. screw-cap bottle is also fitted at the cap with two rubber gaskets, the upper gasket being the puncture-sealing rubber material.

6. If the nitrobenzene is not obtained from a freshly opened bottle of C.P. reagent grade material, it must be purified according to standard procedures (3).

7. The polymerization mixture consists of a 10.0 mole % solution of styrene in solvent (an equimolar mixture of carbon tetrachloride and nitrobenzene) containing 0.1 mole % of stannic chloride catalyst. The molar ratio of monomer to catalyst is accordingly 100:1.

8. Paraffin chips and phosphorous pentoxide are placed in the desiccator to absorb any solvent adhering to the polymer. The pressure in the desiccator was 0.5 mm. Hg.

9. It is necessary to dry the polymer in the sintered glass funnel in which it is filtered and to have the top of the funnel tightly covered with a rubber sheet. If this precaution is not taken, the polymer, which upon drying will become a very fine powder, will tend to disperse all about the desiccator.

3. Methods of Preparation

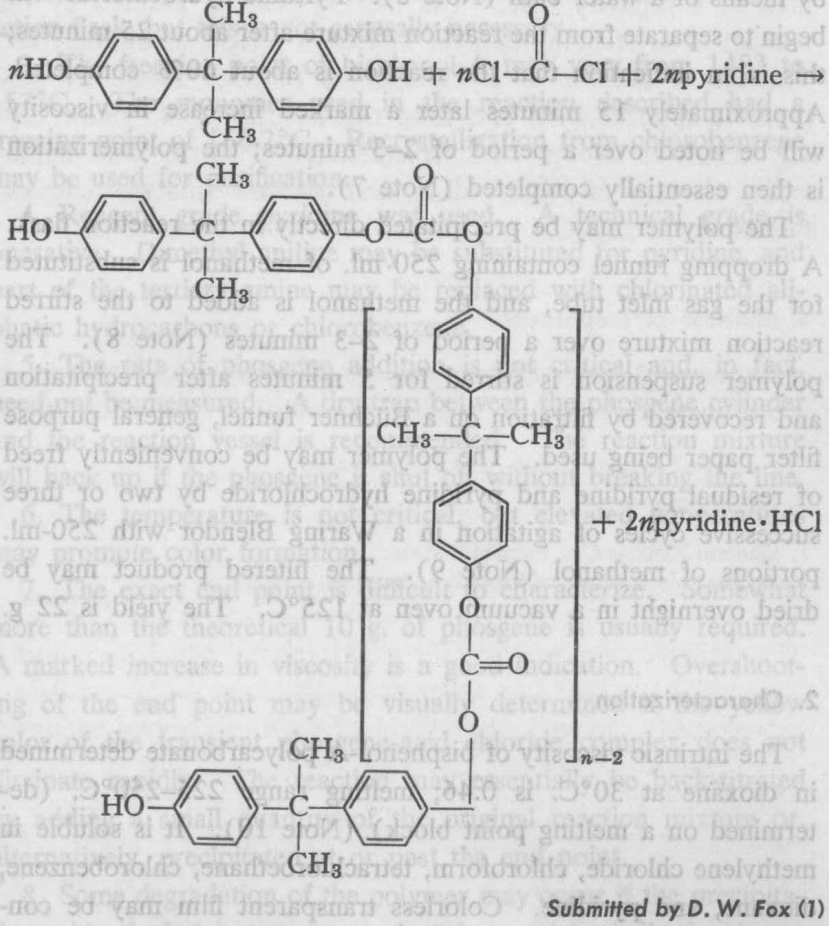
Polystyrene has also been prepared by suspension or pearl polymerization (4), emulsion polymerization (5), solution polymerization (6), and thermal polymerization (7).

4. References

1. Polytechnic Institute of Brooklyn, Brooklyn 1, N.Y.
2. George, Mark, and Wechsler, *J. Am. Chem. Soc.*, 72, 3691 (1950).
3. Vogel, *Practical Organic Chemistry*, third edition, Longmans, Green and Co., New York, 1959, p. 175.
4. Hohenstein (Polytechnic Institute of Brooklyn), U.S. Pat. 2,524,627 (1950) [*C.A.*, 45, 903 (1951)].
5. Combined Intelligence Objectives Sub-Committee Report 79–85 (Schildknecht, *Vinyl and Related Polymers*, John Wiley and Sons, Inc., 1952, p. 16).
6. Hunt (E. I. du Pont de Nemours & Co.), U.S. Pat. 2,471,959 (1949) [*C.A.*, 43, 6002 (1949)].
7. Dow Chemical Company, Product Bulletin, "The Polymerization of Styrene."

Bisphenol-A Polycarbonate

(p,p′-Isopropylidene bisphenol polycarbonate)



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Checked by C. G. Overberger and B. Avchen (2)