

This article was downloaded by:

On: 21 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymer Analysis and Characterization

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646643>

Characterization of Styrene Copolymers Using Size-Exclusion Chromatography with On-line FT-IR Viscometer Detectors

Zengrong Zhang^a; Rolf Saetre^a

^a NOVA Chemicals Corporation, Calgary, Alberta, Canada

To cite this Article Zhang, Zengrong and Saetre, Rolf(2007) 'Characterization of Styrene Copolymers Using Size-Exclusion Chromatography with On-line FT-IR Viscometer Detectors', *International Journal of Polymer Analysis and Characterization*, 12: 3, 185 – 201

To link to this Article: DOI: 10.1080/10236660701223824

URL: <http://dx.doi.org/10.1080/10236660701223824>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Characterization of Styrene Copolymers Using Size-Exclusion Chromatography with On-line FT-IR and Viscometer Detectors

Zengrong Zhang and Rolf Saetre

NOVA Chemicals Corporation, Calgary, Alberta, Canada

Abstract: Size-exclusion chromatography (SEC) provides a rapid method for determining molar mass distributions of macromolecules. In this article, we demonstrate the method of SEC coupled with an on-line Fourier-transform infrared (FT-IR) detector and an on-line differential viscometer developed for copolymer characterization. Using a chemometric technique to analyze the FT-IR spectra allows for determining copolymer concentration and composition. The combination of the FT-IR concentration detector and the viscometer allows the universal calibration method to be used for measuring copolymer molar mass. Molar mass distribution and compositional distribution are described and the method's application demonstrated using several types of styrene copolymers.

Keywords: Copolymer; Fourier-transform infrared spectrometry; Partial least squares; Size-exclusion chromatography; Styrene-butadiene copolymer; Styrene-methylmethacrylate-butadiene copolymer; Styrene-methylmethacrylate-butylacrylate-butadiene copolymer; Universal calibration

INTRODUCTION

In the characterization of polymers, size-exclusion chromatography (SEC) has become a popular technique for determining polymer molar mass averages and molar mass distribution (MMD) since its inception

Address correspondence to Zengrong Zhang, Testing Services, NOVA Chemicals Corporation, 2928 16 St. N.E., Calgary, Alberta, Canada T2E 7K7.
E-mail: zhangz@novachem.com

in the 1960s.^[1] Conventional SEC generally calibrates the molar mass of a given substance to the retention volume using narrow MMD standards. The most commonly used standards are narrow MMD polystyrene (PS) standards since these materials are commercially available and cover an extremely broad range of molar masses. The only case where conventional calibration can be rigorously held true is when there is no variation of structure (e.g., branching, conformation, etc.) between the standards and unknowns. Conventional calibration curves generated from narrow MMD PS standards will generate “polystyrene equivalent” molar masses if applied to other polymers, and this can be misleading. An important breakthrough in SEC calibration was the discovery by Benoit and his coworkers^[2] that SEC separates polymers by hydrodynamic volume. These researchers demonstrated that data plotted in the form of $\log([\eta]M)$ versus V_R , where $[\eta]$ is intrinsic viscosity, M is molar mass, and V_R is retention volume, fell on a single curve for different polymer types and for different branched architectures and copolymers. This single curve can be considered as a universal calibration (e.g., $M_1[\eta_1] = M_2[\eta_2]$, for two polymers 1 and 2). The intrinsic viscosity is a function of molar mass, which is described by the Mark-Houwink relationship $[\eta] = KM^\alpha$, where K and α are constants for a given polymer in a given solvent at a given temperature. If a column has been calibrated with polymer 1 (e.g., PS), the calibration line for polymer 2 (e.g., polyethylene) can be calculated, provided that the constants K and α are available for both polymers with sufficient accuracy. With advances in instrumentation and computer interfacing, the use of on-line viscometers has become popular in SEC for polymer characterizations.^[3–5] Combination of an online viscometer and a concentration detector allows the universal calibration to be used in SEC analyses of polymers for which the Mark-Houwink constants (K and α) are not available.

