

On-Line Monitoring of Polymer Quality in a Batch Polymerization Reactor

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Synopsis

A novel experimental reactor system has been designed to study a variety of problems related to on-line measurements and computer control of batch polymerization reactors. A number of measuring devices such as densitometer, viscometer, size exclusion chromatograph, and torquemeter have been put on-line to a batch reactor and interfaced to a real time computer to monitor monomer conversion and molecular weight during polymerization. A new feature of the experimental setup is its microprocessor-based sampling system which automatically collects samples from the reactor and injects them into the SEC analyzer. Computer software has been developed for on-line acquisition and processing of SEC data. This work demonstrates the feasibility of on-line measurement of monomer conversion and molecular weight. Furthermore, it presents a comparative study of some common techniques employed for off- and on-line measurement of polymer quality.

INTRODUCTION

The slow progress in automatic control of polymerization reactors has been attributed to the lack of robust on-line measuring devices. Hoogenboorn and Shaw¹ pointed out the viscous nature of the polymerization mixture as the main contributing factor for the difficulty of on-line measurements. Polymer quality has been traditionally controlled by measuring the properties of the polymer product off-line and rejecting the off-grade product completely or blending it with good product such that the blended product has desirable properties.

In recent years there has been considerable research in the area of on-line measurements and control of polymerization reactors. In fact, the research is advancing so rapidly that it is anticipated that soon we will see the implementation of higher level optimization schemes to polymerization reactors.² The availability of process computers and the recent developments of on-line measurement techniques have considerably increased the scope of on-line control of product quality in polymerization reactors. The objective of this work was to design and operate a fully automated polymerization reactor system to study the problems related to on-line measurements and real-time computer control of polymerization reactors.

For this purpose, a batch reactor system has been designed and built to study the free-radical polymerization of methyl methacrylate. A num-

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ber of on-line measuring devices such as a densitometer, a viscometer, a torquemeter, and a size exclusion chromatograph have been placed on-line to monitor the density, viscosity, and the molecular weight distribution (MWD) of the polymer product during the course of polymerization. The present paper describes a novel experimental reactor system and the various on-line analytical measurements. It also presents a critical evaluation of these techniques with respect to their accuracy and robustness in estimating on-line important process variables such as monomer conversion, number-average, and weight-average molecular weight.

EXPERIMENTAL REACTOR SYSTEM

A schematic representation of the experimental setup is shown in Figure 1. It is designed in such a way that different on-line measurements from the system can be obtained. The reactor is a 5-L jacketed cylindrical glass vessel. A stirrer-motor assembly is mounted on the reactor for thorough mixing of the reactants. The stirrer has two turns of helical blades and is supported by a bearing at the center of the reactor lid. It is turned by a totally enclosed DC motor and can keep the agitation speed constant. The torque on the stirrer is measured and is available for on-line data acquisition as a 0–10-V output.

The reaction mixture is continuously heated by circulating hot water through the reactor jacket using a thermally protected pump. The cooling of the reaction mixture which is required during the exothermic polymerization is achieved by the cold water flowing through an 0.25 in. stainless steel cooling coil placed inside the reactor. The flow rate of the cooling

