

inlet tube (S) is inserted in (R) below the surface of the reactants. An adapting tube (T), used to carry off the nitrogen effluent to a mercury or mineral oil bubbler (U), is inserted in the curved arm of (R). Temperature control and means of irradiation are accomplished by use of the same Dewar flask (A), platform (B), relay (C), and ultraviolet light source (I) described in Procedure A and illustrated in Fig. 1 (Note 1).

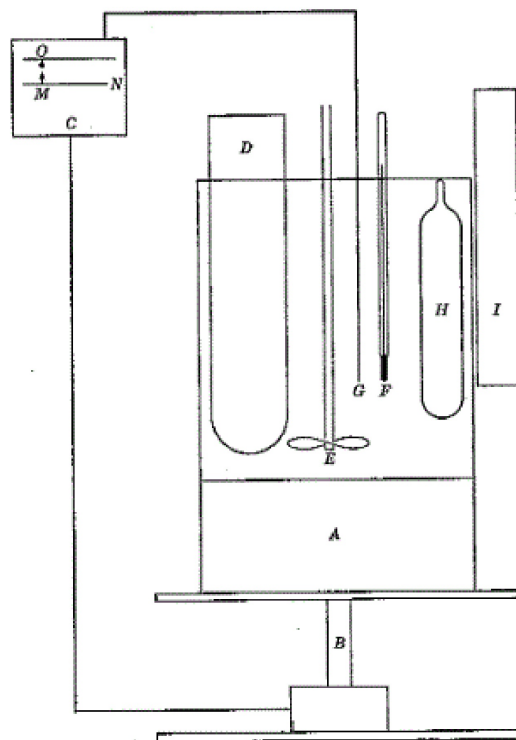


FIG. 1.

Fig. 1

In the reaction flask are placed 150 g of reagent grade toluene, isopropyl acrylate, (150 g, 1.32 moles, Note 5), and benzoin, (1.25 g, 0.006 mol, Note 6). The reactants are cooled to -95° , and the solution is degassed by bubbling a stream of nitrogen through it for 2 h (Note 7). The temperature is lowered to and maintained at $-105^{\circ} \pm 7^{\circ}$ before the reaction is initiated by irradiation from the ultraviolet light source. Nitrogen bubbling and agitation are maintained throughout the entire reaction time.

After 6 h of irradiation, the ultraviolet lamps are turned off, and the reaction mixture is allowed to warm to room temperature. The polymer is isolated as indicated in Procedure A, dissolved in 500 ml of benzene, and then this solution is filtered. The final syndiotactic polymer (23 g, which corresponds to an average rate of polymerization of approximately 2.6%/h) is isolated by freeze-drying this solution.

3. Characterization

The viscosity average molecular weight of the rubbery, partially crystalline, syndiotactic poly(isopropyl acrylate) prepared by the methods described was calculated from the intrinsic viscosity $[\eta]$ in benzene at 30° using the relationship:

$$[\eta] = 1.18 \times 10^{-4} \bar{M}_v^{0.72}$$

derived from measurements on fractions of conventional polymer³ prepared at 44.1°. For the material prepared by Procedure A, $[\eta] = 0.62$ dl/g; for material prepared by Procedure B, $[\eta] = 1.4$ dl/g.

Syndiotactic poly(isopropyl acrylate) gives a typical crystalline powder diffraction pattern with strong scattering from spacings at 7.4 and 4.25 Å; a fiber repeat distance of 5.18 Å; a calculated density of 1.8 g/cc;⁴ and a dilatometric glass transition temperature between 5° and 11° (Note 10). A crystalline melting point, $T_m = 115^\circ$, has been found from dilatometric measurements for a sample of syndiotactic poly(isopropyl acrylate).

Films of conventional poly(isopropyl acrylate) exhibit infrared maxima at 1265 and 920 cm^{-1} , whereas syndiotactic polymer exhibits sharp maxima at 1250 and 924 cm^{-1} . The maxima at 1250 cm^{-1} is not present in spectra of solutions of syndiotactic polymer.