The difficulty with SEC analysis of copolymers is in the measurement of the polymer concentration at each elution volume. The concentration detectors commonly used in SEC analyses are differential refractive index (DRI) and ultraviolet (UV) detectors. Since the composition of the copolymer sample is expected to change as a function of molar mass, the use of a DRI or UV concentration detector will produce a response that will vary with the polymer composition in an unpredictable manner. The use of multiple concentration detection is generally inevitable in the analysis of copolymers. Typically, a combination of UV and DRI detection is used,^[6] but other detector combinations have also been described.^[7] For example, the combination of UV and DRI detection is used to characterize poly(styrene-*b*-methylmethacrylate) block copolymers.^[8] The UV detector set at 262 nm, at which wavelength poly(methylmethacrylate) does not absorb, was used to measure the polystyrene content, and the

DRI was used to measure the total change in refractive index. The UV signal was then used to correct for changes on polymer refractive index and allow the concentration of both components at each elution volume to be calculated. However, one has to keep in mind that dual concentration detection is applicable only for copolymers with two monomers or for binary polymer mixtures. This will be addressed in more detail in a later discussion.

Fourier-transform infrared (FT-IR) spectrometry is an important technique for coupling with SEC. Two main approaches have been used in interfacing SEC and FT-IR. In one method, a sample eluent from the SEC is deposited on a substance using a sample deposition interface.^[9,10] The solid deposit is subsequently analyzed offline by FT-IR.^[11–18] Conversely, the SEC eluent is passed through a flow cell and FT-IR spectra are acquired continuously in on-line FT-IR methods.^[19,20] With the commercialization of a high-temperature flow cell manufactured by Polymer Laboratories,^[21] on-line detection using FT-IR spectrometry is becoming more important in size-exclusion chromatography for copolymer characterization. Size-exclusion chromatography combined with Fourier-transform infrared spectrometry (SEC–FT-IR) has found acceptance in determining compositional distribution of copolymers.^[22] An investigation has been performed to compare on-line flow cell and offline solvent elimination interface for SEC–FT-IR analysis with respect to their chromatographic integrity (i.e., peak asymmetry, chromatographic resolution) and qualitative and quantitative aspects.^[23] The relatively large volume of the flow cell and the inherent deposition characteristics of the solvent elimination interface led to a comparable decrease in chromatographic resolution. The peak asymmetry was not significantly affected by either interface. The sensitivity was found to be higher for the solvent elimination interface and the detection limit worse for the flow cell. However, the repeatability of flow cell SEC–FT-IR was considerably better than solvent elimination SEC–FT-IR due to the well-defined optical path length of the sample in the flow cell.

In this work, we demonstrate the method of SEC coupled with an on-line FT-IR detector and an on-line differential viscometer (SEC–FT-IR–viscometry) developed recently for styrene copolymer characterizations. Molar mass distribution and compositional distribution are described and the method's application demonstrated using several types of styrene copolymers. In order to measure the polymer concentration and chemical composition, a partial least squares (PLS) approach is used when analyzing the FT-IR spectra of the eluting polymer solutions. The combination of the FT-IR flow cell and viscometer allows the universal calibration method to be used for characterization of copolymers.

EXPERIMENTAL SECTION

Chemicals

The antioxidant 2,6-di-*tert*-butyl-4-methylphenol (BHT, 99%) used in this study was purchased from Aldrich and the solvent 1,2,4-trichlorobenzene (TCB, EM Science, Omnisolve grade) from VWR. Polybutadiene (Stereon 40A) was provided by Firestone Polymers and poly(methylmethacrylate) from Aldrich. A narrow MMD polystyrene sample (PS47500, $M_w = 47500$, $M_w/M_n = 1.06$) was obtained from Pressure Chemical Company and a broad MMD polystyrene sample (NBS 706) from National Bureau of Standards. The narrow MMD polystyrene standards used for SEC column calibration were purchased from several suppliers: Tosoh Corporation, American Polymer Standards Corporation, and Polymer Laboratories. The copolymers of styrene and methylmethacrylate (I and II) and copolymer of styrene and butylacrylate (III) were synthesized in our lab using free-radical polymerization. Their chemical compositions (i.e., weight fractions of styrene of 79%, 27%, and 80% for I, II, and III, respectively) were measured using nuclear magnetic resonance (NMR). Styrene-butadiene, styrene-methylmethacrylate-butadiene, and styrene-methylmethacrylate-butylacrylate-butadiene copolymers were synthesized in our lab as described elsewhere.^[24]

Static FT-IR Measurements

Sample solutions were prepared by dissolving an appropriate amount of polymers in approximately 20 mL of TCB at 140°C. Both solvent and samples were weighed to the nearest 0.1 mg. The concentrations of polymer solutions in mg/cm^3 were calculated using the density of TCB (i.e., $1.3257 \text{ g}/\text{cm}^3$ at 140°C). The polymer solutions were transferred with a syringe to the FT-IR flow cell (Polymer Laboratories, 1 mm optical path length, 70 μL in volume, CaF_2 windows) that was preheated to 140°C, and the corresponding FT-IR spectra were obtained by scanning after a one-minute equilibration time. The FT-IR flow cell was mounted on a base plate in the sample compartment of the FT-IR spectrophotometer. Infrared spectra were acquired on a Bruker TENSOR 27 FT-IR spectrophotometer equipped with OPUS operating software. The sample and detector compartments of the spectrophotometer were continuously purged with dried nitrogen gas. The spectra were acquired in the absorbance mode and were background corrected against pure solvent. All spectra were measured at 8 cm^{-1} resolution with 32 scans.