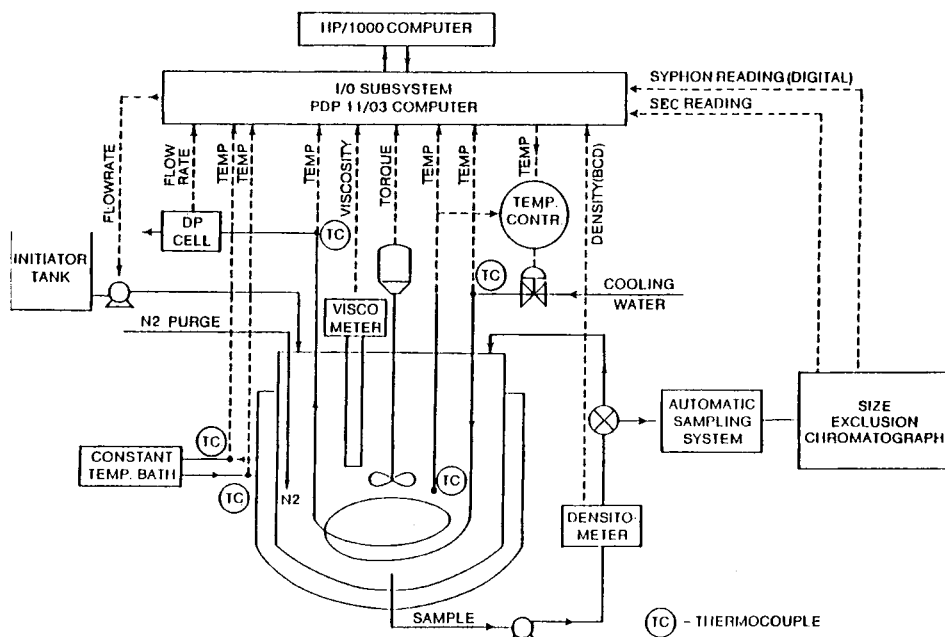


Fig. 1. Schematic diagram of polymerization reactor system.

water is controlled by an analog PI Foxboro controller. A D/P cell is used to measure the flow rate of the cooling water. The inlet and outlet temperatures of the cooling water are measured by thermocouples.

A viscometer (Norcross Corporation Model M8B) is mounted on the reactor lid to measure the viscosity of the reaction mixture during polymerization. The viscometer operates on a falling piston principle. A piston is periodically raised by a lifting mechanism drawing a sample of the liquid into the space which is formed below the piston-rod assembly. The piston is then allowed to fall by gravity expelling the sample through the same path as it entered. The time required for the piston-rod assembly to drop to the bottom of its travel is a measure of the viscosity of the reaction fluid. This measurement is available as an analog signal in the range of 1-5-V for on-line data acquisition.

During the polymerization the reaction mixture is continuously circulated through a densitometer (Anton Parr) by a reciprocating-revolving pump. In our experiments we experienced plugging of the pump at high conversions. These problems were temporarily solved by removing the pump and cleaning the pump head with solvent. To ensure that density is measured at a constant temperature, the reaction mixture is first passed through a stainless steel coil immersed in a thermostatic bath before entering the densitometer. The measured density is available as a BCD output for data acquisition.

From the densitometer the reaction mixture flows through a three-way solenoid valve back to the reactor. This valve is used to collect automatically samples of reaction mixture for SEC analysis. In the present setup we have developed an automatic sampling system that periodically collects a sample and prepares it for automatic injection into the SEC. A schematic diagram of this system is shown in Figure 2. It consists of a sample vessel, two three-way solenoid valves, two metering pumps, and a magnetic stirrer. A pro-

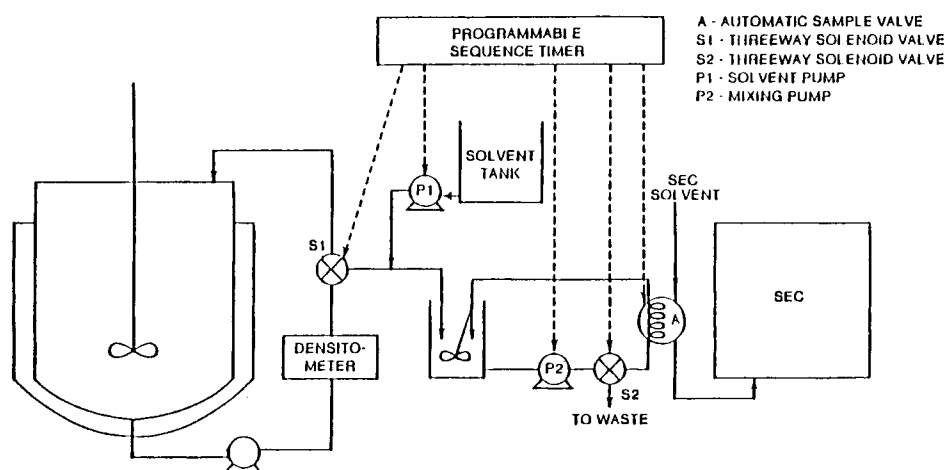


Fig. 2. Automatic sampling system for SEC analysis:

