

Advances in SEC Analysis for Polymer Engineering Applications

Waters

THE SCIENCE OF WHAT'S POSSIBLE.™

Michael O'Leary¹, Baiba Čabovska¹, Bonnie Alden¹, Edouard Bouvier¹, Peter Hancock², Jeremy Shia¹, Mia Summers¹, Marian Twohig¹

¹ Waters Corp. Milford, MA USA ² Waters Corp. Manchester UK

INTRODUCTION

This year marks the 50th anniversary of the first commercial Size Exclusion Chromatography (SEC) system or as it was first described by J.C. Moore¹, Gel Permeation Chromatography (GPC). Since Waters Corp. introduced the Waters GPC 100™ system and associated Styragel® column offerings, significant advances have been made in polymer science and polymer molecular weight characterization based on this technique.

Over the first decades many refinements were introduced on the original concept. With the introduction of improved separation capacity, stable solvent delivery systems, automated sample introduction and robust detector technology, GPC has become an analytical work horse for polymer research and quality control laboratories. However, in the past two decades, little improvement has been made in basic SEC analytical systems to enable direct in-process analysis of polymerization reactions. (Figure 1)

Recent focus on reduced solvent consumption and rapid throughput testing have proven useful, but with a tradeoff between analytical performance (resolution and sensitivity) and speed of analysis due to the inherent fragile nature of the Gel Particle used in the analysis. Further, the dispersion and high dead volume of conventional refractive index detectors have limited the technological development required to break the speed vs. performance trade off for high quality rapid polymer analysis.

This poster highlights the limitations of current SEC technology and the obstacles that must be understood and addressed to advance to the next step in polymer molecular weight characterization. Further, examples provided in this poster illustrates the promise of advanced SEC analysis based on a balanced approach of complete system design that enables direct real time process control of reactions. The examples provided in this study highlight the potential of rapid SEC analysis with high quality data generation for synthetic process optimization and polymer product confirmation.

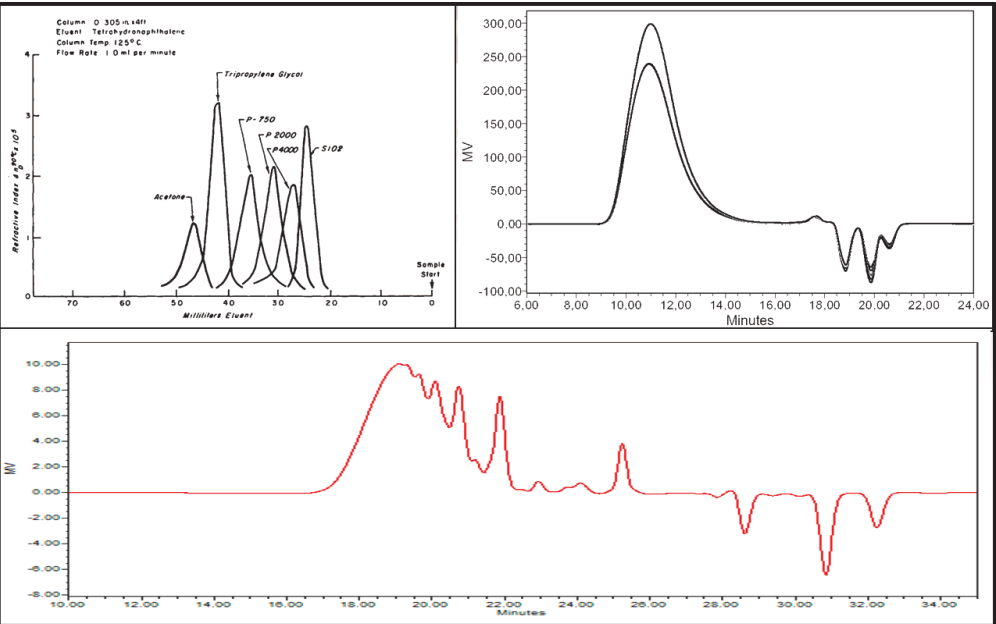


Figure 1. GPC Chromatograms; Top left circa 1965—run time 70 min., Top right circa 1990—run time 35 min. and Bottom circa 1995—run time 50 min.

