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Continuous Production of Polystyrene in a Tubular Reactor: Part I

An experimental analysis of the bulk polymerization of styrene initiated by azobisisobutyronitrile was carried out in a tubular reactor.

The experiments performed in a 2.362-cm I.D., 6-meter long jacketed reactor showed that: (1) it was feasible for a tubular reactor to produce acceptable quality polystyrene for industrial purposes; (2) the quality of the polymer product was reproducible at any time; (3) it was technically feasible for the tubular reactor to replace the stirred-batch kettles as the preliminary stage in the polystyrene manufacturing process, and (4) radial temperature gradients were not a problem for reactor operation.

J. P. A. WALLIS
R. A. RITTER
and
H. ANDRE

The Department of Chemical Engineering
The University of Calgary
Calgary, Alberta T2N 1N4 Canada

SCOPE

Over 50% of the polystyrene manufactured comes from bulk polymerization processes (Bishop, 1971). The major manufacturing process is usually a two-stage process (Boundy et al., 1970), the first stage (stirred-batch kettles) takes the conversion of bulk monomer to 30 to 40% completion. Upon reaching this level of conversion, the greatly increased viscosity of the polymer solution becomes a serious hindrance to the mixing of the polymer syrup resulting in poor control of temperature and, hence, the molecular weight distribution. At the same time there is an increased energy requirement for the mixer. This impairs the economics of the process. Therefore, the polymer syrup is transferred to processing equipment such as screw extruders, plate and frame presses, or temperature controlled towers, which are more suited to handle the viscous mixture.

Despite these problems the stirred kettle is still preferred to the tubular reactor (Bishop, 1971). The stated reason for the lack of use of the tube is the anticipated large temperature gradient across the diameter which causes uneven polymerization rates resulting in poor control of the final product molecular weight distribution.

The results given here show that a tubular reactor can produce industrial grade polystyrene by the free-radical polymerization of bulk styrene initiated by azobisisobutyronitrile (AIBN) in a continuous production tubular reactor. Part 2 of this study considers the modeling and design aspects in relation to industrial application.

CONCLUSIONS AND SIGNIFICANCE

This study showed that: (1) a tubular reactor could produce acceptable quality polystyrene for industrial purposes, (2) the polymer product quality was reproducible, (3) it was technically feasible for a tubular reactor to become the first stage in the manufacture of polystyrene, and (4) radial temperature gradients need not be a problem for reactor operation.

DESCRIPTION OF THE PROCESS

Initiator System

The initiator charge was prepared by dissolving AIBN in toluene to make a 0.325 molar solution (0.346 mole of AIBN dissolved in one liter of toluene at 25°C). A 0.325 molar AIBN solution was the maximum concentration that could be used without AIBN precipitation in the initiator pump since: (1) AIBN solubility in toluene was strongly temperature dependent, and (2) the ambient temperature was nominally 23°C. Toluene was chosen as the solvent for AIBN because it was styrene compatible. The solubility curve for AIBN in toluene may be found in Wallis (1973).

The initiator was injected into the feed stream at the reactor inlet with the aid of a piston pump which was designed such that the piston could be inserted into a cylinder at a controlled speed, thereby displacing AIBN solution from the cylinder. Piston displacement was 6.97 cc/in. of travel.

In order to ensure a clean pumping system, the pump was flushed with toluene with the piston completely in the cylinder. Flushing was followed by vacuum evacuation of the cylinder, then by introduction of the new initiator charge.

Plant Description and Operation

The process flow and instrumentation diagram is shown in Figure 1. The tanks were pressurized with helium. With 20 ppm impurities, helium was the purest of the readily available inert gases, and it had the lowest solubility in styrene and toluene. The Ostwald coefficient was 0.0225 cc gas/cc liquid (Wallis, 1973). In contrast, nitrogen was 10 times more soluble in styrene and toluene while having 200 ppm impurities, mostly oxygen, a detriment to styrene polymerization (Boundy et al., 1970). Styrene from the supplier contained para-tertiary-butylcatechol (p-tbc) inhibitor. This was removed by an easily serviceable in-line stainless steel column filled with white drierite. The drierite was expected to remove over 90% of the p-tbc and most of the water (Boundy et al., 1970). Chemical reaction in the heat exchanger before the reactor removed the remaining inhibitor (Wallis, 1973).

