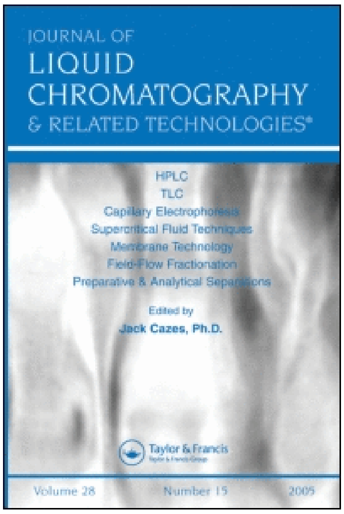

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

On-Line Monitoring of MWD in a Batch Polymerization Reactor by Size Exclusion Chromatography

S. Ponnuswamy[a]; S. L. Shah[a]; C. Kiparissides[ab]
[a] Department of Chemical Engineering, University of Alberta Edmonton, Canada [b] Department of Chemical Engineering, University of Thessaloniki, Greece

To cite this Article Ponnuswamy, S. , Shah, S. L. and Kiparissides, C.(1986) 'On-Line Monitoring of MWD in a Batch Polymerization Reactor by Size Exclusion Chromatography', Journal of Liquid Chromatography & Related Technologies, 9: 11, 2411 — 2423

To link to this Article: DOI: 10.1080/01483918608076874
URL: http://dx.doi.org/10.1080/01483918608076874

JOURNAL OF LIQUID CHROMATOGRAPHY, 9(11), 2411-2423 (1986)

ON-LINE MONITORING OF MWD IN A BATCH POLYMERIZATION REACTOR BY SIZE EXCLUSION CHROMATOGRAPHY

S. Ponnuswamy, S. L. Shah,
and C. Kiparissides*
Department of Chemical Engineering
University of Alberta
Edmonton, Canada

ABSTRACT

A novel highly automated SEC system has been developed for on-line measurement of MWD in a batch solution polymerization reactor. The system includes a liquid exclusion chromatograph, an automatic sampling system, a programmable microprocessor based sequence timer and a process computer. Two main real-time computer programs have been developed to supervise the automatic collection (SEC-Data Acquisition Program) and interprepation (SEC-Data Interprepation Program) of SEC data. Experimental results show that the new system can provide reliable on-line measurements of number average and weight average molecular weights of a sample during the course of polymerization.

INTRODUCTION

In the past, closed-loop control in polymerization reactors was mainly limited to temperature and pressure control. However,

---

* To whom correspondence should be addressed. Current address is Department of Chemical Engineering, University of Thessaloniki, Greece.

0148-3919/86/0911-2411$3.50/0

with the advent of advanced computer process control and the development of new analytical techniques for measurement of polymer quality the scope of closed-loop control in polymerization reactors has largely increased. On-line measurement of molecular weight distribution (MWD) is necessary if the polymer quality has to be controlled during the course of polymerization. One common analytical technique that has been extensively employed to characterize the MWD of a polymer sample is the size exclusion chromatography (SEC). In spite of its wide use as an off-line measurement technique, SEC has not yet been utilized as a routine on-line instrument in the polymerization industry. Past work on SEC analysis has been mainly focused on off- and on-line computer assisted interpretation of SEC data [1, 2, 3, 4, 5]. One of the first applications of SEC for on-line measurement of MWD was reported by Gregges et al. [6]. They modified a conventional SEC by including an automatic sample injection system and a process computer for on-line data acquisition. Recently Roof et al. [7] employed an on-line SEC for the measurement of MWD in a solution polymerization process. They reported that their experience over a period of three years has proven that on-line polymer characterization by SEC is practical.

The present paper describes the development of a novel highly automated SEC system employed for on-line measurement of MWD in a batch solution PMMA reactor. The on-line SEC system includes a Waters Associates - model 244 liquid chromatograph, a sampling system, a programmable sequence timer and an HP/1000 process computer. The novelty of the system lies on its ability to perform on-line determination of MWD of a polymer sample, which is automatically collected, diluted, injected and characterized without any operator intervention. A number of real-time computer programs has been developed to supervise the execution of the various tasks required for the automatic operation of the on-line SEC system. In what follows, a description of the necessary hardware and software in relation to the SEC system is presented. Expererimental on-line measurements of MWD obtained during the operation of the reactor show that the developed system can be effectively used as an on-line sensor in process control applications.