EXPERIMENTAL

Four different measurement experiments are conducted to illustrate the utility of Waters ACQUITY® Advanced Polymer Chromatography™ System (APC™), Figure 2, using the enabling breakthrough APC column technology, Figure 3. Examples provided include a rapid and reliable quality control test of polymer molecular weight, determination of residual component in a polymer reaction, a photo induced polymerization reaction and monitoring a dissolution process used in a polymer blend scheme. The chromatographic experimental test conditions are listed in the table below.

APC MW Conditions	Experiment 1*	Experiment 2*
Eluent/Diluent	THF	Dichloromethane
Solvent Manager	ACQUITY APC p-ISM	ACQUITY APC p-ISM
Flow Rate	1 ml/min	1 ml/min
Sample Concentration	5 mg/gram	40 mg/gram
Sample Manager	ACQUITY APC p-FTN	ACQUITY APC p-FTN
Sample Temperature	25 C	25 C
Sample Volume	20 ul	5 ul
Column Manager	Waters CM-S	Waters CM-S
Active Preheater Temp	40C	40C
Column Temp.	40 C	40C
Column Set	APC XT Columns	APC XT Columns
Column Pore Size	450A, 125A and 45A	450A, 125A and 45A
Column Diameter	4.6 mm	4.6 mm
Column Length	150 mm (each)	150 mm (each)
Detector	ACQUITY APC p-RI	ACQUITY PDA *
Instrument Control	Empower 3	Empower 3
Data Processing	Empower 3 SEC Option	Empower 3
Calibration	Narrow Polystyrene	External Standard
Test Cycle Time	8 min.	8 min.
System Back Pressure	11,000 psi	10,000 psi
* The PDA is connected in series with the RI detector in Exp 1 & 2		
APC MW Conditions	Experiment 3	Experiment 4
Eluent/Diluent	THF	MIBK
Solvent Manager	ACQUITY APC p-ISM	ACQUITY APC p-ISM
Flow Rate	1 ml/min	1 ml/min
Sample Concentration	5 mg/gram	5 mg/gram
Sample Manager	ACQUITY APC p-FTN	ACQUITY APC p-FTN
Sample Temperature	25 C	10 C
Sample Volume	5 ul	5 ul

Table 1. APC Experimental test conditions for QC, residual component analysis, photo polymerization and polymer blend.

Column Manager	Waters CM-S	Waters CM-S
Active Preheater Temp	40C	40C
Column Temp.	40C	40C
Column Set	APC XT Columns	APC XT Columns
Column Pore Size	450A and 125A	200A and 125A
Column Diameter	4.6 mm	4.6 mm
Column Length	75 mm (each)	75 mm (each)

Flexible detection techniques

Low system dispersion

Compatibility with challenging solvents

Precise solvent management

Stable refractive index detection

Rigid, solvent-resilient columns

Versatile column management

Wide range of APC standards

Figure 2. Waters APC System (shown with RI detector)

Application technique for the size based separation of polymers in solution using columns packed with sub-3µm, rigid, high-pore-volume, hybrid particles combined with a fully optimized low dispersion ACQUITY system

- Particles based on BEH chemistry
- Five pore sizes
 - 45 Å (200 – 5,000) 1.7µm
 - 125 Å (1,000 – 30,000) 2.5µm
 - 200 Å (3,000 – 70,000) 2.5µm
 - 450 Å (20,000 – 400,000) 2.5µm
 - 900 Å* (TBD, later in the year)
- Two surface chemistries
 - Organic solvent- XT
 - Aqueous buffers – AQ
- Three column lengths
 - 30 mm
 - 75 mm
 - 150 mm
- Internal diameter: 4.6 mm

Figure 3. Waters ACQUITY APC Columns

RESULTS AND DISCUSSION

Utilizing the ACQUITY APC system a wide variety of experiments can be conducted. In experiment 1, quality control of final polymer product, sample analysis is conducted on 2 different polymer types using the standard molecular weight calculations, figures 4, 5 & 6. In contrast to conventional GPC testing multiple replicates are easily collected in less time than a single traditional test. In addition to rapid analysis high resolution chromatographic data is obtained.

In experiment 2, the solvent APC system was changed while all other components remained constant. Within 30 min the system was equilibrated for the residual competent analysis, figure 7.

In experiment 3, a set of two 75 mm APC columns were utilized to allow for a rapid (150 second) analysis test cycle time. As a result of the rapid size based analysis the reaction was easily followed predicting a complete photo polymerization in 'real time'. Figures 8 & 9 show the polymerization product while figure 10 summarizes the molecular weight moments as a function of reaction time.