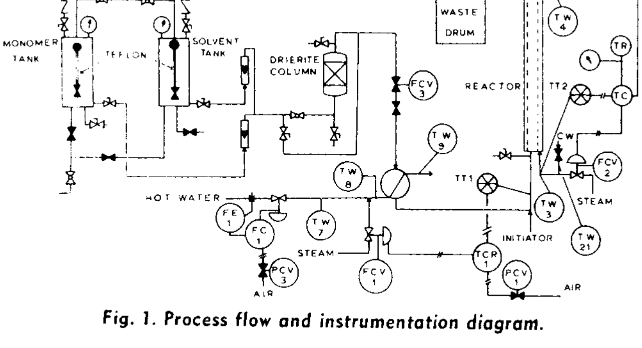


Fig. 1. Process flow and instrumentation diagram.

The reactor, fabricated from a six-meter long type 316 stainless steel tube 2.54-cm O.D. and 2.362-cm I.D. (1-in. O.D., B.W. Gage 20), was enclosed by a copper cooling jacket, 3.493-cm O.D. and 3.213-cm I.D. (1⅜ in. O.D., 0.055-in. wall thickness). Welded to each end of the reactor were 316 stainless steel flanges, the upper flanges being tapered from 2.362 cm to a ⅛-in. NPT over a distance of 1.91 cm to eliminate a potential dead zone at the reactor exit. Cooling water, flowing concurrently with the process stream, was used to control the reactor wall temperature.

Before commencing an experiment the monomer tank was pressurized to 3 atm. and the reactor wall temperature was adjusted to the desired position. The styrene flow rate was adjusted to 2500 to 3000 ml/hr. to completely purge the toluene from the drierite column and the heat exchanger. With liquid flowing, the reactor inlet temperature was set to the desired position. After these preliminary operations, the initiator solution was introduced to the pump. After the purging was completed, the desired styrene flow rate was set and experimentation commenced.

Initiator piston travel, tank pressure, and styrene flow rates were noted at regular intervals for approximately three residence times. This was the assumed length of time needed for the reactor to reach steady state. The calculations forming the basis for this assumption are presented in Wallis (1973). After the first two residence times, a styrene sample was drawn at the outlet of the drierite column to check the inhibitor removal rate. The inhibitor reading for the sample was compared to that for the styrene in the storage tank. The inhibitor determination procedure was adapted from that given by Boundy et al. (1970). The first product sample was taken 30 min. before plant shutdown and a second one just prior to experiment termination. These samples were analyzed immediately for polymer content in accordance with the analytical method of Boundy et al. (1970). Sometimes a third sample was taken at plant shutdown and it was inhibited with p-tbc. The third sample was not analyzed for polymer content, but was occasionally used to verify gel permeation chromatography results on the second sample. In all cases the reator was in operation for at least eight hours before samples were taken.

When all samplings were completed, the shutdown of the plant was commenced. The two temperature control systems and the initiator pump were turned off, then toluene replaced the styrene as the flowing medium for the purpose of flushing the system of the polymer syrup. The toluene purging was continued for about 2.5 reactor volumes, which was adequate to clear the system of polymer material.

A sample of the polystyrene was dissolved in toluene and pumped through a gel permeation chromatograph to obtain the molecular weight distribution of the polymer. A sample chromatogram, shown in Figure 2, indicated the presence of a small quantity of styrene. The percent conversion figures were corrected by ratioing the two areas.

Molecular Weight Analysis—Gel Permeation Chromatography

Each of the two chromatographic columns on the Waters 501 chromatograph used in this study consisted of a pair of 0.61-m long 0.9525-cm diameter stainless steel tubes. Each column was packed with a different porosity styragel. The nominal exclusion molecular weight limits of the column were 2×10^5 and 6×10^5.

The calibration curve for the chromatograph used in this study is shown in Figure 3, in which molecular wieght is plotted against time, instead of counts (1 count —5 ml), since all standards were analyzed at the same flow rate, 1.4114 ml/min. (Wallis, 1973).