SEC–FT-IR–Viscometry Measurements

Samples of experimental resins were dissolved in TCB by heating the mixture for 4 h at 150°C in an oven. BHT was added to the mixture in order to stabilize the polymer against oxidative degradation. The BHT concentration was 250 ppm. Sample solutions were chromatographed on a Waters 150-C high-temperature chromatography unit equipped with four PLgel Mixed B columns (Polymer Laboratories) using TCB as the mobile phase with a flow rate of 1.0 mL/min. BHT was added to the mobile phase at a concentration of 125 ppm to protect SEC columns from oxidative degradation. The sample injection volume was 300 μ L. The SEC eluent was introduced to the FT-IR flow cell via a heated transfer line. The FT-IR flow cell outlet was connected to the differential viscometer (Viscotek Corporation, Model 150R) via a heated transfer line. The FT-IR flow cell was mounted on a base plate in the sample compartment of the FT-IR spectrophotometer. The viscometer was sitting inside the column compartment of the Waters 150-C. The temperatures of the transfer lines, FT-IR flow cell, and the column compartment of the Waters 150-C were kept at 140°C. A Bruker TENSOR 27 FT-IR spectrophotometer was used in these studies. The sample and detector compartments of the spectrophotometer were continuously purged with dried nitrogen gas.

All FT-IR spectra were acquired using OPUS process software. Background spectra of the TCB solvent were obtained prior to each run. All spectra were measured at 8 cm^{-1} resolution with 16 scans (one spectrum in \sim every 6 s). Spectra from individual time slices were analyzed in “real time” for component concentrations using a chemometric technique (i.e., PLS). The concentration data, along with the viscometer differential and inlet pressures, were acquired using OPUS process software. These data were processed using Excel and OMNIC software to provide molar mass and composition distributions.

RESULTS AND DISCUSSION

In on-line flow cell SEC–FT-IR analysis, it is important to employ a mobile phase having low or preferably no infrared absorptions in the analytically important spectral regions for the polymers of interest. Although tetrahydrofuran (THF) is a good solvent for the copolymers investigated in this study, it is not a suitable mobile phase for on-line flow cell SEC–FT-IR analysis since there is very strong solvent infrared absorption band due to the C–H stretching vibrations in the spectral region for the copolymers of interest between 2800 and 3000 cm^{-1} . Typically, chlorinated solvents having low infrared absorption are good

candidates for the mobile phase of SEC-FT-IR analysis. For example, tetrachloroethylene (TCE) will be a good choice of mobile phase for styrene-butadiene copolymer analysis even at ambient temperature. It was found that 1,2,4-trichlorobenzene (TCB) at 140°C is a good solvent for copolymers studied in this work and for other copolymers currently under investigation. To simplify the instrument setup and to avoid frequent solvent switching, TCB was used as the mobile phase in this work.

In order to determine the concentration of an unknown sample, the FT-IR flow cell must be calibrated to generate a calibration curve that correlates the measured absorptions with the known concentrations of standards. This is straightforward for a single component (i.e., homopolymer) system since a linear correlation exists between the sample concentration and the absorbance of a peak. For a multicomponent (i.e., copolymer) system, peaks used for the analysis must be well separated. For styrene copolymers, resolved single peaks or absorption bands for each component are not available. For example, the FT-IR spectra of polystyrene, poly(methylmethacrylate), and polybutadiene in TCB are shown in Figure 1. Due to the strong IR absorptions from solvent TCB, the spectral window that can be used to quantify the sample concentration for this type of polymer is 2800 to 3050 cm^{-1} , in which the spectra overlap seriously (Figure 2).

