

Polymer Reactors and Molecular Weight Distribution: Part I. Free Radical Polymerization in a Continuous Stirred-Tank Reactor

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An investigation was made of the simulation of bulk and solution polymerization of styrene in a continuous stirred-tank reactor (CSTR). A theoretical model from the literature was used to predict conversion, molecular weight distribution (MWD), and molecular weight averages. The kinetic rate constants required to solve the model were also taken from the literature.

Styrene polymerizations were done at steady state in a laboratory-scale CSTR over a range of experimental conditions. The recently developed gel permeation chromatograph (GPC) was used to measure MWD and average molecular weights. Comparisons were made between the theoretically predicted and experimentally determined values.

The effect of solvent was included in the theoretical model but further investigation is necessary before the effects of thermal polymerization, viscosity, and mixing can be included. Where the latter effects were not important, good agreement was obtained between theoretical and experimental values.

Commercial production of a new polymer is generally preceded by several stages of laboratory-scale and pilot-plant production and testing to overcome problems associated with scale-up. Two objectives are to produce a product of a desired specification and to maximize its yield (or minimize its cost). The savings which could be realized by reducing pilot-plant production and testing provide a real incentive for investigating the design, simulation, and optimization of polymerization reactors.

Considerable work has been done on the theoretical description of polymerization reactors (1 to 14), but little experimental work has been done to check the theoretical models (10 to 14), due, until recently, to the lack of a rapid technique for measuring molecular weight distribution. The object of this investigation was to test the validity of a theoretical model for the bulk and solution polymerization of styrene.

This investigation is concerned with the simulation of a bench-scale, continuous, stirred-tank reactor (CSTR) in which monomer conversion and polymer molecular weight distribution (MWD) were used as criteria of simulation. Conversion was chosen since it is a measure of yield and MWD was chosen since many of the important physical properties of the polymer are determined by it. The solution polymerization of styrene (benzene as solvent) was chosen for study since its reaction mechanism has been relatively well established at low conversions (15) and

the required rate constants are available in the literature (15 to 23).

The mass balance equations were solved to predict conversion and MWD. Experimental polymerizations in a CSTR over a range of reaction conditions yielded experimental conversions and MWD's which were compared with the theoretical results.

The recently developed gel permeation chromatograph (GPC) (24 to 27) was used to measure molecular weight distribution. This relatively rapid technique and the availability of a high-speed digital computer (IBM 7040) for solving the theoretical model have made this investigation feasible.

This investigation is part of a larger study, which includes development work on gel permeation chromatography and polymerization studies in batch reactors (28).

THEORY

In the development of the theoretical model the assumptions made were: mixing is perfect, reactor is operating at steady state, k_p and k_t are independent of polymer radical chain length, termination is by combination only, all radicals have the same reactivity, and no density change occurs in the reactor.

The kinetic mechanism selected for the theoretical model is from Bamford et al. (15). It includes transfer to monomer and solvent.

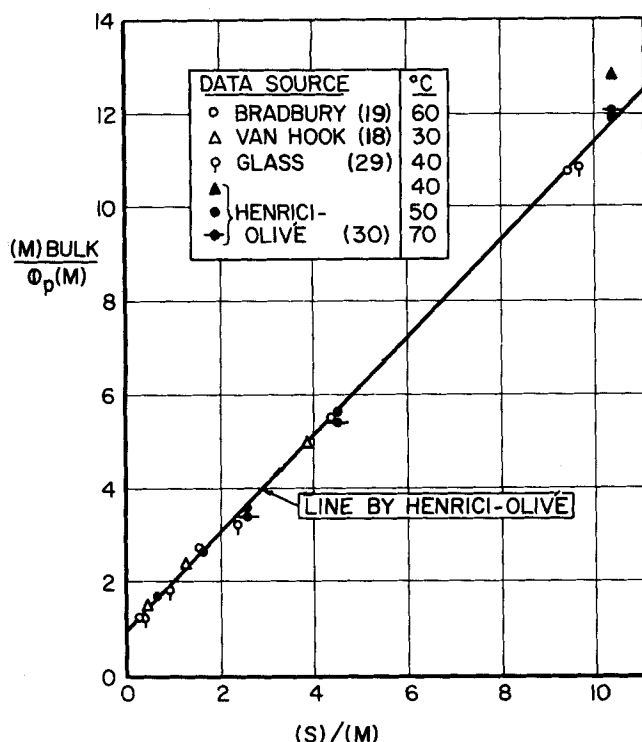


Fig. 1. Correlation of solvent correction factor Φ_p with solvent concentration.