(A) automatic sample valve; (S1, S2) three-way solenoid valve; (P1) solvent pump; (P2) mixing pump.

grammable microprocessor based sequence timer (Potter and Brumfield) is used for switching on-off the pumps, solenoid valves, and the magnetic stirrer. The sample preparation is achieved by appropriate timing of the above devices. The essential steps of the sampling procedure are described by Ponnuswamy.³

A size exclusion chromatograph (SEC Waters Associates Model 244) is employed for molecular weight measurements. Finally, a Hewlett-Packard (HP/1000) minicomputer is used for data acquisition and automatic operation of the reactor system. The H/P 1000 employs a PDP 11/03 computer as an I/O subsystem interface to the process. A hard copy terminal near the reactor site is used for entering commands as well as reporting experimental data. A real-time computer program has been developed for the purpose of on-line monitoring of various variables of the process.

Experimental Procedure

The free-radical solution polymerization of methyl methacrylate (MMA) has been selected to study the problems related with on-line measurements and computer control of polymerization reactors. Toluene was chosen as solvent because of its high boiling-point (120°C) and its low rate constant value for transfer to solvent reaction. Commercial monomer (MMA) supplied by the Aldrich Chemical Co. was vacuum-distilled to remove the inhibitor. The distilled monomer and solvent were then dried with anhydrous calcium chloride to remove any traces of water. Both monomer and solvent are purged with nitrogen to remove any dissolved oxygen which inhibits polymerization. The initiator, benzoyl peroxide, supplied by Aldrich was dissolved in chloroform and recrystallized in methanol before use. The reactor was purged with nitrogen during polymerization to prevent oxygen from being dissolved into the reaction mixture.

Measured quantities of monomer and solvent are charged into the reactor and heated to the required operating temperature. After the reaction mixture has reached the specified reaction temperature, initiator dissolved in toluene is added to the reactor. Immediately afterwards, the reactor system is placed under computer control. On-line measurements of the process variables are continuously made. Off-line measurements are also carried out on samples that are periodically collected from the reactor.

ON-LINE MEASUREMENTS—PREVIOUS WORK

In the past, on-line measurements in polymerization reactors were limited to temperature and pressure. Recently much attention has been given to develop on-line sensors for measuring monomer conversion and MWD. Jo and Bankoff⁴ and Schmidt and Ray⁵ employed an on-line refractometer to measure conversion in solution polymerization reactions and reported reliable results. Abbey⁶ used an on-line densitometer for monitoring conversion in emulsion and solution polymerization reactions and experienced the following problems: pump failure from either monomer attack or polymer scale, monomer phase separation in the density cell, and lag time for rapid polymerization. Schork and Ray⁷ also used a DMA series densitometer for

measuring monomer conversion in emulsion polymerization of methyl methacrylate. They reported very good agreement between conversion results obtained by gravimetry and densimetry. Pollock⁸ employed the same type of densitometer to monitor conversion in emulsion polymerization of vinyl acetate.

It is known that the viscosity of linear polymer solutions is related to the molecular weight of the polymer. Jo and Bankoff⁴ developed an on-line viscometer to measure the variation of viscosity in a solution polymerization CSTR. The measurement was made on-line by monitoring the torque exerted on the split impeller shaft by the deformation of a stainless steel torsion spring. They chose the following model to correlate the viscometer data:

$$\ln(\eta) = b_1 + b_2 X \overline{M}_w^{b_3} \quad (1)$$

where η , X , and \overline{M}_w denote the viscosity, monomer conversion, and weight average molecular weight, respectively. The constants b_1 , b_2 , and b_3 were determined from experimental data. Jo and Bankoff used eq. (1) to estimate on-line the weight-average molecular weight from continuous measurements of viscosity and monomer conversion.

A more direct method of measuring the MWD of a polymer is through the use of size exclusion chromatography (SEC). Although SEC is widely used to measure off-line the MWD of a polymer, there are only few reported applications of use of SEC as an on-line detector. Gregges et al.⁹ modified a conventional SEC to an on-line (MWD) analyzer by including an automatic sample injection system and a process computer for data acquisition. Roof and co-workers¹⁰ field-tested an on-line SEC for a solution polymerization process over a period of 3 years. They reported that their experience has proven that on-line polymer analysis by SEC is practical. Recently, Meira et al.¹¹ employed an on-line SEC for measuring MWD in a solution PMMA CSTR. They reported good reproducibility and precision of the SEC results obtained on-line.