In this work, the PLS technique is used to analyze FT-IR spectra for the determination of polymer concentration and composition. PLS

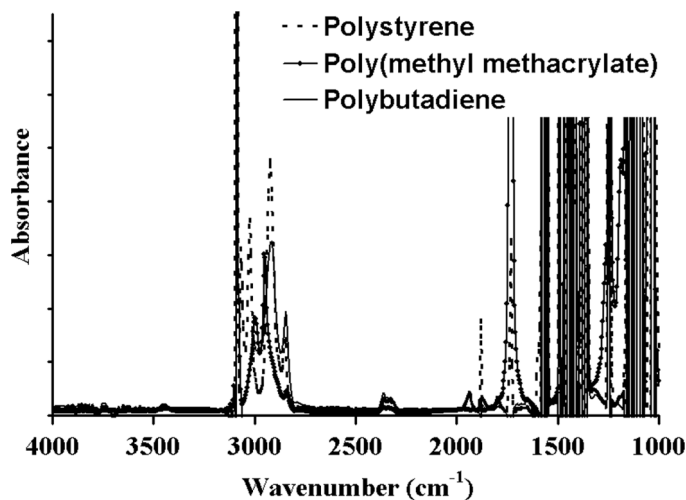


Figure 1. FT-IR spectra of polystyrene, poly(methylmethacrylate), and polybutadiene.

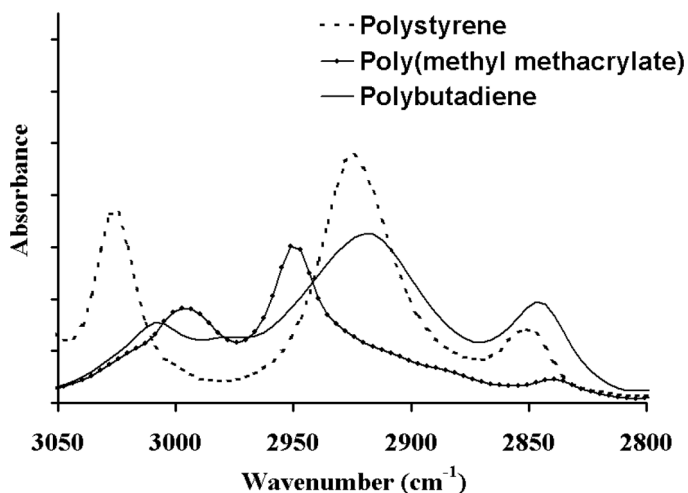


Figure 2. Expanded FT-IR spectra of polystyrene, poly(methylmethacrylate), and polybutadiene.

regression is an extension of a multiple linear regression model. A good tutorial on the PLS algorithm was presented by Kowalski.^[25] In chemometrics, partial least squares regression has become a popular tool for modeling linear relations between multivariate measurements. It has been successfully applied to FT-IR quantitative analyses,^[17,22] and commercial PLS software is available from FT-IR instrument suppliers (e.g., OPUS QUANT, Bruker; TQ Analyst, ThermoNicolet). In our study, the PLS software purchased from Bruker (OPUS QUANT) was used for quantitative FT-IR spectral analyses.

For building a calibration model using the PLS method, a sufficiently large number of samples are made to represent the styrene copolymer systems. This is done by mixing the TCB solutions of individual polymers. For example, PS47500, poly(methylmethacrylate), poly(styrene-*co*-methymethacrylate), and polybutadiene solutions are mixed to prepare samples to represent styrene-methylmethacrylate-butadiene copolymer system. The concentration of each component is calculated based on the polymer masses and the composition of copolymers. Monomers (e.g., styrene, methylmethacrylate, butadiene) are considered as components in these copolymer systems. The spectra obtained from the static FT-IR measurements of sample solutions are input into the OPUS QUANT software along with the component concentrations. The spectra are then defined into two independent sets, one for calibrating the system and the other for validating the model. Both sets consist of about the same number of spectra and each set covers the whole concentration

range. Second derivatives of the spectra in given frequency ranges are used in the calculations.

The PLS method is a “full spectrum method.” However, in some cases spectral noise in the samples may cause the PLS algorithm to interpret these features, which can degrade the model. In these cases it is better to narrow a spectrum down to a few absorption bands. As shown in Figure 1, residual IR absorptions from the solvent TCB are detected after background correction against pure solvent TCB, especially in the frequency range from 3050 to 3150 cm^{-1} and when the wave number is less than 1900 cm^{-1} , due to strong IR absorptions of TCB in these frequency ranges. These contribute in a sample spectrum as spectral noise. Therefore, two absorption bands (3017 to 3032 cm^{-1} and 2831 to 2986 cm^{-1}) in which there is much less spectral noise were chosen for building the calibration model in this study.