The required kinetic rate constants were extracted from the literature (15 to 23). The Arrhenius equations for these constants are

$$\begin{aligned}
 k_p &= 1.051 \times 10^7 \exp(-3,557/T) \quad (20 \text{ to } 22) \\
 k_t &= 1.255 \times 10^9 \exp(-844/T) \quad (20 \text{ to } 22) \\
 k_d &= 1.58 \times 10^{15} \exp(-15,500/T) \quad (16) \\
 k_f &= 2.31 \times 10^6 \exp(-6,377/T) \quad (20) \\
 k_{fs} &= 9.95 \times 10^{10} \exp(-11,000/T) \quad (15)
 \end{aligned}$$

For the catalyst efficiency f , an approximate average of the literature values was taken as 0.60.

The effect of solvent on the polymerization kinetics of styrene has been investigated by several workers (18, 19, 29, 30). Henrici-Olivé and Olivé developed a hypothesis in which they assumed that solvent affected the propagation rate constant k_p but not the termination rate constant k_t (32). From their experimental data (30) they obtained a solvent correction factor Φ_p which is plotted in Figure 1. The data of several other workers (18, 19, 29) are also plotted and good agreement is indicated.

The present authors found that application of Φ_p to either k_p or k_t yielded the same results for conversion and

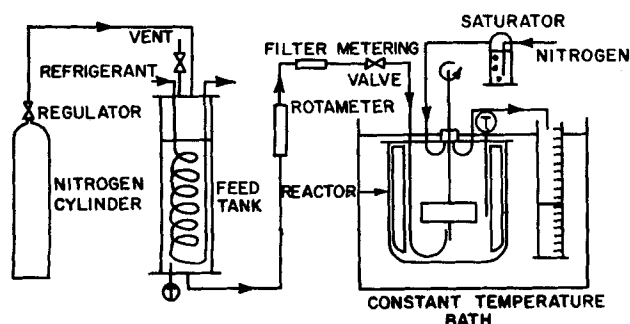


Fig. 2. Schematic diagram of polymerization apparatus.

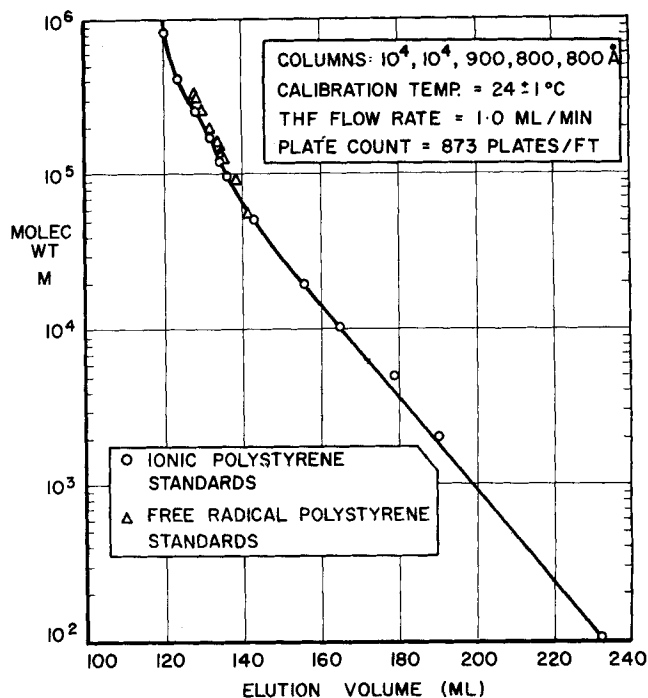


Fig. 3. Calibration curve for gel permeation chromatograph.