Finally, a production blend of 2 polymers was followed using the APC system. The molecular weight profiles of the 2 blend partners are shown in figure 11. The summary data shown in figure 12 indicates the point of complete polymer dissolution while providing confidence in the polymer has not cross linked or degraded during the mixing process.

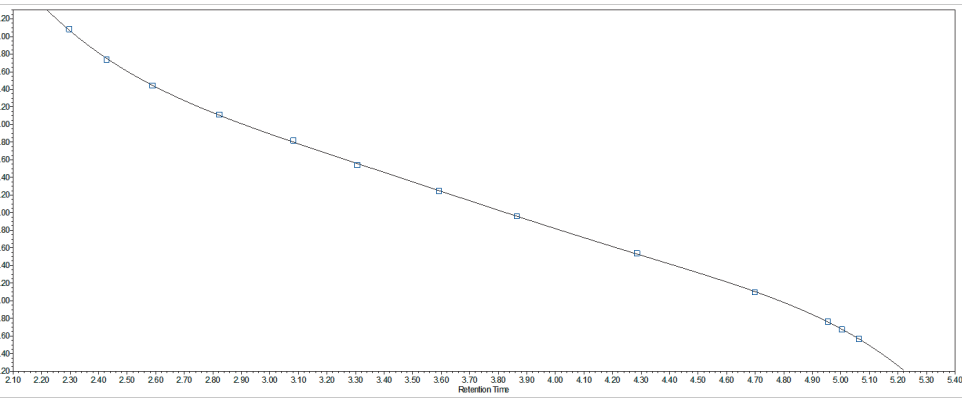