PS47500 and polybutadiene were used for preparing samples to represent styrene-butadiene copolymer system. Styrene and butadiene were considered as the two components for this system. The training set was composed with 27 standards that covered a concentration range of 0–1.95 mg/mL and a composition range of 0–100% (styrene weight fraction). The ranks used in the calibration model were three for the two components. For the styrene-methylmethacrylate-butadiene copolymer system, PS47500, poly(methylmethacrylate), two poly(styrene-*co*-methylmethacrylate) (I and II), and polybutadiene were used to prepare the standard solutions for building the PLS calibration model. Styrene, methylmethacrylate, and butadiene were considered as the three components for this system. The training set was composed with 49 standards that covered a concentration range of 0–1.22 mg/mL and a composition range of 0–80% (styrene weight fraction). The ranks used in the calibration model were four for all three components. PS47500, two poly(styrene-*co*-methylmethacrylate) (I and II), poly(styrene-*co*-butylacrylate), and polybutadiene were used for preparing samples to represent styrene-methylmethacrylate-butylacrylate-butadiene copolymer system. Styrene, methylmethacrylate, butylacrylate, and butadiene were considered as the four components for this system. The training set was composed with 89 standards that covered a concentration range of 0–3.85 mg/mL and a composition range of 0–80% (styrene weight fraction). The ranks used in the calibration model were five, five, six, and five for styrene, methylmethacrylate, butylacrylate, and butadiene, respectively.

Figure 3 shows the calibrations in the PLS calibration model for the three components (styrene, methylmethacrylate, and butadiene) of styrene-methylmethacrylate-butadiene system. Forty-five samples with different concentrations and compositions were used as the validation samples. The concentrations and compositions predicted by the PLS

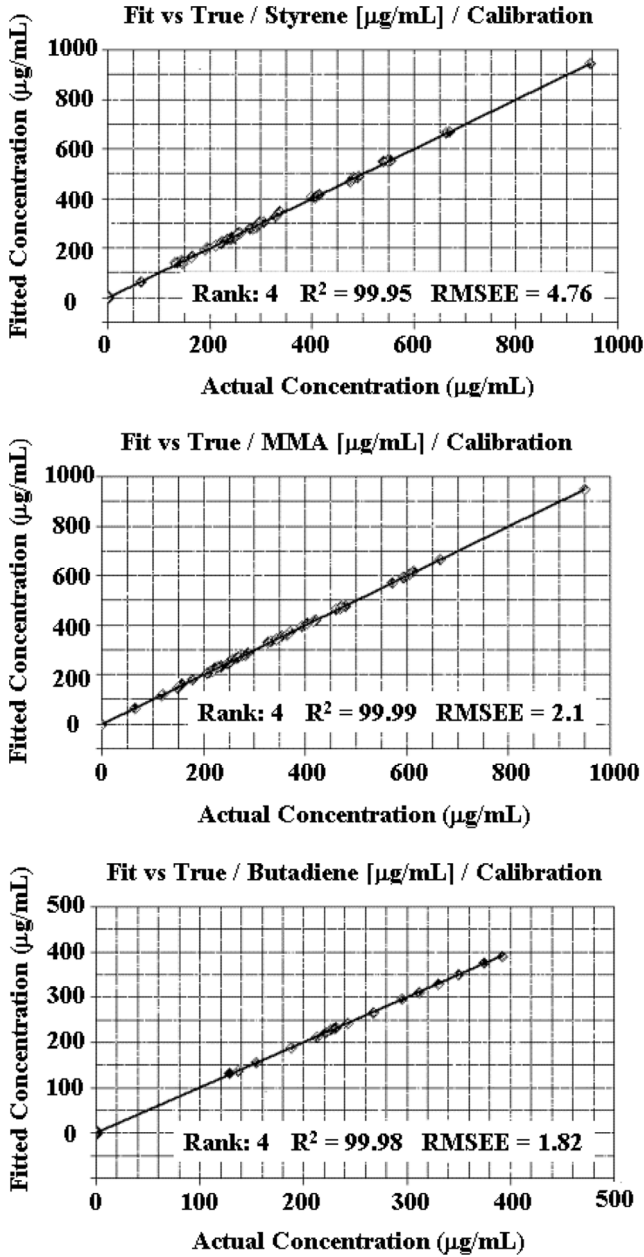


Figure 3. PLS calibration model for styrene-methylmethacrylate-butadiene copolymer system.

