

In-Line Dielectric Monitoring of Monomer Conversion in a Batch Polymerization Reactor

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SYNOPSIS

In-line monitoring of monomer conversion is studied using a low-frequency dielectric sensor during solution polymerization of methyl methacrylate in a laboratory-scale batch reactor. It has been found that the induction period due to the presence of an inhibitor can be determined by the dielectric sensor to detect the starting point of polymerization. The dielectric loss factor that changes with the progress of polymerization is empirically correlated with monomer conversion measured by the off-line gravimetric method at different temperatures and initiator concentrations. It is demonstrated that dielectrometry can be used as an in-line monitoring method in free-radical polymerization. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Control of batch and continuous polymerization reactors is often difficult due to the lack of rapid on-line sensors for measuring important process variables and polymer properties. One of the key process variables to be monitored and controlled in industrial polymerization processes is monomer concentration or monomer conversion. There are several techniques currently available for measuring monomer conversion on-line including refractometry, densimetry, and gas chromatography. However, these methods all require the removal of a sample from the reactor or flow through a detector. At high monomer conversions or solution viscosity, these methods may present some operational problems or there may be a significant measurement delay. In this work, dielectrometry is used to monitor monomer conversion *in-line* in free-radical solution polymerization of methyl methacrylate in a stirred batch polymerization reactor.

Dielectrometry involves measuring the change in the dielectric properties of permittivity and loss factor to monitor changes in the physical properties of

the polymer during processing. Measurements are typically taken using a number of frequencies over several orders of magnitude and the electrical resistivity extracted from the response. Since the electrical resistivity is an electrical measurement and does not directly translate into units of viscosity, the actual values are not normally of direct importance. Previous work has shown that the ion viscosity is a strong function of the degree of reaction and temperature of a polymer resin.¹ A good correlation exists between the change in the electrical resistivity and the actual polymer viscosity during the reaction of thermosetting resins as measured with a rheometer.²

Dielectric analysis has been frequently used in cure monitoring applications, although some reports are available on its application to polymerization monitoring. Carlini et al.³ measured the real (ϵ') and imaginary (ϵ'') parts of the dielectric constant in the microwave frequency range for photoinitiated polymerization of *n*-butyl acrylate. In the microwave frequency range, ϵ' and ϵ'' are dominated by the motion of the monomer dipoles and, therefore, they were able to measure the changing monomer concentration during polymerization by measuring the changing dielectric constant in the microwave region. The dielectric measurements were not made in a reactor because their measurement apparatus

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required that a small closed vial containing the reaction mixture be placed inside a microwave cavity followed by irradiation with UV light to polymerize the sample. The use of dielectrometry to monitor the curing of epoxy resins and other crosslinking reactions has been reported in the literature.³⁻⁵ These studies show that the dielectric loss factor may be quantitatively correlated to the mechanical viscosity.

While most of the published work on dielectrometry involved applications in monitoring the curing of thermosetting resins, very little has been reported on the use of dielectrometry for monitoring the progress of polymerization in industrial polymerization processes. Considering the importance of accurate control of monomer conversion and polymer properties during the synthesis of polymers, one can view the dielectrometry as a potentially attractive in-line monitoring technique. In this work, the applicability of low-frequency dielectric measurements to the in-line monitoring of monomer conversion is investigated experimentally for free-radical solution polymerization of methyl methacrylate (MMA) in a batch reactor.

EXPERIMENTAL

For this work, ϵ' and ϵ'' are measured by an Eumetric System II Microdielectrometer connected to an IDEX sensor (Micromet Instruments, Inc.) placed in a polymerization reactor. The dielectric measurements are made at a frequency of 1 kHz approximately every 20 s during an experiment. The sensor is a coplanar capacitor composed of many

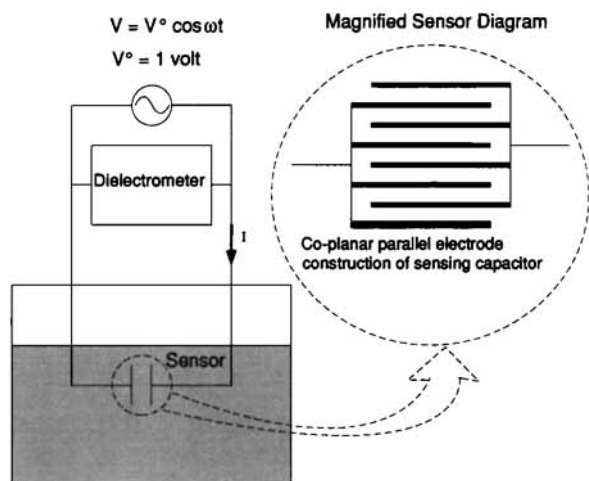


Figure 1 In-line sensing of monomer conversion with the dielectric sensor.

