# The Anionic Dispersion Polymerization
# of α-Methylstyrene

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## Synopsis

A new technique for the anionic polymerization of α-methylstyrene has been developed. By using an aliphatic hydrocarbon as the diluent, hexamethylphosphoramide as promoter, and a poly(vinyl alkyl ether) as interfacial agent, the high molecular weight polymer is obtained as a uniform dispersion. The advantages of the method are high conversions at low viscosities and an economical isolation procedure.

## INTRODUCTION

High molecular weight poly-α-methylstyrene can be conveniently prepared in the laboratory by an anionic solution polymerization. On a larger scale, however, such processes are generally not very attractive, because they necessitate the removal of large amounts of solvent later if the solution is to be kept at a reasonable viscosity level. This situation is still aggravated in the case of α-methylstyrene, where the low ceiling temperature demands that the temperature be kept low and the monomer concentration high. One solution for this problem is the polymerization in a heterogeneous phase, but while a great number of such methods have been described for free radical and organometallic coordination polymerizations, none has yet been reported for an anionic living polymerization.[†]

We have now developed a dispersion technique for the polymerization of α-methylstyrene that offers, for the first time, a convement method for the large-scale preparation of this polymer.

## EXPERIMENTAL

### Materials

The α-methylstyrene, bp 163–165°C, was distilled under vacuum immediately before use to remove stabilizer and possible oligomers. The diluent, a research- or technical-grade heptane (Matheson) was purified by passage through a column of activated alumina. Hexamethylphosphoric

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† It was recently pointed out to us that a patent (U.S. Pat. 3,402,160 (1968)) teaches the anionic polymerization of styrene and α-methylstyrene in a solvent (hexane) in which the polymer is insoluble in the presence of a suspending agent (rubber).

triamide practical, "HMPA," mp 6–8°C (Matheson), was fractionated under vacuum before use.

The initiator n-butyllithium (Alfa Inorganics) was obtained as a 22 wt-% (2.35 molar) solution in hexane. The interfacial agent was EDBM, a tacky, rubber-like poly(vinyl ethyl ether) from Union Carbide, with a reduced specific viscosity at 20°C of 4.0 ± 0.5 (2 g/l.). It was handled as a 6 wt-% solution in α-methylstyrene.

## Polymerization

The reactions were carried out in a 1-l resin flask, equipped with an efficient mechanical stirrer, thermocouple well, gas inlet and outlet tubes, and an injection port closed with a serum stopper. The flask was dried by flaming the outside while passing a stream of argon through the vessel. During the polymerization a slight positive pressure of argon was maintained in the flask.

All liquid transfers were made with carefully dried syringes through the serum stopper. In a typical experiment, e.g., those of Table I, the monomer, diluent, and polyvinyl ether were charged to the flask and cooled to 0°C with an outside bath.

The impurities in the system were deactivated by careful titration with n-butyllithium. To help determine the endpoint, 0.02 ml of HMPA was added as an indicator. The complete removal of impurities is then easily recognized by a persistent lemon-yellow color of the solution. This small amount of HMPA is insufficient to promote the polymerization of more than a trace of monomer. The requisite amount of n-butyllithium was then added rapidly, giving a reddish-brown solution. Upon addition of the rest of the HMPA, a darkening of the solution occurred, followed immediately by the formation of a dispersed polymer phase. The color lightened considerably, turning to light brown or cocoa brown, depending on the particular composition of the reaction mixture. The temperature rose rapidly at this point, reaching a maximum of about 20°C for the most active reactions, then dropping again to 0°C in about 15 min. The dispersion was

TABLE I
Dispersion Polymerization of α-Methylstyrene[a]

| | Levels | |
|---|---|---|
| Variables | (−) | (+) |
| A: Monomer concentration, vol-% | 25 | 33 |
| B: Butyllithium, mole-% of monomer | 0.1 | 0.2 |
| C: HMPA, mole equiv. of B | 2 | 5 |
| D: EDBM, wt-% of monomer | 0.2 | 0.5 |

[a] Experimental conditions: total volume, 400 ml; diluent, technical heptane; temperature, 0°C; reaction time, 1 hr.

kept at this temperature for a total reaction time of 1 hr before carbon dioxide or an alcohol was introduced to terminate the reaction.

## Recovery

After termination, the polymer was recovered by filtration, washing with isopropanol, and drying in a vacuum oven at 100°C for 24 hr. In cases of low conversions, the dispersion had to be diluted with isopropanol to prevent the coalescence of the particles into a tough, hard-to-handle mass. This effect is due to the residual unreacted monomer which swells the polymer and acts as a bonding agent.

## Characterization

The reduced specific viscosities of the polymers were determined at 20°C on chloroform solutions, containing 2 g of polymer per liter of solution.