Inspection of the calibration curve (Figure 4) shows that there is a sharp upswing in molecular weight for elution times of 32 min. or less, and thus it is difficult to assign a calibration molecular weight at the 32-min. time. The exclusion molecular weight is used as the calibration molecular weight at the 32-min. time and is obtained by finding the molecular weight at the point where the extrapolated linear curve meets the extrapolated vertical portion of the calibration curve, as shown by the dotted lines in Figure 3. For this study it is 375,000.

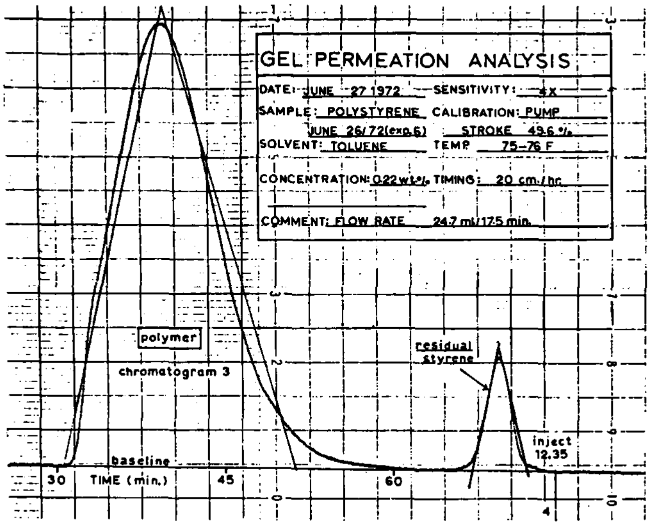
This insensitivity of the chromatograph to high molecular weights resulted in low experimental values of $\overline{M}_z$ (see discussion of results). The reason is the M_i^2 terms in the definition of $\overline{M}_z$ are more sensitive to high molecular weights.

Accuracy of GPC

Since the chromatograph must be calibrated against known standards, the accuracy for GPC studies is dependent on the accuracy of the standards (determined by osmometry and light scattering) and the reproducibility of the instrument.

Alliet (1969) compared GPC molecular weights with osmometry and light scattering values. He concluded GPC $\overline{M}_n$ values were consistently low and $\overline{M}_w$ values consistently high and by approximately the same amount when compared with osmometry and light scattering results. The standard deviations of the duplicate analyses for osmometry and light scattering were 3% and 2%, respectively.

Other studies by Nester/Faust and Dupont obtained comparable results. In general, the expected GPC reproducibility was expected to be 5-10% of a molecular weight.



GEL PERMEATION ANALYSIS
DATE: JUNE 27 1972 SENSITIVITY: 4X
SAMPLE: POLYSTYRENE CALIBRATION: PUMP
JUNE 26/72(exp.6) STROKE 49.6 %
SOLVENT: TOLUENE TEMP 75–76 F
CONCENTRATION: 0.22 wt.% TIMING: 20 cm./hr.
COMMENT: FLOW RATE 24.7 ml/17.5 min.

Fig. 2. Chromatogram of polymer from experiment 6.