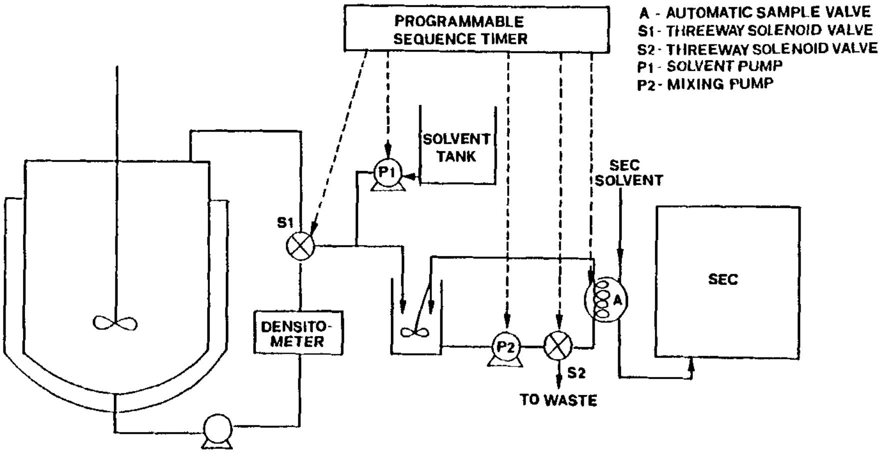

FIGURE 1: Automatic sampling system.

AUTOMATIC SAMPLING SYSTEM

As mentioned above an automatic sampling system was developed to collect periodically polymer samples from the running reactor and prepare them for automatic injection into the SEC. A shematic diagram of the sampling system is shown in Figure 1. It consists of a 50 cm^3 sample vessel, two three-way solenoid valves, two metering pumps, a magnetic stirrer and an automatic sample injection valve. A programmable microprocessor based sequence timer (Potter and Brumfield) that has sixteen output relays is used for switching on-off the pumps, solenoid valves and the stirrer. The sample preparation is achieved by appropriate timing of the above devices. The essential steps required for the analysis of a polymer sample are:

Step 1: A certain quantity of polymer mixture is fed into the sample vessel by switching on the three-way solenoid valve (S1) for a predetermined period of time (0.0-0.1 min).

Step 2: The polymer sample is diluted with THF solvent by operating the valve (P1) for a certain period of time (0.1-0.4 min).

Step 3: The contents of the sample vessel are thoroughly mixed by switching on, first the magnetic stirrer and then the circulation pump (P2) (0.3-0.8 min).

Step 4: The dissolved polymer sample is automatically injected into the SEC by switching on the automatic sample valve (+ 0.8 min).

Step 5: The contents of the sample vessel are emptied to waste by switching on the solenoid valve (S2) (+ 0.8-0.9 min).

Step 6: The sample vessel and the circulation lines are flushed with fresh solvent by operating pumps (P1) and (P2) (0.9-1.5 min).

Through the above described procedure automatic sample collection, preparation and injection into the SEC is achieved. The first number inside the parentheses represents the start time of the corresponding event and the second number denotes its termination time. Since the SEC requires approximately 10-12 minutes for a MWD determination, a total cycle time of 15 minutes has chosen for the real-time implementation of the six-steps sequential operation of the sampling system. Thus, every 15 minutes the sequence timer initiates a new cycle of analysis.

A size exclusion chromatograph supplied by Waters Associates (Model 244) was used in this work to determine the MWD of the polymer PMMA during the course of polymerization. Tetrahydrofuran (THF) was chosen as the carrier solvent. The concentrations of the separated molecules were detected by an RI detector. The RI detector responses (0-10 mV) were first amplified, filtered and then sent to an HP/1000 process computer for further on-line analysis. Two main programs were developed for the automatic collection and interpretation of SEC data. The first program called SEC- Data Acquisition Program (SEC-DAP) stores the SEC data and identifies the start and the end of the chromatogram. The SEC-Data Interpretation Program (SEC-DIP) processes the collected data and calculates the number and weight average molecular weights of a polymer sample. The exact functions of these two programs are described next.

THE SEC-DATA ACQUISITION PROGRAM

The SEC-DAP algorith accomplishes the following functions:

1. Initiation of data aquisition
2. Identification of the start of a chromatogram
3. Identification of the end of a chromatogram
4. Termination of data acquisition

Initiation of SEC-DAP routine is accomplished by reading a digit switch associated with switching of the automatic sample injection valve. This digit switch which is located in the programmable sequence timer turns on at the instant of the injection of a polymer sample into the chromatograph. The program reads the on-status of the switch and starts the acquisition of SEC data. Since the actual chromatogram elutes a few minutes after the sample injection, a dead time can be specified in the program during which SEC data are not stored. However, elution time is counted right from the moment of the sample injection. Few minutes after the injection, the digital switch is turned off so that it can initiate another SEC analysis.