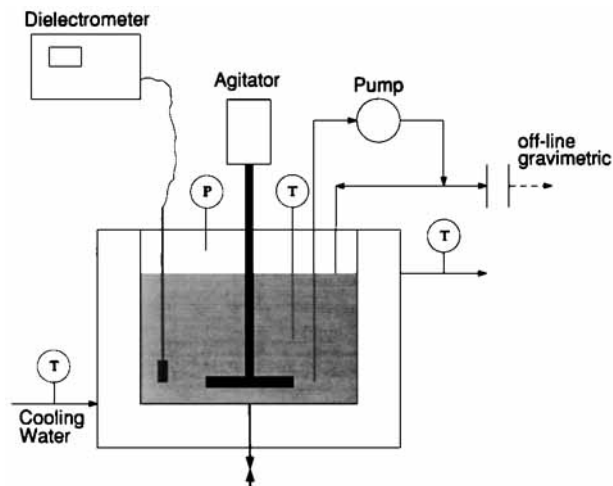


Figure 2 Schematic of the laboratory polymerization reactor system.

interpenetrating electrodes, as shown schematically in Figure 1. The sensor is attached to a small diameter tube and inserted into a polymerizing liquid in the reactor.

A sinusoidal voltage with amplitude of 1 V is imposed across the sensor. The resulting current traversing the sensor is also sinusoidal but out of phase with the voltage signal. The instrument measures the amplitude ratio and phase difference of the signals and, from these, calculates ϵ' and ϵ'' for the polymer solution in contact with the sensor. The contributions of conduction and dipole orientation to the loss factor (ϵ'') can be separated such that the total loss factor is given by

$$\epsilon'' = \epsilon''_{\text{dipole}} + \frac{\sigma}{2\pi\epsilon_0\omega} \quad (1)$$

where σ is the material's conductivity, and ω , the frequency of the applied electric field. From eq. (1), it can be seen that the conduction contribution to the loss factor becomes larger as frequency is decreased. The dipole contribution is also frequency-dependent but is generally very small in relation to conduction at low frequencies. Measurements for the MMA/PMMA system were taken at frequencies on the order of 1 kHz, which is sufficiently low such that the conductive contribution dominates the loss factor and, therefore, changes in loss factor during polymerization represent changes in the material's dielectrical conductivity.

MMA polymerization experiments have been carried out in a 4 L stainless-steel jacketed reactor. Figure 2 shows a schematic diagram of the laboratory

reactor system. A small amount of solution sample is taken for the conversion measurement by the gravimetric method during the experiment through a sampling loop. In a typical polymerization experiment, the reactor is initially charged with 1 L of a liquid mixture containing 25% ethyl acetate solvent, 75% MMA, and a weighed amount of Vazo-67 initiator (DuPont) at room temperature. The reactor temperature is then raised to the set-point temperature and regulated by manipulating the jacket cooling water temperature, which, in turn, is controlled by manipulating control valves for the hot and cold water streams. Isothermal experiments were carried out at 50, 60, and 70°C and at initial initiator concentrations of 0.02, 0.05, and 0.07 mol/L. The dielectric loss factor measured by the dielectric sensor is monitored by a data acquisition computer.