MWD. Since no proof of the hypothesis is yet available, the correction was applied to k_t . Since k_t must also be corrected for viscosity, this approach simplifies the kinetic model but does not change the predicted results.

The theoretical model for free radical polymerization in a CSTR has been derived by previous workers (1, 5, 7, 41). The steady state model involves solution of the algebraic mass balance equations for monomer, catalyst, and each of the live and dead polymer species. The present model differs from previous models in that it incorporates the above-mentioned solvent correction.

EXPERIMENTAL CONVERSION (PERCENT)

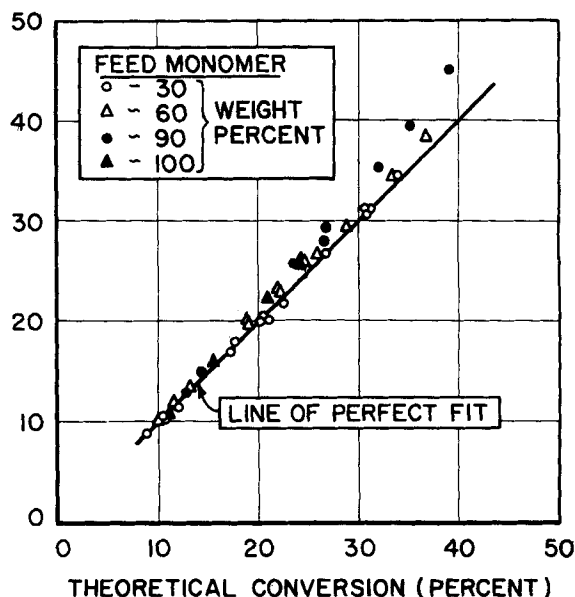


Fig. 4. Comparison of experimental and theoretical conversion.

EXPERIMENTAL -THEORETICAL CONVERSION (PERCENT)

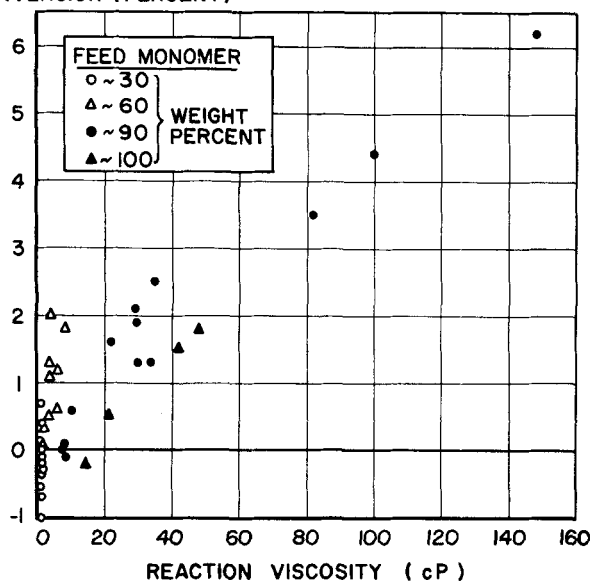


Fig. 5. Effect of reaction viscosity on the deviation between experimental and theoretical conversion.

EXPERIMENTAL PROCEDURE

Reagents and Analytical Techniques

The catalyst, 2, 2'-azobisisobutyronitrile* (Eastman Organic Chemicals), was recrystallized once or twice from absolute methanol. The benzene (Fisher certified grade, thiophene free) was used without further purification, except for one run in which it was distilled. Inhibitor-free styrene was provided by Polymer Corporation, Sarnia, Ontario. It was taken from the overhead stream of their styrene still and was stored at less than 0°C. under nitrogen until used. In one run it was vacuum distilled before use.

Apparatus and Procedure

A schematic diagram of the polymerization apparatus is shown in Figure 2. The reactor diameter and height were 100 and 125 mm., respectively. The impeller (four-blade turbine type) diameter and width were 64 and 12.5 mm., respectively. The four baffles were located at 90-deg. intervals and had a width of 10 mm.

The reactor feed components—styrene, benzene, and AIBN—were premixed under nitrogen before they were added to the refrigerated feed tank. The feed flow was controlled to $\pm 3\%$.