The SEC data that contain the necessary information for the calculation of MWD lie between the start point and the end point of a chromatogram. Thus, it is necessary to identify these two points as the collection of the SEC data proceeds. The sampling time is set to three seconds. To identify the start of a peak twenty consecutive readings are stored in an array. Then, sequences of five readings [i.e. (1, 2, 3, 4, 5), (2, 3, 4, 5, 6) ... (15, 16, 17, 18, 19, 20)] are successively analysed to find a monotonically increasing sequence of five readings. The first reading in a sequence which satisfies the above criterion is identified as the start point of a chromatogram. This criterion works well upon proper differentiation between base-line drift and start point of a chromatogram. Thus, it is required that each successive SEC reading after the start point is higher than the previous value by 10 mV. This 10 mV difference was found to be higher than the usual base-line drift difference of (≤5 mV) between two consecutive readings. If all readings in the array fail to satisfy the criterion for a start point, the program stores the initial five points of the array and adds at the end of the array five new readings. After the identification of the start point, a logical variable LSTART is changed from •FALSE• to •TRUE• and the execution of the start point identification routine terminates.

Subsequently, the SEC-DAP algorithm searches for the peak point of the chromatogram. A similar procedure used for the search of a start point is applied for peak identification. A peak is considered to have been identified, if five readings in a sequence show a monotonic decrease. A logical variable LPEAK is then changed from •FALSE• to •TRUE•.

To identify the end point of a chromatogram, the new SEC data collected after a peak reading are analysed to find whether or not it satisfies the logic for an end point. The first point in a sequence of five readings in which any absolute difference between two consecutive readings is less than 5 mV, is considered to be the end point of a chromatogram. After the identification of the end point, a logical variable LSTOP is changed from •FALSE• to •TRUE•. Then, the program terminates the data collection routine and reinitializes the above logical variables to •FALSE• so that another search for a chromatogram can start. It is possible that another peak due to residual monomer, solvent, etc. may start eluting before the complete elution of polymer. In this case the chromatogram ends in a valley. This situation is also handled by the SEC-DAP. The SEC data stored in a disc file are subsequently processed for determination of molecular weight averages. The SEC data can also be plotted on a HP-plotter or reported on the hard copy terminal operating at the reactor site.

THE SEC - DATA INTERPRETATION PROGRAM

The SEC-DIP algorithm processes the raw data and calculates the $\bar{M}_n$ and $\bar{M}_w$ taking into account the following:

1. Change of the time scale of SEC data to elution volume.
2. Correction of SEC data for base-line drift.
3. Normalization of SEC chromatogram.
4. Correction for axial dispersion.

As mentioned previously, acquisition of SEC data is accomplished in real-time at a sampling rate of 3 sec. These SEC readings collected with respect to time are subsequently corresponded to elution volumes. For this purpose, a constant volume syphon fitted at the outlet of SEC columns was employed. Each time at which the syphon automatically discharges its content, a digit switch closes causing the registration of the corresponding discharge time. The time scale is then easily converted to elution volumes by noting the relation between real-time and registered discharge times.

Since molecular weight calculations are affected by any base-line drift, SEC readings have to be appropriately corrected for it. Assuming, a linear base-line drift, a straight line connecting the start and the end point of a chromatogram is drawn. A correction for base-line drift is applied to SEC data by subtracting from each reading the corresponding value of the linear base-line. The corrected SEC readings are then normalized by dividing each reading by the total area of the chromatogram. These normalized values F(v) are subsequently used to calculate the true chromatogram W(v) of the sample that would have been obtained in absence of axial dispersion.

If we assume a Gaussian spreading function

$$G(v-y) = \frac{1}{\sigma\sqrt{2\pi}} e^{-(v-y)^2/2\sigma^2} \tag{1}$$

of the molecular species with mean retention volume y and peak standard deviation σ, we can express the weight concentration of the polymer sample detected at the elution volume v, which is simply F(v), as