RESULTS AND DISCUSSION

When the kinetic model developed in a laboratory is used to predict changing monomer conversion in a large-scale polymerization reactor, predictions are often inaccurate. There are many factors that contribute to the mismatch between model predictions and actual process data. For example, the effect of mixing is often important in a large-scale polymerization reactor; the kinetic parameters used in the model may not be precise. Another possible cause for such inaccuracy is due to the fact that rate con-

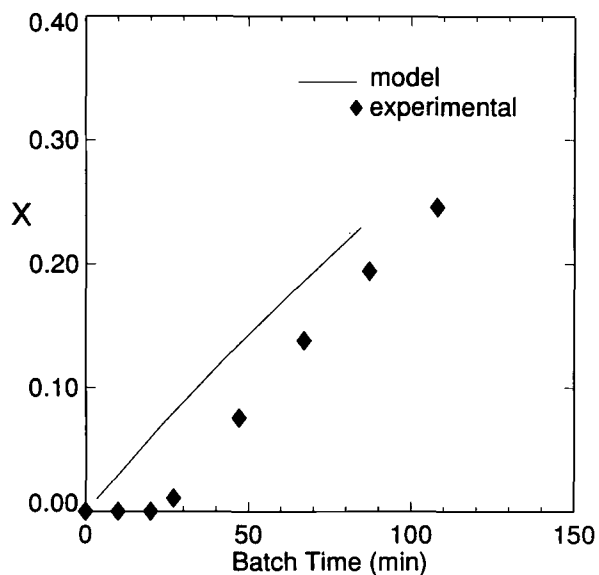


Figure 3 Monomer conversion vs. time (with 10 ppm of MEHQ inhibitor in the monomer).

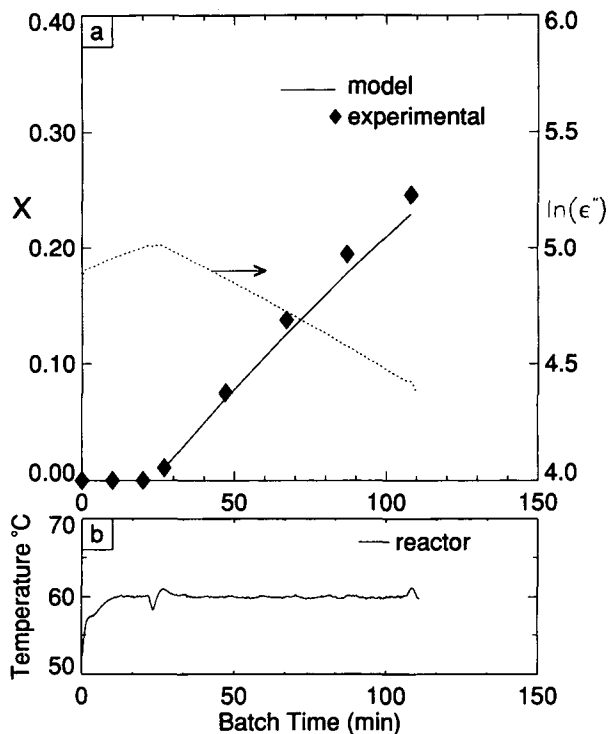


Figure 4 (Top) Monomer conversion and dielectric loss factor vs. batch time; (bottom) reaction temperature profile.

stants for the model were obtained from polymerization experiments in which great care was taken to remove polymerization inhibitors or impurities from the monomer. Such careful procedures are seldom practiced in a large-scale industrial polymerization process. For example, the presence of inhibitors in the monomer will inhibit polymerization until they are completely consumed by free radicals formed from the decomposition of the initiator. This inhibition causes an induction period, which is illustrated in Figure 3. Here, X denotes the fractional conversion of the monomer (MMA). In the monomer used in our experiments, 10 ppm of the monomethyl ether of hydroquinone (MEHQ) inhibitor was present. If the kinetic model does not take the inhibition effect into account, the model predictions will be in error. The solid line in Figure 3 illustrates the prediction of monomer conversion by the model in which the inhibition effect is not included.

