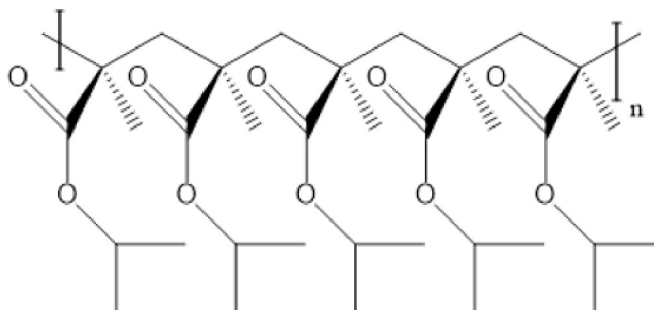


# Isotactic Poly(isopropyl acrylate)

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## 1. Procedure

A 1 l four-necked round bottomed flask is equipped with a mechanical stirrer, a thermometer, and a graduated addition funnel. One neck of the flask and the addition funnel are fitted with rubber serum caps (Note 1). In the flask is placed toluene (525 ml, Note 2); isopropyl acrylate (43 ml 38.8 g, 0.336 mol, Note 3) is charged to the addition funnel. Oxygen is removed from the solvent and the monomer at room temperature by slowly bubbling a stream of nitrogen (Note 4) through the materials for at least 1 h. Degassing is conveniently effected with hypodermic needles inserted through the serum caps. The nitrogen effluent should be vented through a mineral oil or mercury bubbler. Short hypodermic needles inserted through the serum caps serve as convenient vents.

To the toluene is added with stirring 0.024 eq of phenylmagnesium bromide in ether (Note 5) by means of a hypodermic syringe inserted through the serum cap. The mixture is cooled to 0-5°. From the addition funnel is added 5 ml of isopropyl acrylate, and the mixture is allowed to stir at 0-5° for 3 h (Note 6), whereupon it is cooled to -70 to -80° with a Dry Ice-acetone bath. The remaining monomer is added dropwise while the temperature is maintained at -70 to -80°. The mixture is stirred for 1 h and is then held at -70 to -80° overnight without stirring (Note 7).

The polymer is isolated by precipitation at room temperature into a rapidly stirred solution containing 4.5 l of methanol, 800 ml of distilled water, and 175 ml of concentrated hydrochloric acid. The product is removed by filtration and is thoroughly washed with distilled water. After drying to constant weight at 50-60° under reduced pressure, there is obtained 29-33 g (76-86%, Note 8) of isotactic poly(isopropyl acrylate) (Notes 9 and 10).

## 2. Characterization

Isotactic poly(isopropyl acrylate) prepared by this procedure is a granular, hard solid in contrast to normal free-radical prepared polymer which is a rubbery material at room temperature. The intrinsic viscosity of the Grignard-initiated polymer in chloroform at 25° is in the range 5-10 dl/g. The viscosity average molecular weight is calculated from the relationship:

$$[\eta] = 1.4 \times 10^{-4} \bar{M}_v^{0.72}$$

This equation is derived from measurements on fractions of conventional polymer. A preliminary investigation of tactic polymer fractions indicates this relationship to be at least approximately valid.<sup>3</sup> It should be noted that the ratio of viscosity average to number average molecular weight for Grignard-initiated acrylic polymers is large. Mechanistic reasons for the broad molecular weight distribution in these polymers have been discussed.<sup>3</sup>

Isotactic poly(isopropyl acrylate) shows a typical crystalline powder diffraction pattern with strong scattering from spacings at 8.4, 5.15, 4.85, and 4.20 Å.<sup>4</sup> Indeed it is difficult to obtain this polymer as an amorphous solid. Dilatometric measurements indicate a glass transition at -11° and a crystal melting point at 162°. Data now available indicate a fiber repeat distance of 6.32 Å and a density of 1.08 g/cc.<sup>5</sup>

In-depth characterization of the structure of isotactic isopropyl acrylate polymer was not carried out by the original submitters. Details of NMR spectra and of the mechanism of isotactic polymerization have been reported<sup>6</sup> as have studies of the basic physical properties of isotactic poly(isopropyl acrylate).<sup>7</sup> Films of normal free-radically-initiated poly(isopropyl acrylate) exhibit infrared maxima at 1265 and 920 cm<sup>-1</sup>, while crystalline isotactic polymer shows sharp maxima at 1305, 1245, 1210, and 912 cm<sup>-1</sup>. The maxima at 1305, 1245, and 1210 cm<sup>-1</sup> are not present in spectra of solutions of isotactic poly(isopropyl acrylate).