## RESULTS AND DISCUSSION

The anionic polymerization of $\alpha$-methylstyrene in pure hydrocarbons is very slow, due to the fact that both the initiator and active ends are present as unreactive clusters of ion pairs. This is shown by the fact that the addition of a catalytic amount of butyllithium to a solution of monomer in heptane does not produce the brown color of the $\alpha$-methylstyryl anion until minutes later and that it takes hours before the color reaches full strength. It has been shown, however, that even small amounts of ether solvents are sufficient to break up the organometallic aggregates and stabilize the ion pairs.[1]

The initiation rate is thereby greatly increased while there is no marked change in propagation rate. This same effect is observed when a polyvinyl ether is added to the monomer solution. Upon the addition of an initiator, the color of the $\alpha$-methylstyryl anion appears instantly and is completely developed in a few seconds. Again, the propagation rate does not change noticeably and the initiated solution remains essentially unchanged for hours before some insoluble polymer begins to settle out.

In order to increase the propagation rate, the slowly reacting contact ion pairs must be solvated. It has been known for some time that dipolar aprotic solvents have an accelerating effect on anionic reaction rates and that among these hexamethylphosphoramide is exceptionally reactive.[2] We have found that amounts of hexamethylphosphoramide equimolar to initiator are sufficient to produce a dramatic increase in polymerization rate. This observation has since also been reported by other investigators.[3]

The reaction becomes exothermic and the polymer separates out almost immediately. In the presence of the polyvinyl ether, however, it does not settle out as one mass but rather forms a uniform dispersion. To explain the stability of dispersions in hydrocarbons, Mackor has introduced the concept of entropic stabilization.[4] According to this theory, the dispersions are stabilized by the steric barrier of amphipathic polymers, i.e., poly-
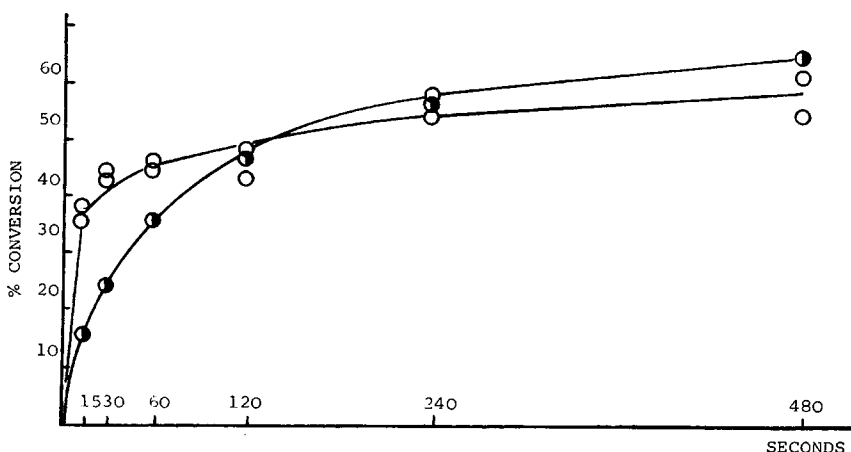
Fig. 1. Rates of conversion in typical dispersion polymerization of α-methylstyrene (40% monomer, 1 mole-% BuLi): (●) solution in benzene; (○) dispersion in heptane.

mers that have dual affinity for the dispersed phase and the medium. The ends of these molecules which are dissolved in the diluent lose translational freedom when two particles approach each other and this leads to entropic repulsion.

The role of the polyvinyl ether in the stabilization of a living poly-α-methylstyrene dispersion can be explained in these terms. As the α-methylstyrene chain grows with its carbanion solvated by the polyvinyl ether, it reaches a size where it is no longer soluble in the hydrocarbon medium. As it precipitates out, it agglomerates with other polymer particles until the ratio of polymer to interfacial agent is such that a further coalescence is prevented by entropic repulsion.

The necessary dual affinity of the polyvinyl ether is provided by the fact that it is soluble in hydrocarbons but remains anchored to the polymer particle through coordination with the polar reaction site. The lower limit of interfacial agent concentration is around 0.1% by weight of monomer. Below that, coarse particles are formed that do not remain in suspension. The molecular weight of the polymer is also critical. The commercial product that we commonly use has a molecular weight of about one million. A much lower molecular weight product, with a reduced specific viscosity of only 0.3, proved to be totally ineffective. It seems that this molecule no longer has the necessary length to form a steric barrier.

The rate of conversion in a typical dispersion polymerization of α-methylstyrene is shown in Figure 1. It is compared to a solution polymerization in benzene, carried out under identical reaction conditions. It is apparent that the dispersion affords a higher initial polymerization rate. At the time of the phase separation, which takes place in the first few seconds, the monomer becomes distributed between the diluent and the dispersed polymer phase. This creates a high local monomer concentration in the individual dispersion particles and consequently a high propagation rate.

When the monomer/polymer equilibrium within each particle has been established, further polymerization can only be sustained by diffusion of additional monomer from the diluent into the polymer and to the site of the reaction. We believe that this process is very slow and does not contribute noticeably to the polymerization within practical limits of time.