To improve model predictions, it is necessary to know when the induction period ends and polymerization begins. It was observed in our experiment that dielectric measurements can be used to determine the start of polymerization. Figure 4 shows the variations in the fractional conversion of the monomer and the dielectric loss factor during the course

of polymerization. The bottom diagram illustrates the reactor temperature profile during the course of polymerization. Except for the first 10 min, the reaction temperature was maintained at 60°C throughout the polymerization. It is seen that the dielectric loss factor (ϵ'') increases initially to a maximum and then decreases gradually as the polymerization proceeds. It was found that during the initial induction period the loss factor increases to a maximum value (ϵ''_{\max}). As the inhibitor is consumed and the polymerization starts, the dielectric loss factor value starts to decrease. The observed decrease in ϵ'' during polymerization is presumably due to decreasing ion mobility as more polymer is produced. Even a small concentration of polymer molecules in solution can decrease the mobility of trace ions present and, therefore, decrease the loss factor. Thus, Figure 4 suggests that one can easily detect the beginning of polymerization by monitoring the changes in the dielectric loss factor. When the induction period is correctly known, the same kinetic model used in Figure 3 provides a more accurate prediction of monomer conversion as shown in Figure 4.

The fractional monomer conversion and the logarithm of the maximum value of ϵ''_{\max} to the loss factor ϵ'' are plotted against the batch reaction time in Figure 5. The ratio is taken in order to normalize loss factor measurements against batch-to-batch variations of ion concentrations. Furthermore, ϵ'' is chosen as the denominator for convenience, since the ratio then becomes an increasing function as monomer conversion increases. As mentioned in the

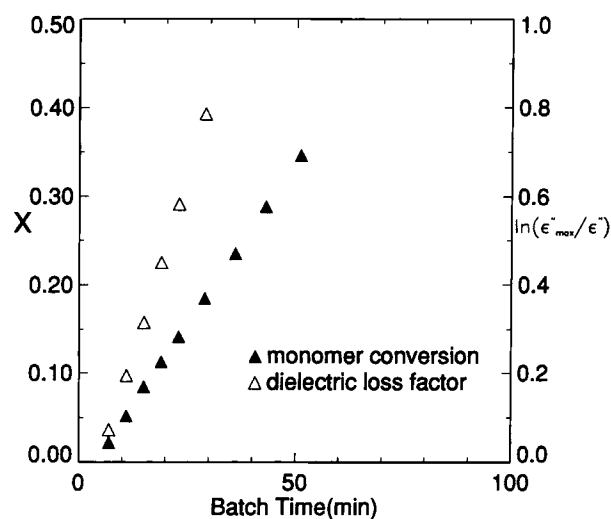


Figure 5 Monomer conversion and dielectric loss factor for a typical polymerization.

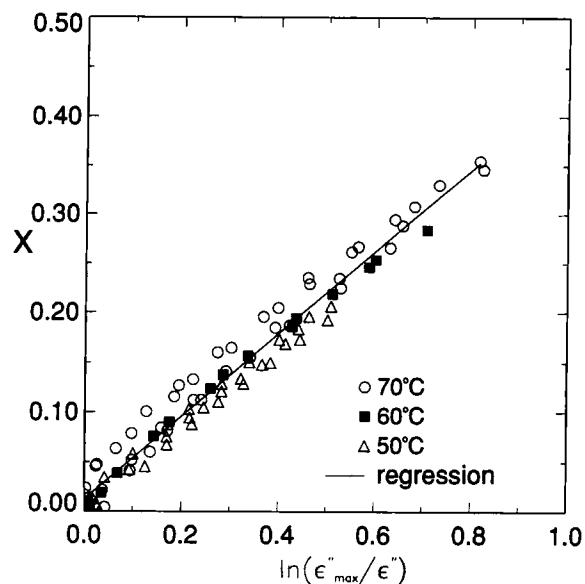


Figure 6 Monomer conversion vs. dielectric loss factor at three reaction temperatures.

above, the time at which ϵ''_{\max} is reached represents the start of polymerization.

To find a correlation between the fractional monomer conversion and the dielectric loss factor, conversion is plotted against $\ln(\epsilon''_{\max}/\epsilon'')$ in Figure 6. Notice that all the data points obtained at three different temperatures are fitted into a single