In spite of the recent advances made in the development of on-line polymer sensors, undoubtedly, the weakest link in any polymerization control study is the measuring devices. It therefore seemed to be desirable to conduct experimental studies to evaluate the robustness and accuracy of the on-line instruments used to measure continuously monomer conversion and MWD in a polymerization reactor.

CONVERSION MEASUREMENTS

There are several methods available to measure the extent of monomer conversion to high polymer during the course of polymerization. These include dilatometry, gravimetry, gas chromatography, IR spectroscopy, refractometry, densimetry, etc. Despite the large number of methods available, only a few can be used for on-line measurement of conversion. In this work, conversion was measured by three different methods, namely, gravimetry gas chromatography and densimetry. The first two methods were exclusively employed for off-line determination of monomer conversion.

Gravimetry

Gravimetry is the most direct method of determining conversion of monomer to polymer. A sample withdrawn from the reactor is placed in a pre-weighed aluminum dish and weighed accurately using an electronic balance. The sample is then dried in a vacuum oven and finally heated to 60–80°C to remove any traces of monomer and solvent. Subsequently, the dish is cooled and weighed again. Monomer conversion is then calculated taking into account the amount of initiator in the isolated polymer. This method of determining conversion is necessarily time consuming. Furthermore, it becomes increasingly difficult to remove traces of residual monomer and solvent from the polymer sample at high conversions.

Gas Chromatography

Though gas chromatography is perhaps better suited than any other method to follow the course of polymerization, it has not yet been extensively used. As a rule the presence of polymer in the reaction mixture does not hinder the use of GC. Berezkin et al.¹² compared the widely used dilatometry with GC methods to determine kinetic parameters in polymerization reactions and concluded that GC is the preferred method in most cases. The following are some of the problems that may be encountered when using GC analysis in polymerization studies.

1. At high conversions the polymer sample may not be drawn into the GC syringe easily. In this case, the polymer sample can be dissolved in a solvent and then injected into the GC.

2. Plugging of injection port with polymer may occur in course of time. This is resolved by removing the port and cleaning off the polymer with a solvent.

3. The temperature at the injection port should be such that polymerization and depolymerization reactions do not occur. Most of these problems can be avoided by using a headspace analyzer.¹³

In this work an HP GC (Model 5710 A) with a thermal conductivity detector was employed. A GC package program supplied by Hewlett-Packard was used for calculating the concentrations of monomer and solvent in the sample. The toluene solvent served as an internal standard for the GC analysis since its weight fraction remained constant during the course of polymerization. Therefore, knowledge of the exact volume of the injected sample was not necessary.

Densimetry

Since the density of polymer is higher than the density of monomer, the density of the polymerization mixture increases during the course of reaction. Hence density measurements can be efficiently used to follow the course of polymerization and variation of monomer conversion. Precision densitometers with provision for continuous on-line measurements are available in the market. We used an oscillator-based model distributed by Anton Paar for off- and on-line determination of the density of the reaction mixture. The measuring principle of the instrument is based on the change

of the natural frequency of a hollow oscillator when filled with different liquids or gases. The instrument requires some initial calibration. However, frequent recalibration of the instrument is not necessary as long as the density cell remains free of polymer scale. After calibration, the density of the polymerization mixture can be easily determined. These density measurements can be converted to conversion values by two different methods described in the following section.

Analysis of On-Line and Off-Line Conversion Results

For the purpose of comparison, conversion results obtained off-line by GC analysis and gravimetry are plotted in Figure 3. The symbols T , ϕ_s , and $[I_0]$ denote temperature, solvent volume fraction, and initial initiator concentration, respectively. It can be observed that conversion results calculated by the two methods agree considerably well up to about 40% conversion. Above this value, gravimetric results appear to be higher than those obtained by GC. This behavior was attributed to two possible sources of error, namely, incomplete removal of the trapped monomer and solvent and further polymerization of the residual monomer in the polymer sample during the drying stage. The presence of residual monomer and solvent in the dried polymer sample at high conversions was confirmed by dissolving the dried polymer in THF and injecting it into an SEC. Two distinct peaks corresponding to monomer and solvent were identified. These errors were absent at lower conversions due to the fast and complete removal of residual monomer and solvent from polymer samples.