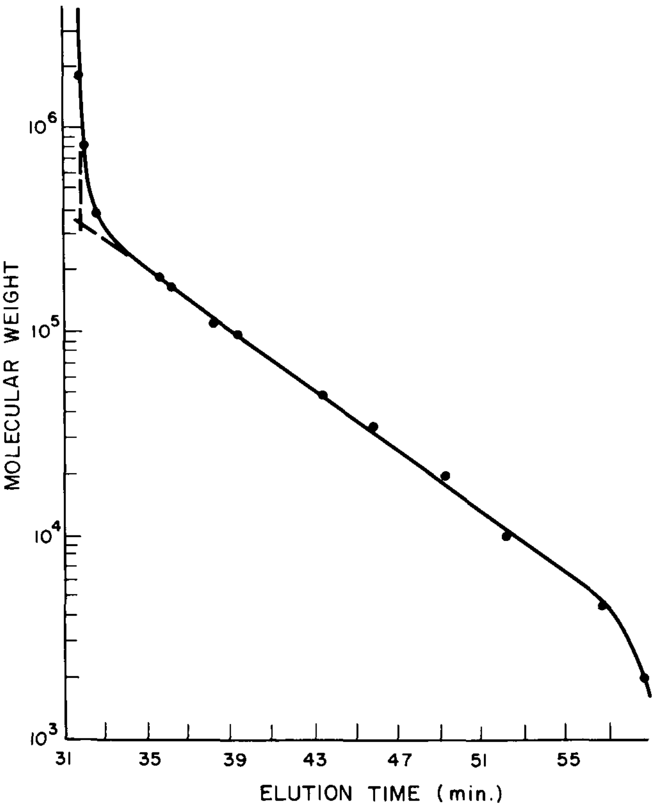
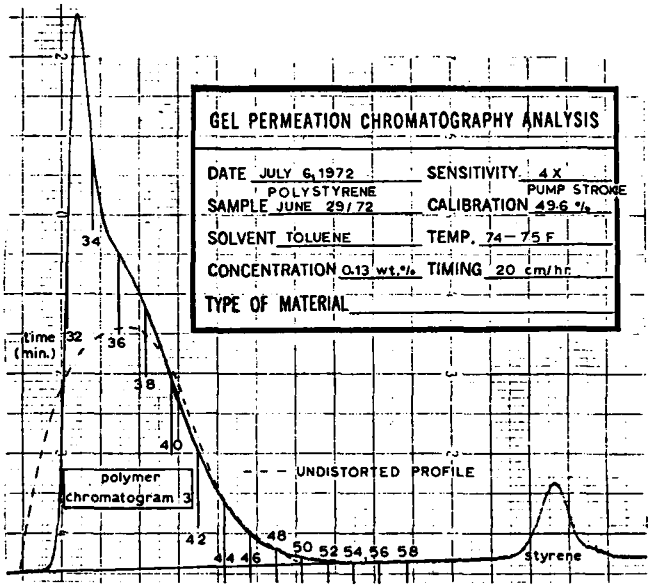


Fig. 3. Molecular weight calibration curve for GPC.



GEL PERMEATION CHROMATOGRAPHY ANALYSIS
DATE JULY 6, 1972 SENSITIVITY 4 X
SAMPLE POLYSTYRENE JUNE 29/72 CALIBRATION PUMP STROKE 49.6 %
SOLVENT TOLUENE TEMP. 74–75 F
CONCENTRATION 0.13 wt.% TIMING 20 cm/hr.
TYPE OF MATERIAL

Fig. 4. Chromatogram of polymer from experiment 8.

GPC Peak Broadening

The phenomenon of the GPC prediction of a broader molecular weight distribution compared with the actual distribution is called *instrumental spreading*. This spreading is caused by imperfect instrument resolution and diffusion effects.

While there are numerous publications on the correction for instrumental spreading, initial procedures require reverse flow chromatograms of the calibration standards. Instrument limitations do not allow reverse flow chromatograms to be run on the Waters 501. This is not serious as new correction methods do not require one.

Hamielec and Ray (1969) have developed an analytical

TABLE 1. REACTOR EXPERIMENTAL CONDITIONS

Experiment	T_w (°K)	Residence time,⁽²⁾ (s)	C_{I0}⁽³⁾ m/l	C_{m0}⁽³⁾ m/l
1	353	8106	0.00447	7.99
2	358	8106	0.00447	7.99
3	353	8106	0.00447	7.99
4	353	8032⁽¹⁾	0.00853	7.88
5	358	8032	0.00853	7.88
6	363	4309	0.00458	7.98
7	363	5283	0.00359	8.01
8	348	9569	0.00174	8.06
9	353	8106	0.00447	7.99

(1) The drierite was replaced prior to experiment 4.

(2) The residence times were based on the styrene density at 30°C.

(3) C_{I0} and C_{m0} were evaluated at the reactor inlet temperature 353°K for all experiments.

method with which experimental GPC results may be dispersion corrected if the spreading is Gaussian. Gaussian spreading is the usual assumption made by many workers; in particular, it is used by Tung and Runyon (1969) whose method is described later. The results of Hamielec and Ray for the expressions of the ratios of the corrected to the uncorrected GPC results are

$$\frac{\overline{M}_n(h)}{\overline{M}_n(\infty)} = \exp(D_2^2/4h) \tag{1}$$

$$\frac{\overline{M}_w(h)}{\overline{M}_w(\infty)} = \exp(-D_2^2/4h) \tag{2}$$

$$\frac{\overline{M}_z(h)}{\overline{M}_z(\infty)} = \exp(-3D_2^2/4h) \tag{3}$$

$$\frac{\overline{D}_n(h)}{\overline{D}_n(\infty)} = \exp(-D_2^2/2h) \tag{4}$$

More general correction methods are available if the dispersion is skewed, Balke and Hamielec (1969). Skewing is only important for molecular weights over 500,000 (Alliet, 1969).