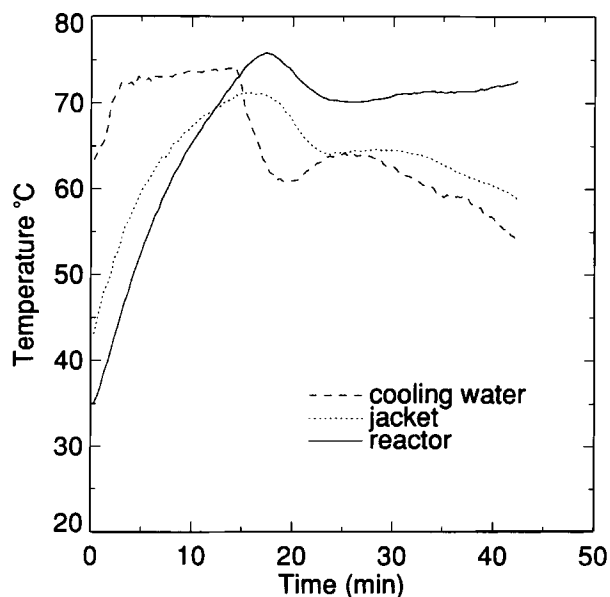


Figure 7 Temperature profiles in a batch test experiment: initial initiator (Vazo-67) concentration = 0.15 mol/L; solvent volume fraction = 0.2; reaction volume = 2 L.

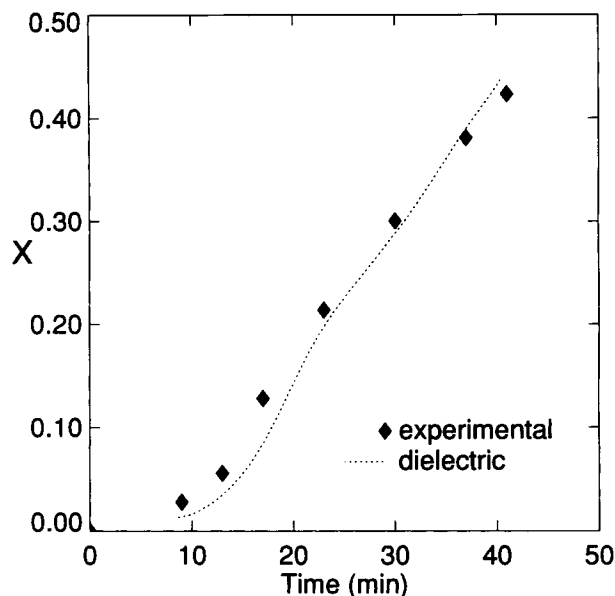


Figure 8 Comparison of monomer conversion calculated from in-line dielectric measurements to conversion determined by the gravimetric method.

straight line, indicating that the measured dielectric loss factor can be used to determine the fractional monomer conversion. One can observe that the normalized dielectric loss factor is not quite sensitive to reaction temperature, at least in the temperature range employed in our experiments. The correlation between the monomer conversion and dielectric loss factor is constructed using the following simple form:

$$X = a_1 + a_2 \ln \frac{\epsilon''_{\max}}{\epsilon''} \quad (2)$$

where X is the fractional monomer conversion. From least squares, the values of coefficients a_1 and a_2 were found to be 0.0123 and 0.416, respectively.

Correlation (2) was examined by running a new polymerization experiment and the results are shown in Figures 7 and 8. Conditions for this experiment were slightly different from the conditions used for the experiments that were used to generate the empirical correlation. In this experiment, the initial initiator concentration was increased to 0.15 mol/L, the solvent volume fraction decreased to 0.2, and the reactor volume was doubled to 2 L. Figure 7 represents the temperature profiles and Figure 8 represents a comparison of off-line gravimetric measurements and the conversion estimated from

the dielectric measurement using the correlation presented in eq. (1). Although there was a significant temperature variation during the early stage of polymerization, the predicted monomer conversion is reasonably accurate. Thus, this experimental result indicates that dielectrometry can be used effectively for in-line monitoring of monomer conversion in free-radical MMA polymerization.

CONCLUDING REMARKS

In this work, experimental results have been presented to illustrate the use of a dielectric sensor as a potential in-line monitoring device for monomer conversion measurement. It was observed that the dielectric sensor can be used to detect the beginning of polymerization in the presence of an inhibitor in the reacting fluid. The experimentally observed changes in dielectric loss factor values were correlated to monomer conversion and the resulting correlation was found to be insensitive to temperature variations under the experimental conditions used in this study. It is suggested that more fundamental studies be carried out in the future to elucidate the relationship between the dielectric loss factor and the concentration of the polymer.

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