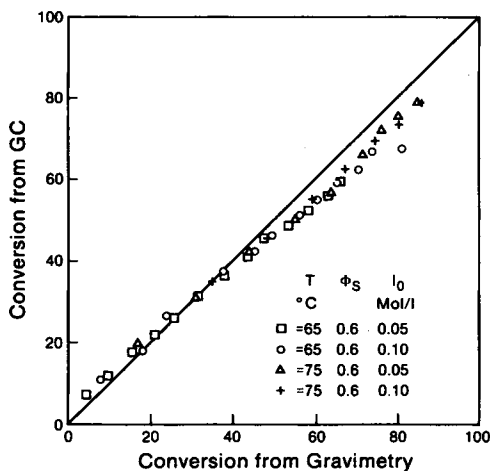


Fig. 3. Comparison of conversion results from gravimetry and GC analysis:

	T (°C)	ϕ_s	$[I_0]$ (mol/L)
□	65	0.6	0.05
○	65	0.6	0.10
△	75	0.6	0.05
+	75	0.6	0.10

GC analysis can lead to erroneous results due to possible polymerization of monomer to polymer inside the GC columns or/and possible depolymerization of polymer at the injection port. However, the vapor phase thermal polymerization of MMA is negligible, which eliminates this source of error. Furthermore, the actual injection port temperature of 150°C is lower than the temperature (>200°C) at which depolymerization would occur. Based on the above arguments, it was concluded that conversion results from GC analysis were relatively more accurate than those obtained by gravimetry. Additional evidence of this result is provided hereinafter.

As mentioned previously, density data were converted to conversion measurements by two different methods. According to the first method, an empirical correlation between density and GC conversion measurements was developed. Figure 4 shows the variation of density with conversion for different polymerization conditions. It should be noted that all density measurements were made at a constant temperature of 40°C. From Figure 4, it can be seen that two different least squares lines are required to fit the data. One line corresponds to an initial initiator concentration of 0.05 g mol/L and the other to a concentration of 0.10 g mol/L. Furthermore, if the volume fraction of the solvent is changed, a different straight line has to be fitted to the new density-conversion measurements. It is obvious that this procedure of fitting a straight line to the experimental data for each set of experimental conditions is not convenient. Hence a second method was developed to directly relate density measurements to conversion.

Let W be the total weight of the initial mixture in the batch reactor. W remains constant and is equal to

$$W = W_m + W_p + W_s + W_i \quad (2)$$

where W_m , W_p , W_s , and W_i are the weights of monomer, polymer, solvent, and initiator, respectively. The total volume of the polymerization mixture

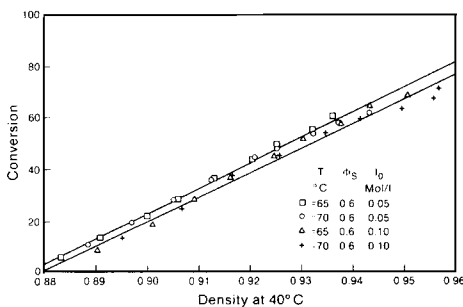


Fig. 4. Variation of density of reaction mixture with conversion:

	T (°C)	ϕ_s	$[I_0]$ (mol/L)
□	65	0.6	0.05
○	70	0.6	0.05
△	65	0.6	0.10
+	70	0.6	0.10

can be obtained by adding the volumes of monomer, polymer, solvent, and initiator assuming ideal mixing of these components, that is,

$$V = \frac{W_m^0(1-x)}{\rho_m} + \frac{W_m^0x}{\rho_p} + \frac{W_s}{\rho_s} + \frac{W_i}{\rho_i} \quad (3)$$

where ρ_m , ρ_p , ρ_s , and ρ_i are the densities of monomer, polymer, solvent, and initiator, respectively. x is the fractional monomer conversion. The density of the mixture can be expressed as