$$F(v) = \int_{-\infty}^{\infty} W(y)G(v-y)dy \tag{2}$$

The above is the well known Tung's axial dispersion equation. Many approaches [8, 9, 10] have been proposed to solve Tung's equation (2) to obtain the true distribution W(v) of the polymer sample. In this work, we follow the method of Yau et al. [10] to correct the chromatographic dispersion effect in F(v) and to calculate directly the $\bar{M}_n$ and $\bar{M}_w$ values. The method of Yau et al. uses the true linear calibration curve and the chromatographic dispersion parameter σ to obtain more accurate estimates of $\bar{M}_n$ and $\bar{M}_w$. This method permits the use of very dissimilar (MWD) standards and samples of the same polymer type while still effectively compensating for axial dispersion. The equations developed by Yau et al. for $\bar{M}_n$ and $\bar{M}_w$ of a polymer sample are:

$$\bar{M}_n = 1/\int_{-\infty}^{\infty} F(v)/\bar{M}_n(v)\,dv \tag{3}$$

$$\bar{M}_w = \int_{-\infty}^{\infty} F(v)\bar{M}_w(v)\,dv \tag{4}$$

where $\bar{M}_n(v)$ and $\bar{M}_w(v)$, the number- and weight-average molecular weights of an infinitesimal fraction of sample at retention volume v, are given by the following equations.

$$\bar{M}_n(v) = \frac{F(v)}{F(v+D_2\sigma^2)}\, e^{-1/2(D_2\sigma)^2} M_t(v) \tag{5}$$

$$\bar{M}_w(v) = \frac{F(v-D_2\sigma^2)}{F(v)}\, e^{1/2(D_2\sigma)^2} M_t(v) \tag{6}$$

$M_t(v)$ is the peak position molecular weight versus elution volume true calibration curve and it is expressed as

$$M_t(v) = D_1 e^{-D_2 v} \tag{7}$$

D_1 is related to the intercept and D_2 to the slope of the linear calibration curve.

Once the calculation of $\bar{M}_n$ and $\bar{M}_w$ has been completed, the SEC-DIP program prints out the following information on an hard copy terminal located near the reactor.

(i) The time and the SEC reading at the sample injection, the start point, the peak point and the last point of the chromatogram.

(ii) A full listing of raw SEC readings.

(iii) A plot of the original chromatogram.

(iv) The values of $\bar{M}_n$, $\bar{M}_w$ and polydispersity index.

Any section of the results (i)-(iv) can be reported or not by appropriate definition of the program's output flags.

DISCUSSION OF RESULTS

Six narrow PMMA molecular weight standards supplied by Polymer Laboratories Inc. were used to calculate the molecular weight calibration curve (7) and an average value for the dispersion parameter σ. A semi-log plot of known molecular weight standards versus elution volume produced the linear calibration curve of Figure 2. The chromatograph was operated under the following conditions.

Columns : μ-Styragel 10^3, 10^4 and 10^5 Å
Solvent : Tetrahydrofuran (THF)
Flowrate : 3.0 ml/min
Detector : RI(8x), ambient temperature

Although the value of the dispersion parameter did slightly vary for the various standards, a single average value of $\sigma^2 = 0.40$ was selected for all subsequent dispersion corrections.

The reproducibility of SEC data was tested by injecting the same polymer sample several times and analysing the resulting chromatograms. The results of the analysis are reported in Table 1.

TABLE 1

Reproducibility Results of SEC Analysis

Injection Number	Number Average Mol. Weight	Weight Average Mol. Weight
1	3.95E4	7.50E4
2	3.97E4	7.31E4
3	4.33E4	7.70E4
4	4.45E4	8.04E4
5	4.13E4	8.15E4
6	4.01E4	7.48E4
7	4.54E4	7.31E4
Average	4.20E4	7.64E4
Std. deviation	2.23E3	3.13E3