Figure 4. Full calibration of APC in < 30 min

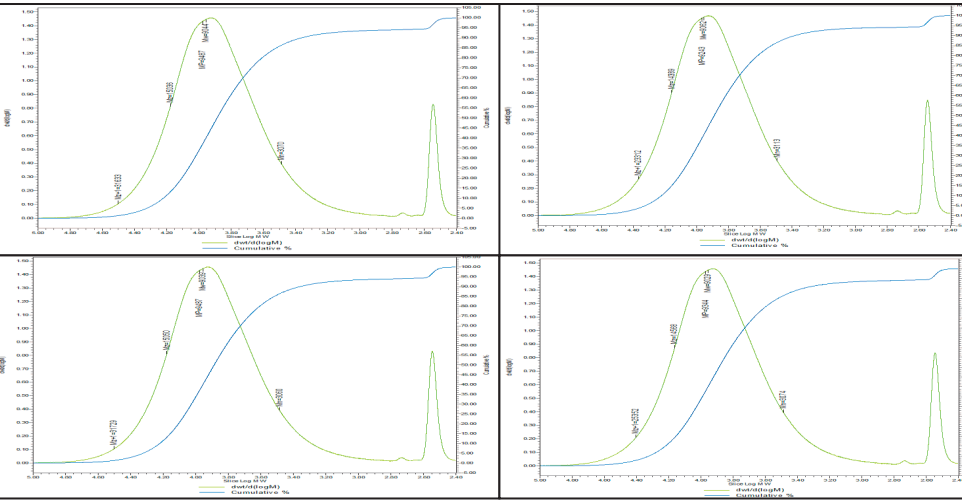


Figure 5. Experiment 1, QC testing of Acrylate polymer in < 35 min

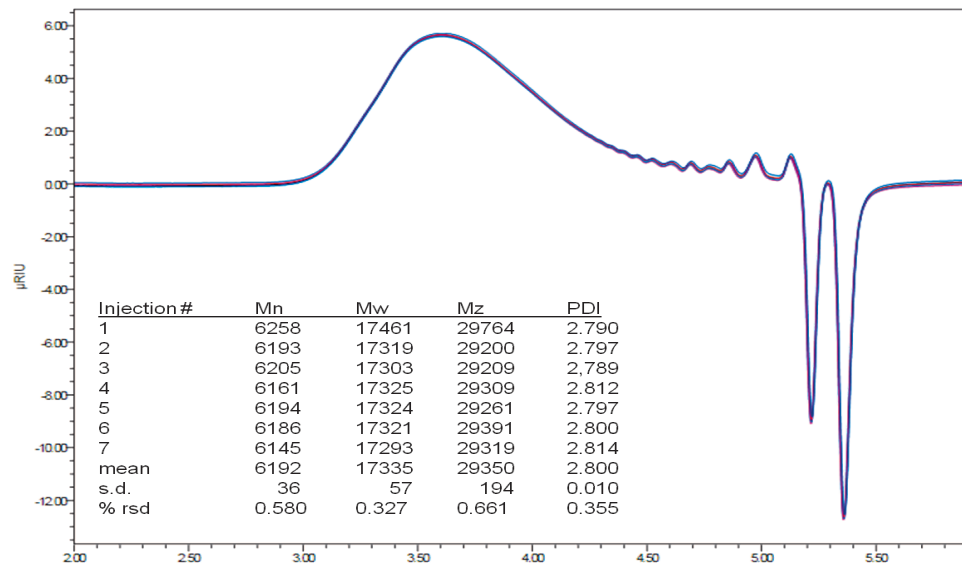


Figure 6. Seven replicate injections of Polyester in < 60 min

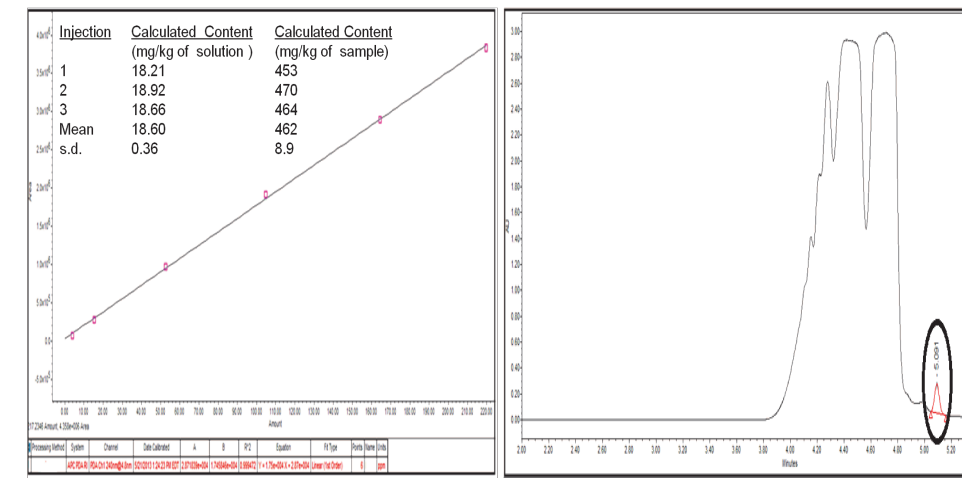


Figure 7. Experiment 2 showing the analysis of the trace polymer residual component in a polymer solution