The reactor was run essentially full. Four reactor volumes of feed were passed through the reactor to reach steady state, although there was generally no significant change in the effluent after three reactor volumes. Reaction temperature was maintained constant by a temperature-controlled bath. The stirrer speed was kept constant at 300 rev./min.

Polymerizations were done at three levels of catalyst concentration (0.2, 0.3, and 0.4 wt. %), four levels of monomer concentration (30, 60, 90, and 100 wt. %), and three levels of temperature (65°, 75° and 85°C.).

The conversion of the styrene to polystyrene was measured by the usual precipitation technique (31).

The molecular weight distributions of the precipitated polystyrene samples were measured with a GPC. The GPC and its operation have been adequately described in recent publications (24 to 27). In this investigation five columns in series were used, with maximum rated porosities of 10⁴, 10⁴, 900, 800, and

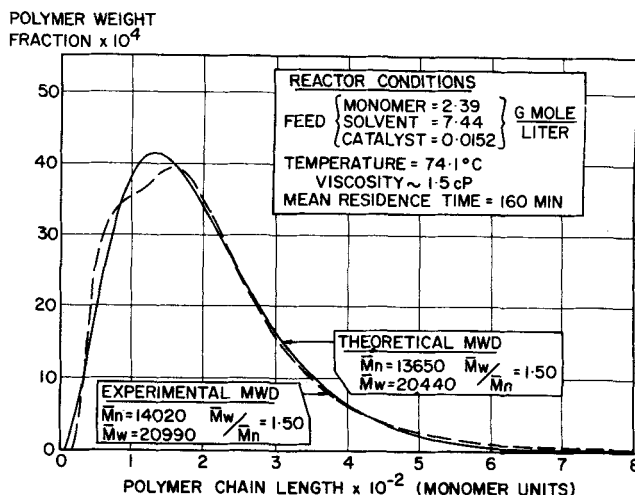


Fig. 6. Comparison of theoretical and experimental MWD at high solvent concentration and low reaction viscosity.

800 Å. in the direction of solvent flow. The GPC solvent was tetrahydrofuran (THF) flowing at 1.0 ml./min. The operating temperature was $24^\circ \pm 1^\circ\text{C}$. One milliliter of sample solution (0.5 wt. % polystyrene in THF) was injected for each analysis.

The GPC was calibrated with ionically polymerized and free radical polymerized polystyrene standards. The calibration curve, shown in Figure 3, indicates good agreement between the two types of standards.

To obtain absolute MWD's it was necessary to correct the GPC chromatogram for the spreading due to axial dispersion in the GPC columns (33 to 36). Computer programs for this purpose were provided by L. H. Tung, Dow Chemical Company, Midland, Michigan. The required GPC resolution factor was determined with the reverse flow technique of Tung et al. (35).

RESULTS AND DISCUSSION

In this section the theoretical and experimental results for conversion, MWD, and molecular weight averages are compared and discussed. Four important considerations in the discussion of the results are the effects of solvent, thermal polymerization, viscosity, and mixing.

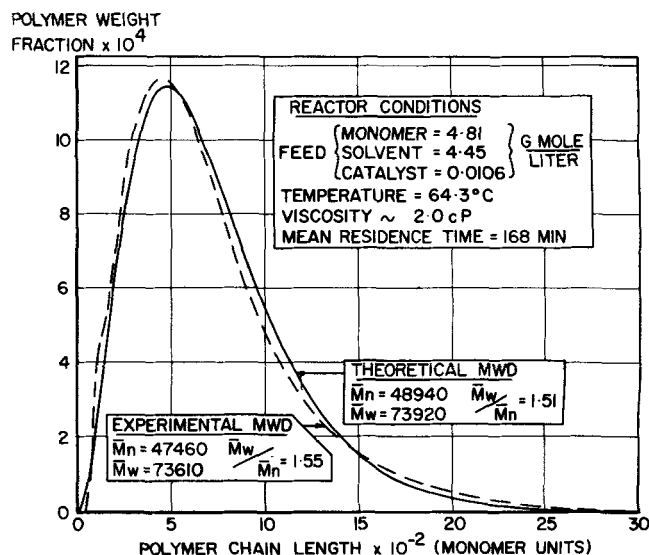


Fig. 7. Comparison of theoretical and experimental MWD at intermediate solvent concentration and low reaction viscosity.