The Gaussian assumption expressions defined by Equations (1) to (4) were used for two reasons:

1. High molecular weight species are not being manufactured, and
2. There is a 400,000 molecular weight resolution limit on the columns of the chromatograph used in this study, and therefore it is impossible to correct for the dispersion effects of high molecular weights.

Determination of the Dispersion Parameter *h*

The method of correction due to Balke and Hamielec (1969) is simple and direct. Rearrangement of Equation (4) for the polydispersity ratios yields the following expression for the parameter h:

$$h = \frac{D_2^2}{2[\ln(\overline{D}_n(\infty)) - \ln(\overline{D}_n(h))]} \tag{5}$$

The dispersity ratio $\overline{D}_n(\infty)$ is obtained from the chromatogram of the standard. Since the standards from the supplier include values for $\overline{M}_n$ and $\overline{M}_w$, the polydispersity ratio $\overline{D}_n$ can be calculated. Assuming $D_n = D_n(h)$, the parameter h can be obtained from Equation (5). The greatest error in this method results from the determination of $\overline{D}_n(\infty)$. This determination is difficult because of the almost monodisperse nature of the standards. A small error in measuring the peak heights at the tail of the chromatogram can cause inaccurate values of $\overline{D}_n(\infty)$.

The method of correcting the chromatograms developed by Tung and Runyon (1969) involves curve fitting the leading half of the chromatogram by a normalized Gaussian type function. Since the curves of the calibration standards are presumed to be Gaussian in shape, a dispersion correction can then be made. The function used to fit the chromatogram is

$$f(v) = \exp(-h_c(v - v_p)^2) \tag{6}$$

where v_p is the elution volume at the peak of the chromatogram. The parameter h_c is obtained by a least squares curve fit of the leading half of the chromatogram.

This curve fitting of the chromatogram is avoided by using a property of the normal curve. At one standard deviation the ratio of the ordinate to the maximum ordinate is

$$\frac{0.2420}{0.3989} = 0.607$$

Then $v - v_p$ is found from the chromatogram at the point where the ordinate is 0.607 of the maximum peak height; h_c is determined by equating $f(v)$ to $\exp(-0.5)$,

$$h_c = \frac{0.5}{(v - v_p)^2} \tag{7}$$

This greatly simplifies the method and avoids dubious measurements in the tail of the chromatogram.

In some cases h_c is not equal to the spreading parameter h and further corrections are required. For this study $h_c = h$. There is little difference between them, most of the scatter being attributable to error in reading the chromatogram.

The average value of h_c, for molecular weights under 400,000, is used in Equations (1) to (4) because of the ease and reliability in which it may be obtained. The value used for $D_2^2/(4h)$, the correction parameter in Equations (1) to (4), is 0.041 (Wallis, 1973).

Experimental Conditions

Experimental conditions of high reactor wall temperature and initiator concentration are considered to be a sufficiently severe test of the reactor's capability to produce adequate quality polystyrene since the rate of reaction and temperature gradients are high. Since most industrial grade polymers ($\overline{M}_w > 150{,}000$) are made under conditions less severe than those considered above, the reactor can be used to manufacture industrial grade polymers (see Table 1 for experimental conditions).

A reasonable set of conditions for reactor testing was considered to involve experimental conditions resulting in weight average molecular weights in the 80,000 to 140,000 range. However, in one experiment the production of polymer with an average molecular weight over 200,000 demonstrated the reactor capability for making high molecular weight polystyrenes. It should be noted that polymers with weight average molecular weights over 150,000 were not amenable to analysis by the available GPC. Figure 4 shows how the insensitivity of the chromatograph skewed the chromatogram for the high molecular weight experiment (experiment 8).