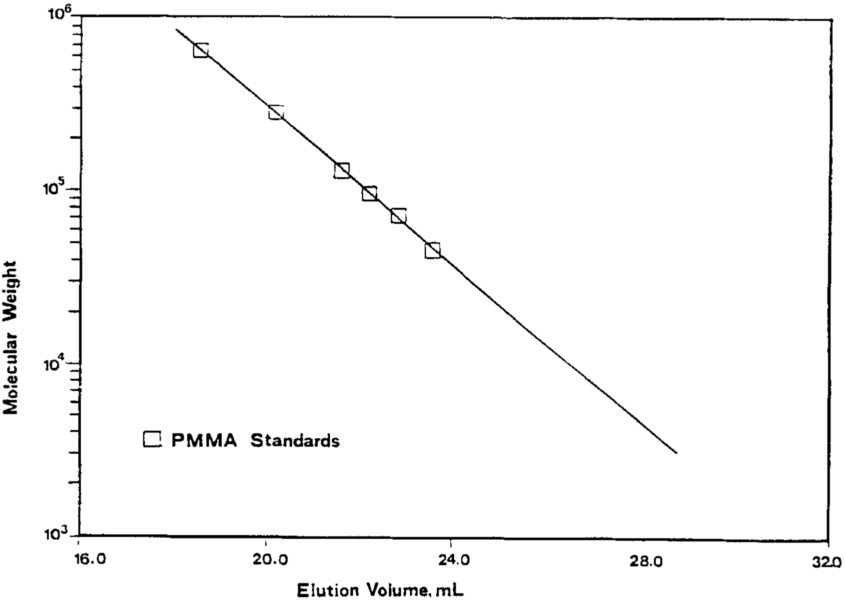

FIGURE 2: Linear calibration curve .

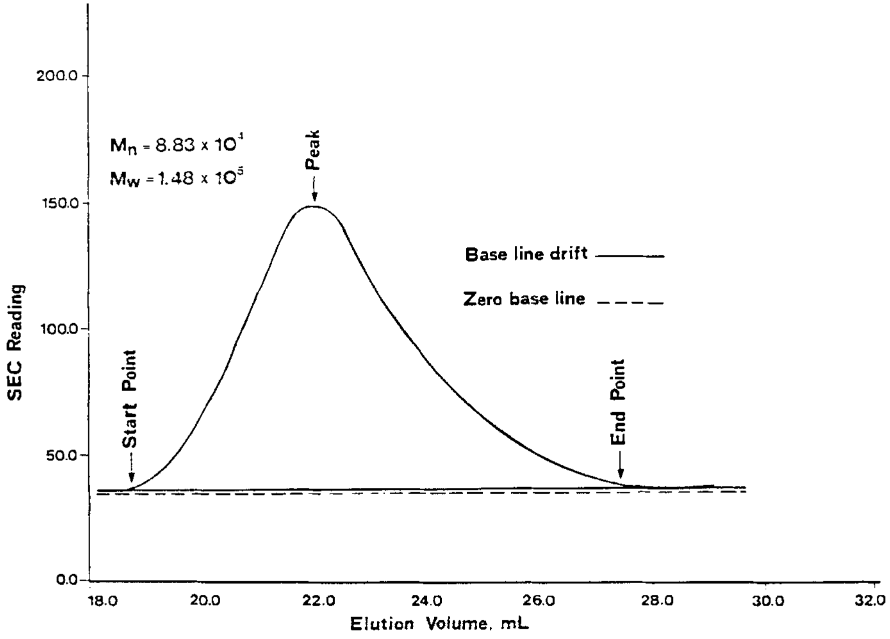

FIGURE 3: Typical chromatogram.

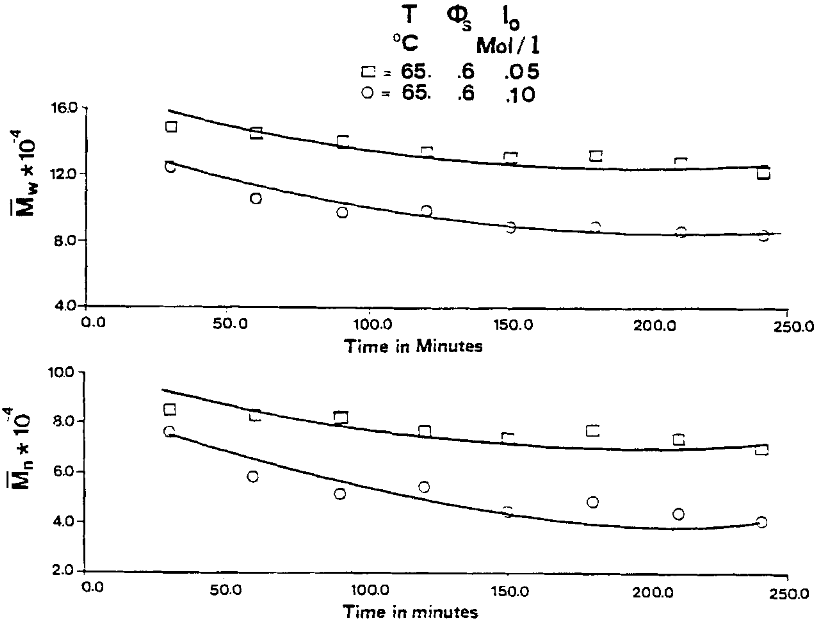

FIGURE 4: On-line monitoring of $\bar{M}_n$ and $\bar{M}_w$ values during the solution polymerization of MMA in a batch reactor (Φ_s: volume fraction of solvent, I_o: initial initiator concentration, T: polymerization temperature).