### 3. Notes

1. The submitters used rubber stoppers, catalog No. 8826, supplied by the A. H. Thomas Co., Philadelphia, PA. Size 15 stoppers are convenient for use with a 24/40 standard taper joint.
2. It is essential that this polymerization be conducted under anaerobic, anhydrous conditions. The toluene may be conveniently dried by azeotropically removing the water. The toluene should be stored over sodium metal or calcium hydride.  
The attainment of very high molecular weights requires scrupulous purity of the reaction mixture and the absence of even small amounts of water, alcohol, oxygen and peroxides. All transfers should be conducted under a nitrogen atmosphere. Merely pouring isopropyl acrylate through air is sufficient to introduce significant amounts of oxygen.
3. Isopropyl acrylate is most conveniently prepared by direct esterification of glacial acrylic acid (Rohm & Haas Co., Philadelphia, PA), with concentrated sulfuric acid or *p*-toluenesulfonic acid as the catalyst. The monomer may also be prepared by transesterification.<sup>8</sup> Freshly distilled, uninhibited monomer should be used for the polymerization. Traces of alcohol are conveniently removed by distillation from boric acid.<sup>9</sup> The monomer should be distilled from a good inhibitor, collected in an ice-cooled receiver, and stored under nitrogen over calcium hydride in a refrigerator. The monomer has the following properties: bp 110-111° (760 torr), 53-54° (95 torr);  $n_D^{20}$  1.4059;  $d_4^{20}$  0.893.
4. The submitters used prepurified nitrogen (Air Reduction Sales Co.) without further purification.
5. The Grignard reagent should be 3.6*N* phenylmagnesium bromide in ether. The submitters found that the best results were obtained when the Grignard reagent was prepared under helium.<sup>10</sup> Commercial phenylmagnesium bromide (Arapahoe Chemicals, Inc., Boulder, CO) or the reagent prepared under nitrogen may also be used.
6. The isotacticity and the viscosity average molecular weight are greatest when this pre-reaction technique is employed. Polymer of lower tacticity and molecular weight results when this step is omitted.
7. The viscosity of the reaction mixture increases markedly during the course of the reaction; therefore it is advisable to discontinue stirring.
8. The yield of isolated polymer is based on the total weight of monomer charged. In addition to the isolated solid polymer, the aqueous methanol contains polymer of very low molecular weight.<sup>3</sup>

9. Isotactic poly(*sec*-butyl acrylate), poly(*tert*-butyl acrylate), and poly(cyclohexyl acrylate) can be prepared by the procedure described. These polymers are also crystalline as prepared.<sup>4</sup>
10. Isotactic poly(methyl methacrylate) can be prepared by the method described; however, the prereaction technique appears to be much less effective for methyl methacrylate and is omitted. The following procedure is used to prepare isotactic poly(methyl methacrylate).

Freshly distilled, uninhibited, oxygen-free methyl methacrylate (32 ml, 30 g, 0.3 mol) is added to 0.024 eq of phenylmagnesium bromide in 525 ml of anhydrous, oxygen-free toluene at 0-5°. The mixture is stirred at 0-5° overnight. The polymer is isolated by precipitation at room temperature into 10 volumes of rapidly stirred petroleum ether. The residual solvent is removed from the polymer under reduced pressure, and inorganic salts are removed by suspending the product in a stirred mixture of 1.7 l of water, 300 ml of methanol, and 90 ml of concentrated hydrochloric acid for 2 h. The polymer is then thoroughly washed with distilled water and dried at 50-60° under reduced pressure. There is obtained 23-25 g (77-83%) of isotactic poly(methyl methacrylate).

Isotactic poly(methyl methacrylate) is usually amorphous as obtained by this procedure; suitable treatment is required to develop crystallinity.<sup>11</sup> The properties of isotactic poly(methyl methacrylate) have been discussed in detail.<sup>11,12,13</sup>

11. Solutions of lithium aluminum hydride in diethyl ether have been used to prepare isotactic poly(isopropyl acrylate).<sup>14</sup> Stereoregular polymers are obtained from acrylate esters with unbranched ester side chains by using calcium or strontium complexed with diethylzinc.<sup>15,16</sup>

#### 4. References

1. *Rohm and Haas Co., Bristol, PA 19007; the assistance of Dr. R. K. Graham in revising this procedure is thankfully acknowledged.*
2. *General Electric Co., Research and Development Laboratory, Schenectady, NY, 12345; current address of Katchman - General Electric Co., Selkirk, NY 12158; Bostick - General Electric Co., Mount Vernon, IL 62864.*
3. Goode, W. E.; Owens, F. H.; Myers, W. L. *J. Polym. Sci.* **1960**, *47*, 75.
4. Garrett, B. S.; Goode, W. E.; Gratch, S.; Kincaid, J. F.; Levesque, C. L.; Spell, A.; Stroupe, D. J.; Wattanabe, W. H. *J. Am. Chem. Soc.* **1959**, *81*, 1007.
5. Unpublished results.
6. Fowells, W.; Schuerch, C.; Bovey, F. A.; Hood, F. P. *J. Am. Chem. Soc.* **1967**, *89*, 1396.
7. Mark, J. E.; Wessling, R. A.; Hughes, R. E. *J. Phys. Chem.* **1966**, *70*, 1895; Wessling, R. A.; Mark, J. E.; Hamori, E.; Hughes, R. E. *J. Phys. Chem.* **1966**, *70*, 1903; Wessling, R. A.; Mark, J. E.; Hughes, R. E. *J. Phys. Chem.* **1966**, *70*, 1909.
8. Rehberg, C. E. *Org. Syn. Coll. Vol. 3*, 1955; p 146.
9. Lemon, R. C.; Goldsmith, W. E. Brit. Patent 812,498, 1969; *Chem. Abst.* **1959**, *53*, 16968d.
10. Owens, F. H.; Fellmann, R. P.; Zimmerman, F. E. *J. Org. Chem.* **1960**, *25*, 1808.
11. Goode, W. E.; Owens, F. H.; Fellmann, R. P.; Snyder, W. H.; Moore, J. E. *J. Polym. Sci.* **1960**, *46*, 317.
12. Fox, T. G.; Garrett, B. S.; Goode, W. E.; Gratch, S.; Kincaid, J. F.; Spell, A.; Stroupe, J. D. *J. Am. Chem. Soc.* **1958**, *80*, 1768.
13. Stroupe, J. D.; Hughes, R. E. *J. Am. Chem. Soc.* **1958**, *80*, 2341.
14. Tsuruta, T.; Makimoto, T.; Nakayama, Y. *Makromol. Chem.* **1966**, *90*, 12.
15. Furukawa, J.; Tsuruta, T.; Makimoto, T. *Makromol. Chem.* **1960**, *42*, 165.
16. Makimoto, T.; Tsuruta, T.; Furukawa, J. *Makromol. Chem.* **1961**, *50*, 116.