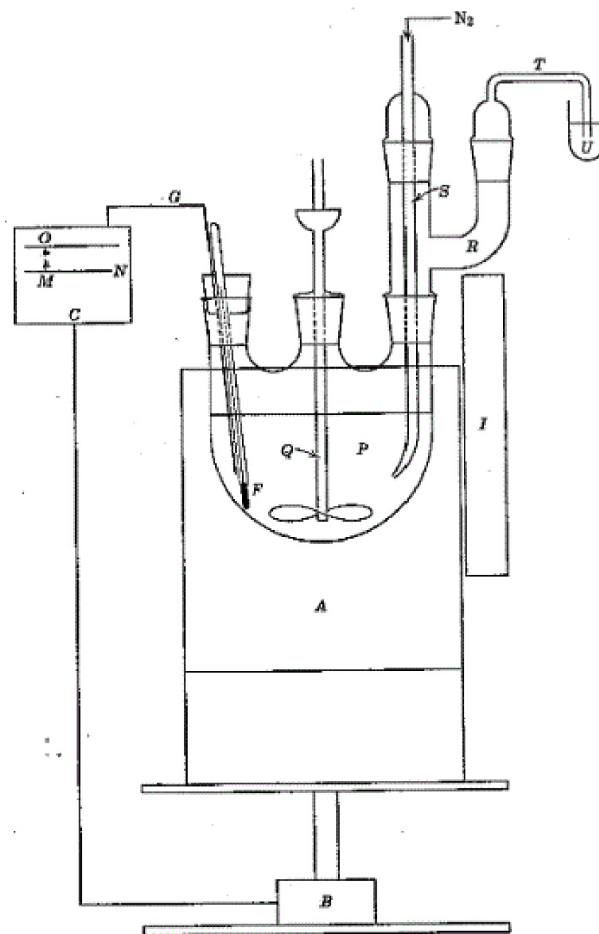


Fig. 2.

Fig. 2

4. Notes

1. The submitters used a Jack-O-Matic, model HD-4, as the platform (available from Instruments for Industry and Research, 108 Franklin Avenue, Cheltenham, PA). The checkers reported satisfactory temperature control by manual adjustment and stirring liquid nitrogen into 1-propanol.
2. A Pyrex[®] ampoule (diameter= 2.5 cm, length = 17 cm), fitted with a 10/30 standard taper joint and constricted below the joint, was used as the reaction vessel.

3. The submitters used the Gardsman, Model J, Indicating Pyrometric Controller (available from West Instrument Corporation, 525 North Noble Street, Chicago 22, IL) as a relay (shown in section C of Fig. 1). A manually operated setting arm (M) is set at the desired position on the temperature scale (N). When a decrease in temperature occurs in the bath, the current generated by the thermocouple (the leads of which must be reversed to accomplish low temperature location) activates the pointer (O). The relay is energized, and the Jack-O-Matic rises at the point where (M) and (O) coincide. When the pointer (O) exceeds the position of (M), the relay is de-energized, and the Jack-O-Matic falls to its normal position. The repetition of this action provides temperature control to within $\pm 7^\circ$ at very low temperature (-100°) and to within $\pm 3^\circ$ at higher temperature (-50°).
4. The submitters used two pairs of 15-watt Sylvania Blacklight bulbs (wavelength = 320-420 nm, 100% transmission at 360 nm). The lights were placed in position so that their beams struck the reactants at an angle of 45° to each other. A Hanovia Inspectolite may also be used, but, because this is a 100-watt source, the amount of photosensitizer used should be reduced proportionately.
5. Isopropyl acrylate was distilled from diphenylpicrylhydrazyl just before use; bp = 111° (760 torr), $53-54^\circ$ (95 torr), $n_D^{20} = 1.4059$, $n_4^{20} = 0.893$.
6. Reagent grade benzoin, which serves as the photosensitizer, was used as received from Eastman Organic Chemicals Company.
7. It is essential that the polymerization be conducted in the complete absence of oxygen.
8. If the reaction mixture contains peroxidic impurities, a higher yield of lower molecular weight polymer is obtained. The checkers reported a yield of 4.5 g of polymer with $[\eta] = 0.27$ dl/g.
9. Syndiotactic poly(methyl methacrylate) can be prepared by Procedure A, but a Dry Ice-acetone mixture is used in the cylinder (D). Forty grams of freshly distilled uninhibited methyl methacrylate and 0.0002 g of benzoin are placed in the reaction vessel, and the solution is degassed. The reactants are irradiated at a constant temperature of $-48^\circ \pm 3^\circ$ for 5 h with a 100-watt Hanovia Inspectolite (or equivalent), mounted 6 in from the reaction vessel. The average rate is approximately 0.3%/h, and the viscosity average molecular weight is approximately 3×10^6 . The properties of syndiotactic poly(methyl methacrylate) have been discussed in detail.^{5,6}
10. Conventional polymers prepared at 44.1° have a glass transition temperature of less than -2° .

5. References

1. Rohm & Haas Co., Bristol, PA 19007.
2. General Electric Co., Research Laboratories, Schenectady, NY 12345; current address Katchman - General Electric Co., Selkirk, NY 12158; Bostick - General Electric Co., Mount Vernon, IL 62864.
3. Cohn, E. S.; Orofino, T. A.; Scogna, L. L., unpublished results.
4. Yanai, H. S., unpublished results.
5. 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.
6. Fox, T. G.; Goode, W. E.; Gratch, S.; Huggett, C. M.; Kincaid, J. F.; Spell, A.; Stroupe, J. D. *J. Polym. Sci.* **1958**, *31*, 173.