Experimental Error

Reproducibility of conversion and molecular weights was determined by repeating the first experiment on two occasions, as the third and the last (ninth) in the experimental series. That is, experiments 1, 3, and 9 were equivalent. The experimental conversions, presented in Table 2, demonstrated this equivalence as well as the ability of the reactor to produce acceptable conversions of polystyrene.

The standard deviation of the conversions due to analytical technique and handling S_a was estimated by pooling all the standard deviations of each experiment. Experiment 8 was excluded since only one conversion was obtained. The standard deviation in conversion for each experiment was determined from two separate analyses. These eight standard deviations were pooled using the following expression:

$$S_a{}^2 = \frac{\sum_{j=1}^{9} (\overline{X}_1 - \overline{X}_2)_j}{2 \times 8} \quad (\text{excluding } j = 8)$$

The value of S_a was 1.1, the units being percent conversion.

To determine the experimental reproducibility the conversions from experiments 1, 3, and 9 were pooled. The average conversion was 19.82%, and the standard deviation, in percent conversion, was 0.85 (19.82 ± 0.85). Comparing the standard deviations due to technique and that due to repetition (the latter including error due to technique), 1.1 and 0.85, respectively, led to the conclusion that the analytical technique was the main contributor to error in the conversions. The implication was that predetermined conversions could be obtained in the equipment.

An estimate was made of the errors in the GPC molecular weight results. Pooling the molecular weights for experiments 1, 3, and 9 with those from the uncured polymer from experiment 1 (1* Table 3) gave estimations of the standard deviation of process performance. The relative errors for one standard deviation of $\overline{M}_n(\infty)$, $\overline{M}_w(\infty)$, $\overline{M}_z(\infty)$, and $\overline{D}_n(\infty)$, were 2.6%, 4.5%, 5.5%, and 4%, respectively. The standard deviations of molecular weights and polydispersity ratio compared favorably with the GPC variability (5 to 10%) reported in the literature. Thus analytical technique, not process variability, was the major contributor to the errors in the experimental results. Therefore, a polystyrene of predetermined molecular weight could be experimentally produced.

The reactor operated smoothly and reliably for all experiments. This implies that radial temperature gradients were not a problem. Results in part two of this study delineate more fully the temperature rise expected under different conditions.

Clearly a single tube of dimensions used in this study has a small product capacity. Industrial quantities may be produced by using 1000 or more parallel tubes (for example, heat exchanger bundle).

TABLE 2. EXPERIMENTAL CONVERSIONS

Experiment	Uncorrected conversion, %		Correction factor	Average conversion, %
1	19.92	22.15	0.954	20.1
2	25.8	23.7	0.956	23.7
3	22.05	20.26	0.953	20.2
4	27.5	29.0	0.983	27.8
5	32.2	34.4	0.962	32.1
6	23.2	23.2	0.941	21.8
7	20.55	21.32	0.955	20.0
8	10.72	—	0.963	10.3
9	19.87	20.01	0.961	19.2

The average conversion is the average of samples 1 and 2 multiplied by the correction factor. The correction factor is due to the residual monomer in the styrene.

CONCLUSIONS

An analysis was made of the bulk polymerization of styrene initiated by azobisisobutyronitrile in a tubular reactor.

The experiments, performed in a jacketed reactor, showed that:

1. It was feasible for a tubular reactor to produce acceptable quality polystyrene for industrial purposes.
2. The quality of the polymer product was reproducible.
3. It was technically feasible for the tubular reactor to replace the stirred batch kettles as the preliminary stage in the polystyrene manufacturing process, and
4. Radial temperature gradients were not a limitation in reactor operation.

ACKNOWLEDGMENT

The authors wish to express their sincere appreciation to the National Research Council of Canada for its financial support.