* The Chemical Abstracts name is 2, 2'-azobis (2-methylpropionitrile). The abbreviation AIBN will be used.

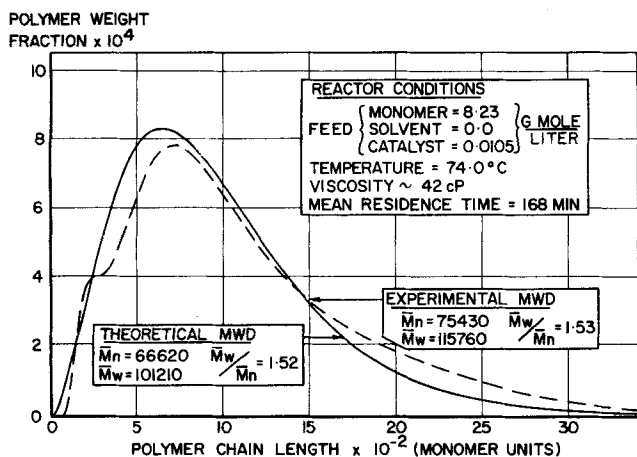


Fig. 8. Comparison of theoretical and experimental MWD at zero solvent concentration and intermediate reaction viscosity.

Solvent

The comparison of experimental and theoretical conversions in Figure 4 shows good agreement at the high solvent concentration over the entire conversion range studied. Similarly the MWD's (Figures 6 and 7) and the number and weight averages (Figures 11 and 12) show good agreement at the high solvent concentrations. Before the solvent correction was applied the agreement was poor.

Thermal Polymerization

Thermal polymerization was not included in the theoretical model since there is still some doubt as to its exact mechanism (15) and reported values for the thermal initiation rate constant show considerable variation.

The theoretical conversions shown in Figure 4 were corrected for thermal polymerization according to the data of Roche and Price (31). The mean residence time and the approximate monomer concentration at steady state were used to calculate the thermal polymerization contribution. In most cases the correction for thermal polymerization improved the agreement between theoretical and experimental conversions.

Although the theoretical MWD's shown in Figures 6 to 10 and the theoretical averages shown in Figures 11 and 12 do not include thermal polymerization, its contribution

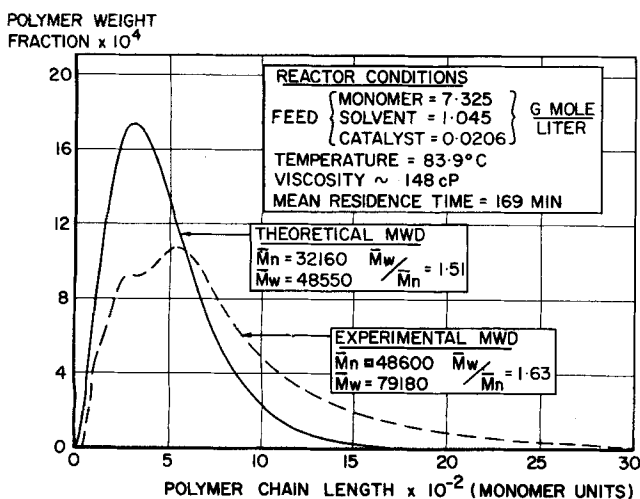


Fig. 9. Comparison of theoretical and experimental MWD at low solvent concentration and high reaction viscosity.