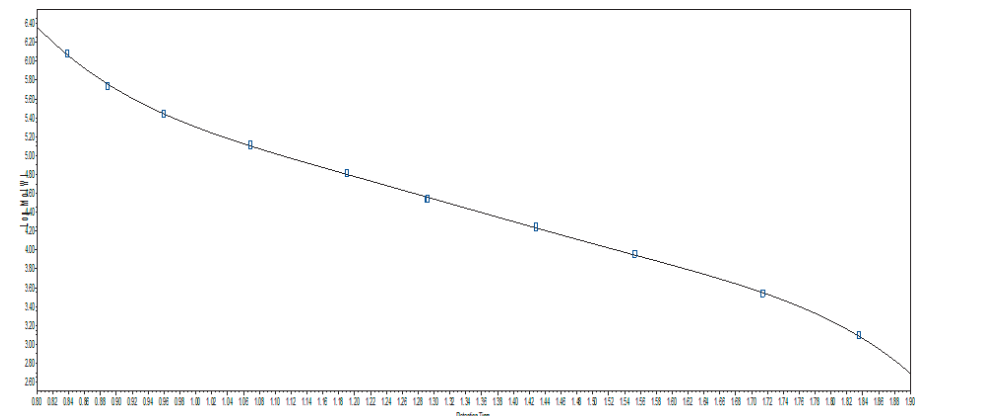


Figure 8. Full calibration of APC in < 10 min

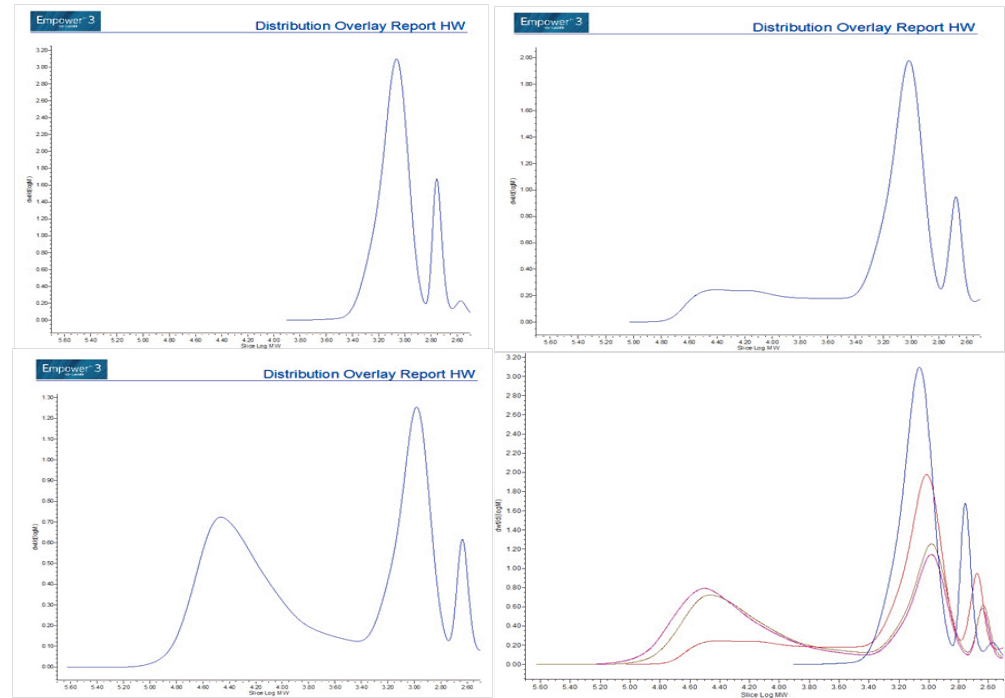


Figure 9. Experiment 3, APC Chromatograms showing the photo induced polymerization as the reaction progresses.

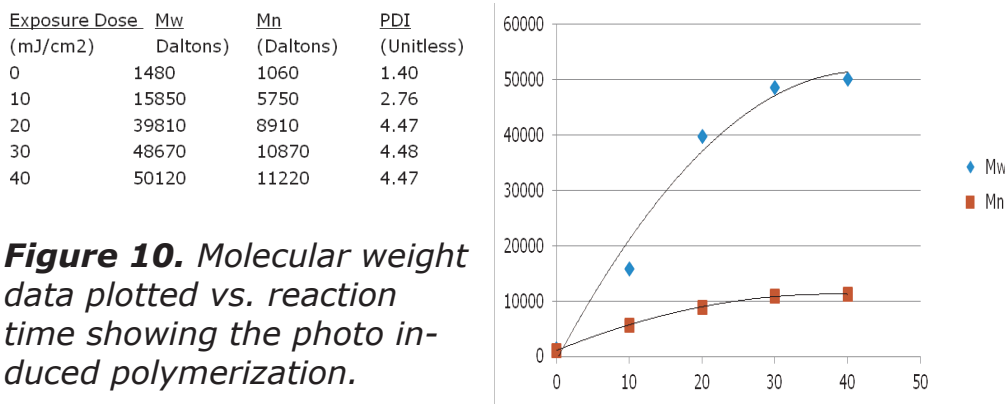


Figure 10. Molecular weight data plotted vs. reaction time showing the photo induced polymerization.

