Poly(methyl methacrylate) Suspension Polymer

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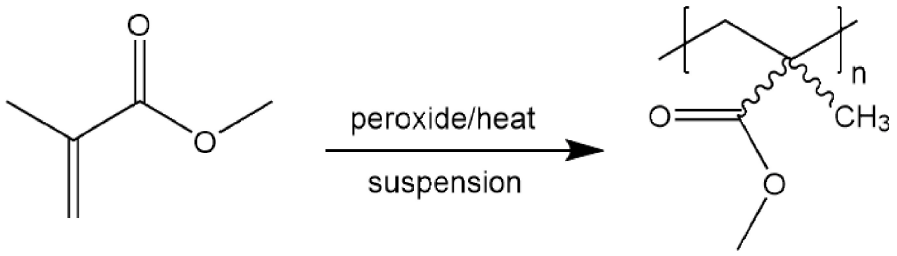

1. Procedure

Into a 3 l three-necked flask are charged 1.5 l of distilled water, 15 g of Cyanamer A-370 (Note 1), 8.5 g of disodium phosphate (Na_2HPO_4), and 0.5 g of monosodium phosphate (NaH_2PO_4). The flask is fitted with a thermometer, a condenser, and a half-moon glass stirrer (Note 2); the mixture is warmed to 30-35° (Note 3) and stirred until clear.

In a 1 l beaker are mixed 500 g of distilled methyl methacrylate (Note 4) and 5 g of benzoyl peroxide (Note 5) until clear. This solution is added to the flask. The half-moon paddle is adjusted to about 1/2 in below the top surface, and agitation is begun at about 400 rpm.

The reactor is flushed lightly with nitrogen gas for 1-2 min to remove atmospheric oxygen. The agitator speed is adjusted to 250 rpm and the reaction mixture is heated at 76-78° for 2.5 to 3 h (Note 6).

The mixture is cooled to room temperature, and the polymer is recovered by filtration in a Büchner funnel (Note 7). The polymer is washed several times with water and dried at 65° for 5 to 10 h.

The yield is 450-475 g (90-95%) of clear polymer beads. Using chloroform, an intrinsic viscosity of 1.87-1.90 dl/g is obtained (Note 8). This intrinsic viscosity may be lowered by the addition of tert-dodecanethiol (Aldrich) to the monomer mixture (Note 9).

2. Notes

1. Cyanamer A-370 is a water-soluble modified polyacrylamide resin from American Cyanamid Company as a free-flowing powder.
2. The half-moon stirrer used was obtained from the H. S. Martin Company and was the 125 mm size.
3. Heat was supplied by a hot water.
4. *Caution! Distilled methyl methacrylate that is free of inhibitor can polymerize exothermically in the presence of light. Store distilled methyl methacrylate in a cool, dark place.*
5. *Caution! Dry benzoyl peroxide is known to spontaneously detonate on handling. To avoid this hazard a wet grade of benzoyl peroxide, e.g., Lucidol-78 (78% benzoyl peroxide), available from Lucidol Division of Pennwalt Corp., may be used.*
6. A definite exotherm occurs after about 45 minutes. This exotherm should be controlled by the addition of cold water to the bath so that the *reaction temperature does not rise above 80°.*

7. Good filtration properties are obtained using a porcelain Büchner funnel (size No. 4 or 5). The best filter paper for this filtration was found to be the M grade from Sparkler Manufacturing of Mundelein, IL. Volan 181 glass cloth or fine nylon cloth also serve well. Optimum filtering is attained if the cooled reaction mixture is diluted with an equal amount of cold water before filtering.
8. Using the relationship[3] $[\eta] = 2.8 \times 10^{-5} M^{0.8}$, the molecular weight of such polymers ranged from 1.07×10^6 to 1.09×10^6. Actual intrinsic viscosities of three different polymers were 1.89, 1.88, and 1.90 dl/g.
9. The addition of 3.7 g of tert-dodecanethiol (0.75%) to the monomer-catalyst solution gave a polymer having an intrinsic viscosity of 0.47-0.49 dl/g. This is equivalent to a molecular weight range of 1.90×10^5 to 2.01×10^5.

3. References

1. *Pittsburgh Plate Glass Co., Springdale, PA 15144; the assistance of M. E. Hartman (PPG Industries, Allison Park, PA 15101) in revising this procedure is thankfully acknowledged.*
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3. Prepr. Pap.--Am. Chem. Soc., Div. Paint, Plastics and Printing Ink Chem. American Chemical Society Meeting, Boston, April 1959, p. 136.