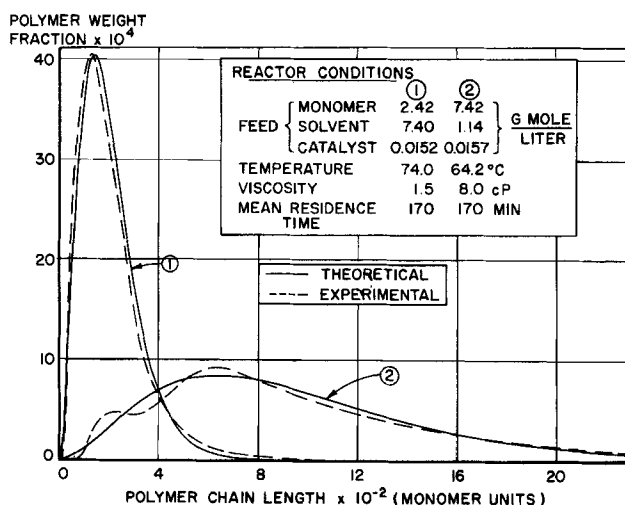


Fig. 10. Comparison of theoretical and experimental MWD at high and low solvent concentrations and low reaction viscosities.

at the lower temperatures is small. A separate study of pure thermal polymerization and its MWD will be conducted to determine the correct mechanism and rate constants. When these are available it will be included in the theoretical model.

The cause of the small secondary peaks in some of the MWD's (Figures 8 to 10) is not known but they may be due to slight mathematical instabilities in Tung's method of correcting for the imperfect resolution of the GPC (34 to 36). Other methods of correcting (33, 42) will be investigated to establish the cause of these secondary peaks.

Viscosity

Reactor viscosity (Newtonian), measured with a Brookfield viscometer, was found to have a significant effect on the difference between experimental and theoretical con-

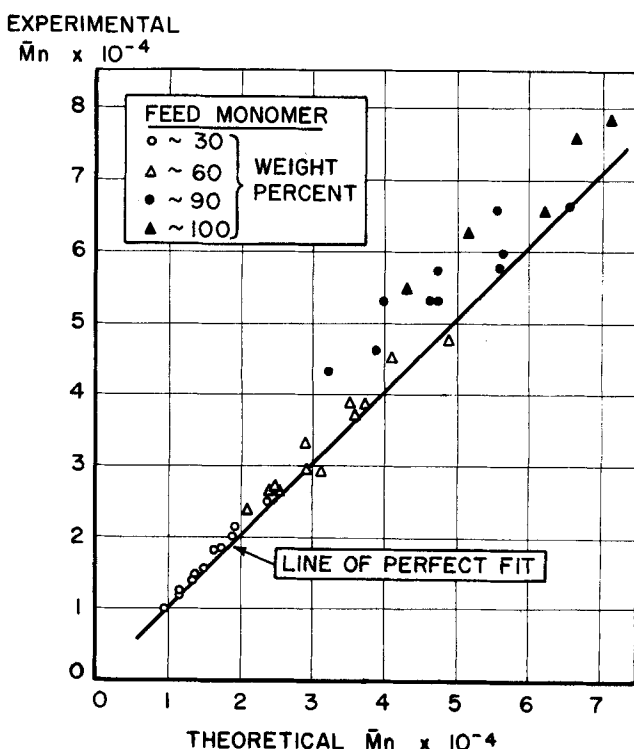


Fig. 11. Comparison of experimental and theoretical number average molecular weight.

EXPERIMENTAL

$\bar{M}_w \times 10^{-4}$

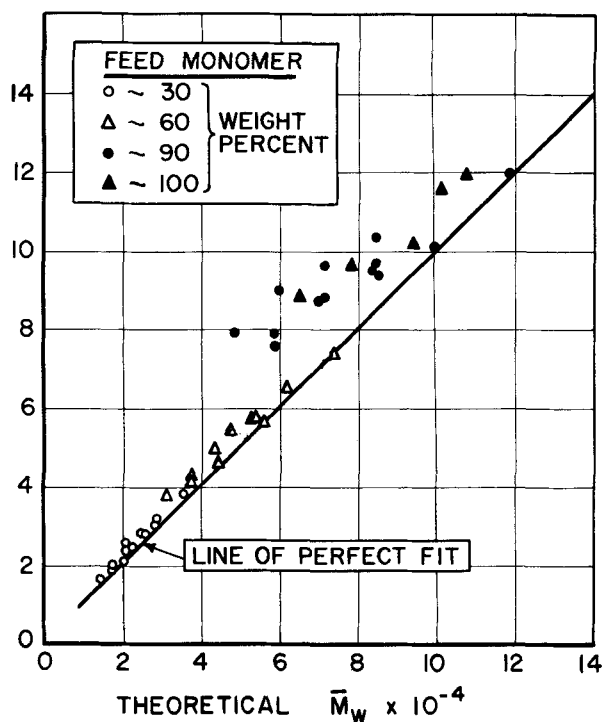


Fig. 12. Comparison of experimental and theoretical weight average molecular weight.