It can be seen that the calculated values of $\bar{M}_n$ and $\bar{M}_w$ for different runs do not show any significant difference. The percent relative standard deviation for $\bar{M}_n$ and $\bar{M}_w$ is equal to 5.3 and 4.1, respectively.

A typical chromatogram obtained on-line during the operation of the reactor is shown in Figure 3. The $\bar{M}_n$ and $\bar{M}_w$ values are printed on the upper left part of the chromatogram. It should be noted that the accuracy of these molecular weight determinations from SEC experiments depends on many factors such as sample dilution, sample volume, sample viscosity, etc [10]. It is important that polymer samples are diluted enough to prevent column overloading and band broadening due to viscous streaming. A rough guide for sample dilution is that an injected sample should have a viscosity no greater than twice that of the mobile phase. In the automatic sampling system, the solvent pump rate can be adjusted so that a desired sample dilution is obtained. Finally, it is important to ensure that an unknown polymer sample is eluted within the linear range of the calibration curve.

The automatic SEC system described above has been successfully used to monitor the molecular weight development, Figure 4, in a batch solution PMMA reactor [11]. The total time for analysis of a polymer sample was 15 minutes. This included the time required for the sample preparation. Further reduction in the analysis time can be achieved with the use of Bondagel columns which can reduce the total analysis time to 5-6 minutes.

Our experience has shown that SEC can be employed as an on-line detector for measurement of MWD. On-line knowledge of $\bar{M}_n$ and $\bar{M}_w$ values during the polymerization would permit the application of optimal closed-loop control in the polymerization reactors. This problem is discussed elsewhere by Ponnuswamy et al. [12].

REFERENCES

[1] Moore, L.D. and Overton, J.R., Gel-Permeation Chromatography Data Acquisition with PDP-8/1 and AX08 Laboratory Peripheral, J. Chromatography, 55, 137 (1971).

[2] Ouano, A.C., Horne, D.L. and Gregges, A.R., Gel-Permeation Chromatography 9. Instrumental Design and Computer Interfacing of a GPC Molecular Weight Detector System, J. Polym. Sci., Polym. Chem. Ed., 12, 307 (1974).

[3] Ouano, A.C., Gel-Permeation Chromatography 12. Computer - Assisted Gel-Permeation Chromatography and Low-Angle Laser Light-Scattering Photometry, J. Chromatography, 118, 303 (1976).

[4] Vandemark, F.L. and Attebery, J.M., Polymer Characterization by GPC Using On-line Data Processing, Chromatography Newsletter, 7, 34 (1979).

[5] Meira, G.R. and Johnson, A.F., Acquisition and Reduction in Real-Time with a Process Computer, Polym. Eng. Sci., 21, 57 (1981).

[6] Gregges, A.R., Dowden, B.F., Barrall, E.M. and Horikawa, T.T., Automation of Analytical Instruments 2. Modification of a Gel-Permeation Chromatograph for Automatic Sample

Injection and On-line Computer Data Recording, Separation Sci., 5, 731 (1970).

[7] Roof, L.B., Porter, G.T., Fuller, E.N. and Mowery, R.A., On-line Polymer Analysis by Liquid Chromatography, Proceedings of the 4th IFAC-PRP Automation Conf., ed. A. Van Cauwenberghe, Pergamon Press, Belgium (1980), p. 47.

[8] Ishige, T., Lee, S.-I. and Hamielec, A.E., Solution of Tungs Axial Dispersion Equation by Numerical Techniques, J. Appl. Polym. Sci., 15, 1607 (1971).

[9] Yau, W.W., Kirkland, J.J. and Bly, D.D., Modern Size Exclusion Chromatography, Wiley, New York (1979).

[10] Yau, W.W., Stocklosa, H.J. and Bly, D.D., Calibration and Molecular Weight in GPC Using a New Practical Method for Dispersion Correction - GPCV2, J. Appl. Polym. Sci., 21, 1911 (1977).

[11] Ponnuswamy, S.R., On-line Measurements and Control of a Batch Polymerization Reactor, Ph.D. Thesis, Dept. Chem. Eng., University of Alberta, Canada (1984).

[12] Ponnuswamy, S.R., Shah, S.L. and Kiparissides, C., Optimal Feedback Control of a Batch Polymerization Reactor, 1985 ACC Proceedings, Boston, MA, (1985), p. 860.