While the polymerization rate already indicates that the polymerization is more like a bulk than a solution polymerization, this is conclusively shown by experiments which, through a proper choice of reaction conditions, give polymer yields that are comparable to bulk polymerization yields. This is shown in Table III. The experimental conditions are explained in Tables I and II.

The anionic polymerization of $\alpha$-methylstyrene is an equilibrium reaction without termination or chain transfer. As a consequence of the low heat of polymerization, even at 0°C a substantial amount of monomer remains in equilibrium with the growing polymer chains. This equilibrium concentration is known and can be used to calculate the theoretically obtainable

TABLE II
Experimental Design

| Exp. no. | Variables[a] | | | |
|---|---|---|---|---|
| | A | B | C | D |
| 1 | − | − | − | − |
| 2 | + | − | − | + |
| 3 | − | + | − | + |
| 4 | + | + | − | − |
| 5 | − | − | + | + |
| 6 | + | − | + | − |
| 7 | − | + | + | − |
| 8 | + | + | + | + |

[a] See Table I.

TABLE III
Results

| Exp. no. | Yield, g | Yield, % | % sol.[a] | % blk.[b] | $\eta_{sp}$ |
|---|---|---|---|---|---|
| 1 | 44.9 | 49.5 | 81 | 55 | 0.36 |
| 2 | 67.2 | 55.9 | 79 | 62 | 0.47 |
| 3 | 79.7 | 88.0 | 144 | 97 | 0.60 |
| 4 | 85.8 | 71.5 | 101 | 79 | 0.33 |
| 5 | 63.3 | 69.8 | 114 | 77 | 0.60 |
| 6 | 91.4 | 75.8 | 107 | 84 | 0.55 |
| 7 | 64.5 | 71.2 | 117 | 79 | 0.38 |
| 8 | 92.0 | 76.2 | 108 | 85 | 0.31 |

[a] Yield calculated as if it were a solution polymerization of the same monomer concentration.

[b] Yield calculated as if it were a bulk polymerization with the same amount of monomer.

polymer yields for solution or bulk polymerizations. According to Mc-Cormick,[5] the equilibrium monomer concentration at 0°C is about 0.75 mole/l. Since the volume of the reactions in Table III is 0.4 liter, it follows that 0.3 moles, or 35.4 g, of monomer would remain unreacted if we ran the reaction as a solution polymerization. The maximum yield would therefore be 55.2 g at the lower and 85.1 g at the higher level of monomer concentration. As a bulk polymerization, the reaction volume would be either 100 or 133 ml and therefore 0.075 and 0.1 mole, or 8.85 and 11.8 g, of monomer would be left at equilibrium, giving maximum obtainable yields of 81.7 and 108.7 g at the two monomer concentration levels. These figures have been used to calculate the yields in columns 4 and 5 of Table III. It shows that all but two of the reactions gave yields that are greater than theoretically possible for a solution polymerization with the same monomer concentration and are close to those of bulk polymerizations. It is obvious, however, that bulk polymerizations with conversions this high would be intractable solids and hence quite impractical.

Another difference between solution and dispersion polymerizations is found in the dependence of the molecular weight on the initiator concentration. For anionic living polymerizations in solution, there is a simple relationship between these two. For a given yield of polymer (determined by temperature and monomer concentration), the molecular weight increases as the amount of initiator decreases. On the other hand, for a given amount of initiator, the molecular weight increases with the polymer yield. This holds no longer true in the case of dispersion polymerizations, as shown in Table III. In addition, Table IV shows that even a small change in the composition of the diluent has a pronounced effect on the polymerization. In a living dispersion polymerization the molecular weight is determined by the ratio of the components within each particle, which can apparently be quite different from the gross composition and responds to minor changes in the solvent.

The anionic dispersions of $\alpha$-methylstyrene are living polymers like the corresponding solution polymers. As such they can be used to prepare polymers with specific endgroups or as starting materials for block copolymers. The lower viscosity compared to a solution of the same polymer concentration greatly facilitates any subsequent chemical reaction.

TABLE IV

| Exp. no. | Yield, g | Yield, % | $\eta_{sp}$ |
|---|---|---|---|
| 1 | 8.9 | 49 | 0.60 |
| 2 | 9.2 | 51 | 0.62 |
| 3 | 8.8 | 49 | 0.76 |
| 4 | 11.8 | 65 | 0.39 |
| 5 | 12.7 | 70 | 0.27 |
| 6 | 11.7 | 65 | 0.36 |

Experimental conditions: 20 ml monomer; 0.07 g EDBM; 0.25 mole BuLi; 0.1 ml HMPA; 0°C; 30 min; exps. 1–3: pure heptane; exps. 4–6; 80/20 heptane/toluene.

The technique of anionic dispersion polymerization has been used to polymerize ring-substituted α-methylstyrenes such as 4-isopropenyltoluene, 4-isopropenyl-*o*-xylene, and others and can, of course, be extended to other anionic polymerization reactions. We find it, however, particularly useful in cases where low reaction temperatures and high monomer concentrations are necessitated by a low ceiling temperature.

## References

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