versions, as shown in Figure 5. The effect of viscosity is also apparent in the experimental MWD's (Figures 8 and 9) and molecular weight averages (Figure 13). The experimental values are shifted to the high molecular weight side of the theoretical values. This is due to the gel or Trommsdorf effect (37) in which the termination rate constant is reduced due to the decreased mobility of the polymer free radicals in the viscous reaction mixtures. Hence, the probability of propagation (15) is increased and the polymer radicals grow longer before terminating.

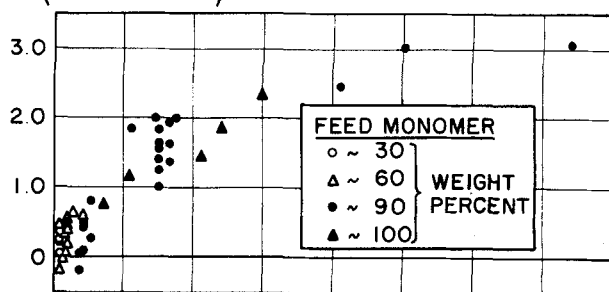
An additional viscosity effect may be operative in the slight viscosity dependence of the experimental \bar{M}_w/\bar{M}_n ratio (Figure 13). Not only should the mobility of a polymer free radical depend upon viscosity, but also upon its molecular weight. The probability of propagation of the larger polymer free radicals should be increased more than that of the smaller radicals (that is, k_t should decrease with increasing chain length). Hence, a spreading of the MWD would be expected as reflected in an \bar{M}_w/\bar{M}_n greater than the theoretically predicted 1.50 to 1.52. In the theoretical model it was assumed that the rate constants were independent of radical chain length.

Figure 10 illustrates that good agreement is obtained for broad or narrow MWD's provided the viscosity is less than about 10 centipoise.

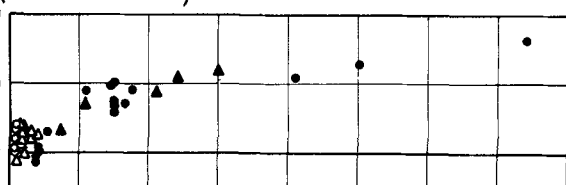
The viscosity effect was not included in the theoretical model since no quantitative relationship among k_t , f , and viscosity was available. Harada et al. (13, 14) developed a relationship among k_t , k_p , f , and polymer weight fraction, based upon their experimental conversions in a batch reactor. However, viscosity would appear to be a better correlating basis, since two samples of identical polymer weight fraction could have quite different viscosities, depending on their MWD.

An approximate model by Rabinowitch, describing the diffusion control of second-order reactions, has been con-

$\Delta \bar{M}_w \left(\frac{\text{EXPERIMENTAL}}{\text{THEORETICAL}} \right) \times 10^{-4}$



$\Delta \bar{M}_n \left(\frac{\text{EXPERIMENTAL}}{\text{THEORETICAL}} \right) \times 10^{-4}$



$\Delta (\bar{M}_w/\bar{M}_n) \left(\frac{\text{EXPERIMENTAL}}{\text{THEORETICAL}} \right)$

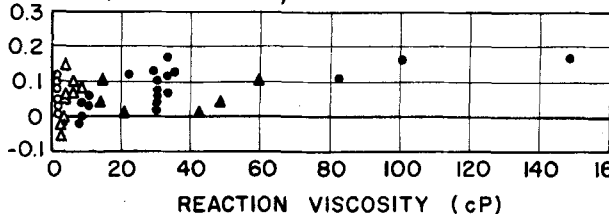


Fig. 13. Effect of reaction viscosity on the deviation between experimental and theoretical weight and number average molecular weights and their ratio.

sidered by Vaughan (38) and Robertson (39) to describe the gel effect in vinyl polymerization. Vaughan estimated the critical viscosity at which termination should become diffusion controlled as 200 centipoise. The results in Figures 5 and 13 indicate that termination is affected at much lower values of viscosity.