$$\rho_{\text{mix}} = W/V \quad (4)$$

From eqs. (2)-(4), the following expression for the monomer conversion is obtained:

$$x = \frac{(1/\rho_{\text{mix}}^0 - 1/\rho_{\text{mix}})}{w_m^0(1/\rho_m - 1/\rho_p)} \quad (5)$$

where ρ_{mix}^0 and w_m^0 denote the density of the mixture and monomer weight fraction at 0% conversion. In eq. (5) all variables but ρ_{mix} and x are known. Thus, by measuring on-line or off-line ρ_{mix} , the fractional monomer conversion can be calculated. It should be noted that density measurements must be made at a constant temperature to eliminate any error due to temperature fluctuations.

Equation (5) was applied to off-line and on-line density measurements to calculate the time variation of monomer conversion at different polymerization conditions. A comparison of conversion results obtained by GC analysis and densitometry is shown in Figure 5. It can be easily seen that conversion result obtained by the two methods agree reasonably well. This

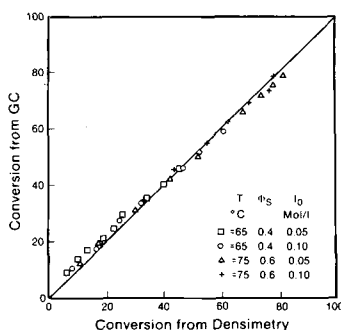


Fig. 5. Comparison of conversion results from densitometry and GC analysis:

	T ($^{\circ}\text{C}$)	ϕ_s	$[I_0]$ (mol/L)
□	65	0.4	0.05
○	65	0.4	0.10
△	75	0.6	0.05
+	75	0.6	0.10

confirms our earlier conclusion that our gravimetric conversion measurements were prone to significant errors at high conversions.

For the purpose of conversion monitoring of solution polymerization of MMA, we have found that the DMA densitometer with a precision of $\pm 10^{-4}$ g/cm³ was capable of predicting monomer conversion to $\pm 0.2\%$ of the real value. In the presence of temperature, polymer scale, and other sources of error, conversion resolution is expected to decrease. Our own experience has shown that in the absence of systematic errors density measurements can be used for off- and on-line monitoring of monomer conversion.

MOLECULAR WEIGHT MEASUREMENTS

Since many polymer properties are related to the MWD, it would be desired to measure this quantity on-line. SEC has been extensively used for off-line determination of MWD. However, there is only a limited number of reports about on-line determination of MWD by SEC. This is mainly due to problems related to the robustness of the instrument, automatic sample collection and preparation, measurement delays, etc. Instead of the direct measurement of MWD, an on-line viscometer or torquemeter can be used to obtain an indirect measure of molecular weight. The ability of these measuring devices to provide on-line information about the molecular weight of a polymer is examined next.

Size Exclusion Chromatography

A real-time computer program has been developed for automatic acquisition and processing of SEC data. This program performs the following tasks:

1. Initiation of SEC data acquisition routine.
2. Identification of the start of a peak.
3. Identification of the end of a peak.
4. Termination of SEC data collection.

Initiation of data acquisition is accomplished by reading the status of a digit switch that turns on at the time a sample is injected automatically into the SEC system. Consecutive readings are then analyzed for identification of the start and end of the chromatogram. The program stops the data acquisition routine, once the end of the chromatogram has been found. Subsequently, the SEC data are normalized and corrected for possible base line drift, axial dispersion, and solvent flowrate fluctuations. Base line drift is accounted for by assuming a linear drift from the initial base line value (start of a peak) to the final value (end of a peak). A correction for axial dispersion is obtained by solving the well known Tung's equation.

$$F(v) = \int_{-\infty}^{\infty} W(y)G(v - y) dy \quad (6)$$

where $F(v)$ and $W(y)$ denote the experimental and true chromatograms, respectively. $G(v - y)$ represents a gaussian instrumental spreading function. A method proposed by Yau et al.¹⁴ was employed to calculate the corrected values of \bar{M}_n and \bar{M}_w . The method requires a calibration curve

which relates the molecular weights of known PMMA standards with elution volume. In this work the chromatograph was operated under the following conditions:

Columns: μ -Styragel 10^3 , 10^4 , and 10^5 Å
 Solvent: tetrahydrofuran (THF)
 Flow rate: 3.0 mL/min
 Detector: refractive index ($8\times$)

Six narrow MWD (PMMA) standards (ranging from 45,000 to 680,000) were used to obtain the molecular weight calibration curve shown in Figure 6. A typical SEC chromatogram obtained on-line during the operation of the batch reactor is shown in Figure 6. This chromatogram corresponds to a polymer with $\bar{M}_n = 8.83 \times 10^4$ and $\bar{M}_w = 1.48 \times 10^5$. The accuracy of these results is largely dependent on factors which are discussed by Yau et al.¹⁴

It is important that the samples are diluted enough to prevent the overloading of the columns and significant band broadening due to viscous streaming.

Viscosity Measurements

Even though it was demonstrated that SEC analysis can be used as an on-line detector for monitoring the variation of \bar{M}_n and \bar{M}_w , this measurement involves a time delay of about 10 min. The alternative was to have a more rapid on-line measurement of molecular weight average. In this context, an on-line falling piston type viscometer was used to measure every minute the variation of viscosity of the reacting mixture.

The variation of viscosity with conversion is plotted in Figures 7 and 8 for different polymerization conditions. These figures clearly show the effect of molecular weight on viscosity. It can be observed that the viscosity values obtained at low initiator concentrations are higher than those corresponding to high initiator concentrations, which signifies the dependence of viscosity on molecular weight. Furthermore, viscosity does depend on polymerization temperature and monomer conversion.

In the past several empirical correlations were proposed to correlate viscosity data with temperature, conversion and molecular weight of a polymer. These correlations, although difficult to support theoretically, provide a good description of experimental data. Recently, viscosity correlations

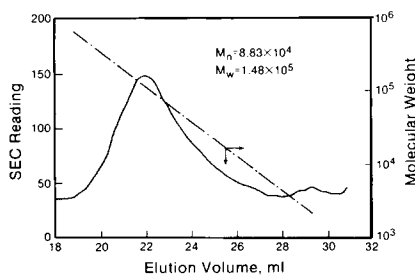


Fig. 6. SEC calibration curve and typical chromatogram.

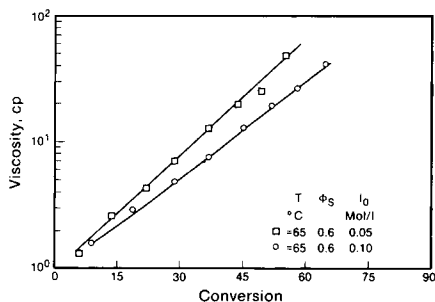


Fig. 7. Variation of viscosity of reaction mixture with conversion at 65°C:

	T (°C)	ϕ_s	$[I_0]$ (mol/L)
□	65	0.6	0.05
○	65	0.6	0.10

based on the free volume concepts and chain entanglement theory have been derived to describe the dependence of viscosity for concentrated polymer solutions on temperature, molecular weight, free volume and polymer concentration (Graessley,¹⁵ Ferry,¹⁶ and Hamer¹⁷). In this work, a modified form of eq. (1) was developed to correlate viscosity data with temperature T , conversion X , and number-average molecular weight \bar{M}_n :

$$\ln(\eta) = (\alpha_1 + \alpha_2/T) + (\alpha_3 + \alpha_4/T)X\bar{M}_n^{1/2} \quad (7)$$

The parameters α_1 , α_2 , α_3 , and α_4 were estimated by fitting viscosity measurements to experimental conversion, and \bar{M}_n results obtained at different temperatures. Figure 9 shows a comparison between measured and estimated viscosity values using eq. (7). The correlation seems reasonably good at least in the low viscosity region. Equation (7) can be rearranged to get \bar{M}_n in terms of solution viscosity η and monomer conversion X . Our analysis of viscosity data was not exhaustive, which means that other correlations might have provided a better fit of the experimental data. Nevertheless, it

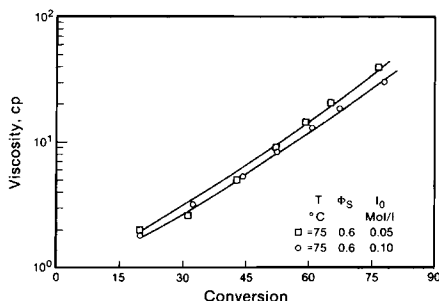


Fig. 8. Variation of viscosity of reaction mixture with conversion at 75°C:

	T (°C)	ϕ_s	$[I_0]$ (mol/L)
□	75	0.6	0.05
○	75	0.6	0.10

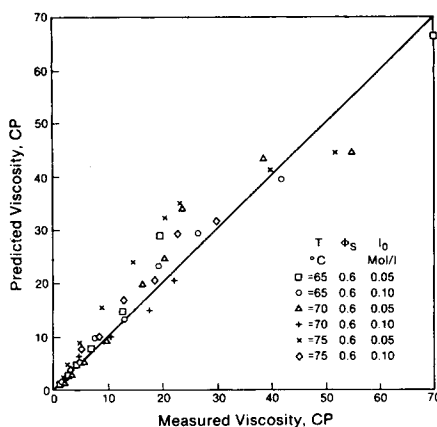


Fig. 9. Comparison of measured and calculated viscosity values:

	T (°C)	ϕ_s	$[I_0]$ (mol/L)
□	65	0.6	0.05
○	65	0.6	0.10
△	70	0.6	0.05
+	70	0.6	0.10
×	75	0.6	0.05
◇	75	0.6	0.10

can be deduced that the degree of polymerization in the solution polymerization of MMA can be inferred from on-line measurements of solution viscosity, conversion, and polymerization temperature. It should be pointed out here that for control purposes \bar{M}_n estimates obtained from viscosity and conversion measurements can be updated, if necessary, when molecular weight averages determined by SEC analysis become available. This combined on-line estimation of \bar{M}_n could provide eventually better control of polymerization reactors.

Torque Measurements

Since the viscosity of the polymerization mixture increases during the course of reaction, the torque exerted on the constant RPM stirrer by the reaction mixture increases too. By measuring the torque exerted on the stirrer, it is possible to estimate the molecular weight of polymer if a reliable correlation relating torque and molecular weight can be found. Figure 10 shows the variation of torque with conversion for two different initiator concentrations. As with viscosity measurements, the effect of molecular weight on torque measurements can be easily observed. Torque measurements were not further analyzed because of their low reproducibility caused by the varying friction at the bearing site of the stirrer-motor assembly.

CONCLUSION

In this paper, the experimental facilities that are required for on-line measurement of polymer quality in a batch polymerization reactor have been described. It can be appreciated that the reactor system requires ex-

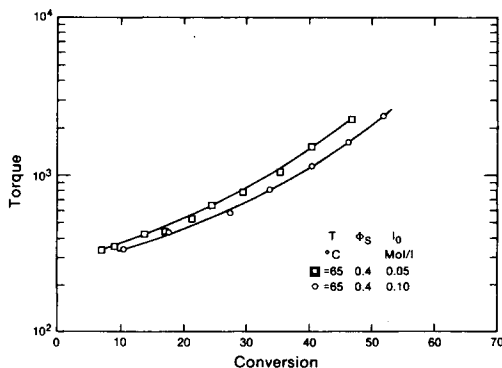


Fig. 10. Variation of torque with conversion:

	T ($^{\circ}\text{C}$)	ϕ_s	$[I_0]$ (mol/L)
□	65	0.4	0.05
○	65	0.4	0.10

tensive instrumentation to monitor on-line the variation of properties like density, viscosity, and MWD of the reacting mixture. Analysis of conversion results obtained by three different methods, namely, gravimetry, gas chromatography, and densimetry, has shown that gravimetric results are prone to error especially at high conversions. It has been demonstrated that the densitometer provides sufficient resolution for on-line measurement of monomer conversion.

A fully automated SEC system has been developed to monitor the variation of MWD during the course of the reaction. The automatic sampling system along with the developed software for on-line acquisition and analysis of SEC data form an important contribution to automatic analysis of polymer MWD. Finally, the analysis of on-line viscosity data has shown the ability of the employed viscometer to provide on-line molecular weight information.

This study has demonstrated that, with the development of improved on-line instrumentation, advanced computer control of polymer properties can be possible.

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