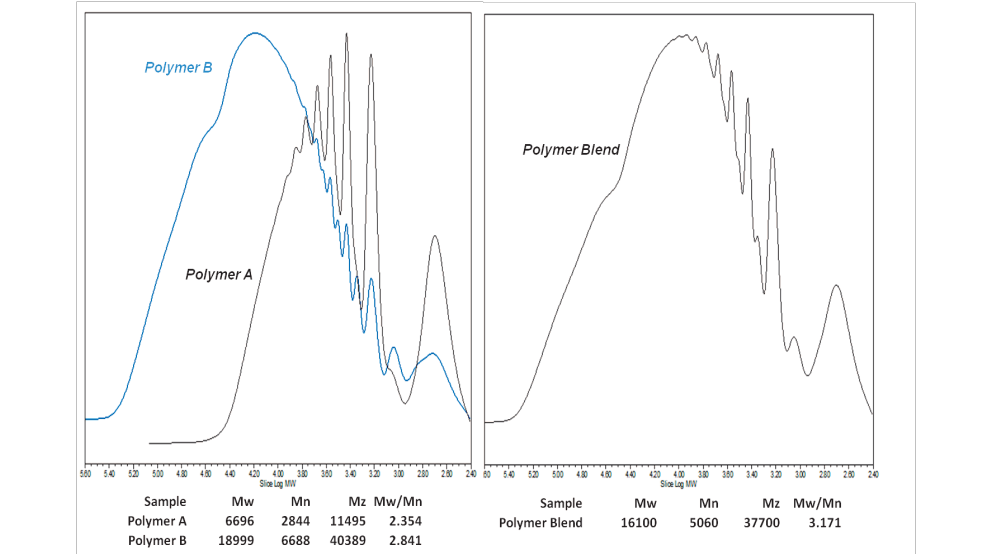


Figure 11. Experiment 4 APC chromatograms of component polymers used in blend dissolution study.

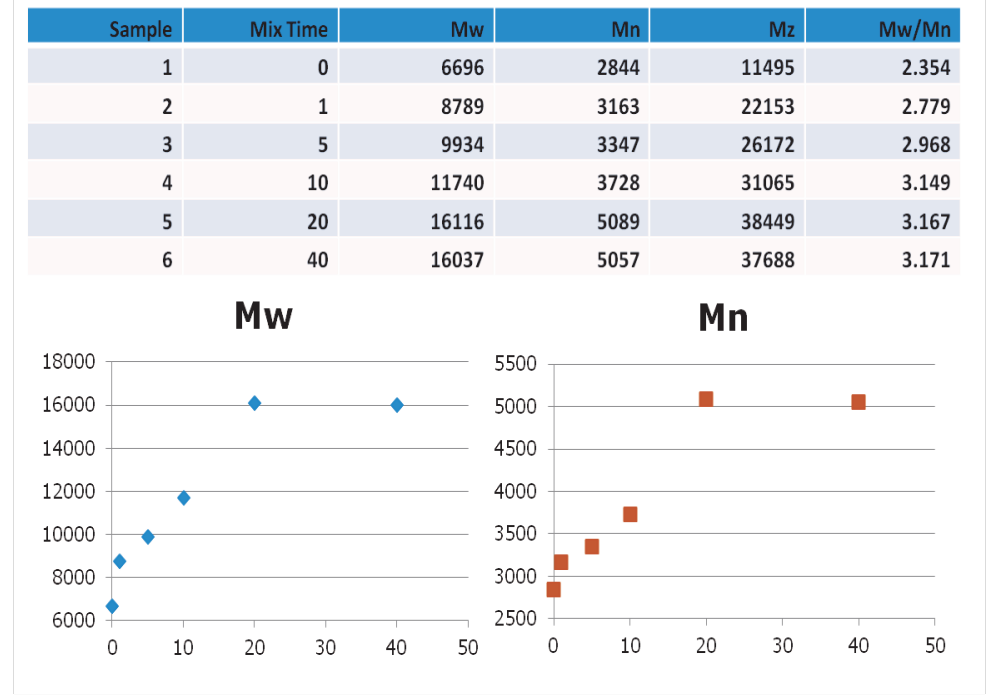


Figure 12. Molecular weight vs. mixing time of blend

CONCLUSION

- New ACQUITY APC System
 - Brings all the advantages of sub-2µm & sub-3µm particles to polymer characterization (GPC/ SEC)
- Analysis time reduction by 5x (at minimum) to 20x (and more)
 - Rapid equilibration and calibration
 - Enables 'real time' studies
- New columns compatible with any solvent
 - Rigid, BEH particles
 - Use one column set for different solvents
 - Supports in situ testing
 - Achieve better results faster
 - Higher resolution, especially in low M Wt area

References

1. J. C. Moore; Gel Permeation Chromatography. I. A New Method for Molecular Weight Distribution of High Polymers. J. Polymer Science: Part A **1964**, 2, 835-843