Future work will be aimed at establishing a quantitative relationship for the effect of viscosity on conversion and MWD.

RESPONSE

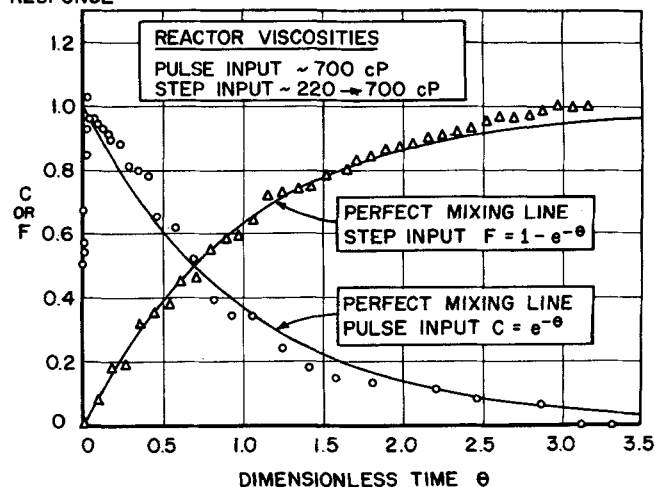


Fig. 14. Tracer response of the polymerization reactor to a pulse input and a step input.

MIXING

The assumption of perfect mixing was made in developing the theoretical model. To confirm the validity of this assumption, tracer response tests were done in the polymerization reactor using pulse and step inputs (40) in glycerine or a glycerine-and-water mixture.

The responses, as measured by refractive index change, are shown in Figure 14. They indicate a reasonably close approach to perfect mixing at viscosities considerably higher than those encountered in the polymerization runs. However, the responses cannot distinguish between perfect mixing on a molecular scale (micromixing) and mixing on a macroscopic scale (macromixing or segregated flow) (40).

Calculations by Tadmor and Biesenberger (6) show that micromixing and segregated flow in a steady state polymerization reactor give the same conversion if the polymer chains are long. The long-chain condition is fulfilled in this investigation. Therefore the deviations between theoretical and experimental conversions in Figures 4 and 5 are attributed only to a viscosity or gel effect.

For chain addition polymerization with termination, their calculations also show a broadening of MWD and an increase in \bar{M}_n , \bar{M}_w , and \bar{M}_w/\bar{M}_n for segregated flow. Viscosity would have the same effect but would also shift the peak of the MWD to a higher molecular weight, as was observed in Figures 8 and 9. It should be noted that not only does increasing viscosity decrease k_t , but it also increases the probability of segregated flow. The two effects cannot be distinguished from the results of this investigation.

CONCLUSIONS

The theoretical CSTR model for styrene polymerization simulated the behaviour of a bench-scale reactor at viscosities less than about 10 centipoise. The effect of solvent on the reactor output was accurately represented in the theoretical model by data taken from the literature. For accurate simulation over a wide range of experimental conditions, the effects of thermal polymerization, viscosity, and mixing must be accounted for.

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NOTATION

- C = tracer response to an idealized pulse input, dimensionless
 F = tracer response to a step input, dimensionless
 f = catalyst efficiency, fraction of catalyst free radicals that initiate polymer molecules
 k_d = reaction rate constant for catalyst decomposition, sec.^{-1}
 k_f, k_{fs}, k_p, k_t = reaction rate constant for transfer to monomer, transfer to solvent, propagation, and termination, respectively, $\text{liter}/(\text{g.-mole})(\text{sec.})$
 M = monomer molecule or monomer concentration, g.-mole/liter
 M_{bulk} = bulk monomer concentration, g.-mole/liter
 \bar{M}_n = number average molecular weight

- \bar{M}_w = weight average molecular weight
 S = solvent concentration, g.-mole/liter
 T = temperature, $^{\circ}\text{K.}$
 θ = residence time of reactor contents, dimensionless
 Φ_p = correction factor for solvent effect, dimensionless

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