NOTATION

C_{I0} = initiator concentration at reactor inlet, g mole/l
C_{m0} = monomer concentration at reactor inlet, g mole/l
D_2 = slope of the molecular weight calibration curve equation, counts^{-1}
$\overline{D}_n$ = polydispersity ratio, ratio of weight average to number average molecular weight
$\overline{D}_n(h)$ = polydispersity ratio corrected for instrumental spreading
$\overline{D}_n(\infty)$ = polydispersity ratio obtained from the chromatogram

TABLE 3. EXPERIMENTAL MOLECULAR WEIGHTS

Expt.†	$\overline{D}_n(h)$	$\overline{M}_n(\infty)$	$\overline{M}_n(h)$	$\overline{M}_w(\infty)$	$\overline{M}_w(h)$	$\overline{M}_z(\infty)$	$\overline{M}_z(h)$
1	1.64	74,600	77,700	132,700	127,400	187,400	165,800
2	1.69	70,700	73,600	129,200	124,100	187,700	166,000
3	1.63	73,200	76,200	129,400	124,400	184,400	162,900
4	1.89	53,600	55,700	110,000	105,600	177,900	157,400
5	1.91	51,500	53,600	106,300	102,200	173,400	153,400
6	1.75	57,600	60,000	109,500	105,200	163,200	144,400
7	1.65	70,400	73,300	126,100	121,100	181,400	160,400
8	1.51	122,400	127,400	199,700	191,800	259,400	229,900
9	1.62	72,200	75,200	126,500	121,600	181,900	160,800
1*	1.67	74,000	77,100	133,900	128,500	190,000	168,000
5*	1.76	54,700	56,900	104,800	100,200	161,400	142,800

† Expt. = experiment.
The corrected molecular weights were evaluated with $h = h_c$.
The last two sets of molecular weights (1* and 5*) were obtained from the uncured polymer sample.
The molecular weights were the average of three or four chromatograms for each experiment.
The uncured polymer weights were the average of two chromatograms.

$f(v)$ = normalized Gaussian function to curve fit the leading half of the chromatogram of the polymer standards

h = instrumental spreading correction parameter, counts^{-2}

h_c = instrumental spreading correction parameter obtained from the leading half of the chromatogram, counts^{-2}

M_i = calibration molecular weight at a particular elution volume

$\overline{M}$ = cup averaged molecular weight, or molecular weight

$\overline{M}(h)$ = corrected chromatogram molecular weight

$\overline{M}(\infty)$ = chromatogram molecular weight

T_w = wall temperature of the tubular reactor, °K

v = elution volume from the chromatograph, counts

v_p = elution volume at the peak of the polystyrene standard, counts

$\overline{X}$ = cup averaged conversion

Subscripts

n = number average

w = weight average

z = z average

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Continuous Production of Polystyrene In A Tubular Reactor: Part II

An analysis of the bulk polymerization of styrene by azobisisobutyronitrile in a tubular reactor was made. Rigorous models were developed and verified. A diffusion model gave predictions of molecular weights and conversions that were 2% higher on the average than the experimental values. Another model, a plug flow contraction of the diffusion model, predicted molecular weights and conversions that were 6% higher on the average than the experimental values.

The diffusion model showed that optimal conversions could be obtained by proper reactor operation. Tentative studies for optimal conversion with minimal molecular weight dispersion indicated the reactor should be operated at a wall temperature 5° to 10°C below that required for optimal conversion.

J. P. A. WALLIS
R. A. RITTER
and
H. ANDRE

Department of Chemical Engineering
The University of Calgary
Calgary, Alberta T2N 1N4 Canada

SCOPE

More than half of today's polystyrene comes from a two-stage bulk polymerization process. The first stage, often called a *prepolymerizer*, consists of stirred-batch kettles. Here conversion of the monomer goes to 30 to 40% completion. Because of viscosity considerations and energy requirements for the mixers, the syrup is transferred to other processes to complete the polymerization.

Despite the widespread use of the kettles, a disadvantage is the relatively larger capital outlay and higher operating costs incurred in comparison with those of a tubular reactor system. Even with a seeming economic advantage, the tubular reactor is little used for commercial polystyrene production (Bishop, 1971), apparently because a large temperature gradient across the tube diameter causes uneven polymerization rates, resulting in poor control of the final product molecular weight distribution. According to Boundy et al. (1970), this temperature rise should be restricted to 10° to 20°C.

The purpose of this study is to investigate the reactor diameter—temperature gradient—product quality functionality by mathematical models which have been verified with experimental data. Also studied are optimal reactor conditions for maximum conversion with minimal molecular weight dispersion.