calibration model match well with the expected concentrations and compositions. The relative standard deviations (RSD) are 0.6% and 1.8% for concentration and composition measurements, respectively. For the styrene-butadiene and styrene-methylmethacrylate-butylacrylate-butadiene copolymer systems, the concentrations and compositions predicted by the corresponding PLS calibration models also match well with the expected concentrations and compositions. Twenty-four samples with different concentrations and compositions were used as the validation samples in the PLS calibration model for the styrene-butadiene system; the relative standard deviations (RSD) are 0.5% and 0.4% for concentration and composition measurements, respectively. Eighty-one samples with different concentrations and compositions were used as the validation samples in the PLS calibration model for the styrene-methylmethacrylate-butylacrylate-butadiene system; the relative standard deviations (RSD) are 1.0% and 1.8% for concentration and composition measurements, respectively.

As Mark-Houwink constants are not available for styrene copolymers, an SEC with an on-line viscometer and a concentration detector (e.g., FT-IR detector in this work) is needed, i.e., universal calibration, to determine the molar mass distribution of these polymers. Applying the above PLS calibration models to the FT-IR spectra allows for determining the concentration and composition (i.e., the weight fractions of monomers) of the eluting copolymer at each slice. For example, for a three-component copolymer system, the corresponding concentrations C_α , C_β , and C_γ for each component are predicted from the PLS calibration model. The copolymer concentration C can be calculated by $C = C_\alpha + C_\beta + C_\gamma$, as well as the copolymer composition (i.e., the weight fractions w_α , w_β , and w_γ of the monomers α , β , and γ) by $w_\alpha = C_\alpha/C$, $w_\beta = C_\beta/C$, and $w_\gamma = C_\gamma/C$.

A differential viscometer (Viscotek Corporation, Model 150R series viscometer) is coupled with SEC to measure the viscosities of the eluting polymer solutions. It is well known that this viscometer actually measures the pressure difference ΔP at the differential pressure transducer between the inlets of the sample capillary and the reference capillary, which have a common outlet, and the overall pressure P_i at the inlet of the bridge. Specific viscosity (η_{sp}), which is defined as $\eta_{sp} = (\eta - \eta_0)/\eta_0$ (where η is the viscosity of the sample solution and η_0 is the viscosity of the pure mobile phase), is thus obtained from the differential pressure and the inlet pressure by $\eta_{sp} = 4\Delta P/(P_i - 2\Delta P)$. Since the concentrations in SEC are typically very low, the intrinsic viscosity $[\eta]$, which is defined as the limiting value of η_{sp}/c for $c \rightarrow 0$, can be approximated by $[\eta] = \eta_{sp}/c$.^[26]

The universal calibration is constructed in the form of $\log([\eta]M)$ versus retention time t_r since the flow rate is set at 1 mL/min and the retention time equals retention volume. A total of 16 narrow molar mass

distribution polystyrene standards (molar mass range 5×10^2 to 5×10^6) were used to construct the calibration curve, and the values for concentration and specific viscosity at the peak positions were used. For the four PLgel Mixed B columns used in this study, the data points fit into a linear relationship.

When two detectors are used in a SEC system, it is essential that the time difference for the eluting polymer to reach the two detectors (inter-detector volume) be known precisely. Otherwise, the calculated values will contain significant errors. There are a number of approaches that can be used to determine the inter-detector volume. The most common one is to measure the difference between peak positions from the two detectors using a narrow molar mass distribution polymer standard. Using this approach, an inter-detector delay time of 0.52 min was obtained when the flow rate was set at 1.0 mL/min in our work, in which the two detectors were configured in series in the order of FT-IR detector and differential viscometer. It was found that the inter-detector volume as measured from the difference in peak retention volumes of narrow molar mass distribution standards from one detector to another varied with molar mass when the detectors were in a parallel configuration. In the series configuration no such dependence was observed. This agrees well with the observations by Balke and his coworkers when they investigated the use of dual detectors in SEC.^[27,28] It could partly account for difficulties in analyzing narrow molar mass distribution polymers in parallel configuration systems and may be due to flow rate variation in different branches of the parallel configuration during elution of a sample.

In order to optimize a chromatographic condition (i.e., sample concentration) for a maximum response from the FT-IR detector with reasonably good chromatographic resolution, a broad molar mass distribution polystyrene sample (NBS 706) was analyzed under different sample concentrations. The weight-average molar mass of this sample is about 250000 and the number average molar mass is about 115000.^[3] As shown in Figure 4, distortions of the differential molar mass distribution curves (i.e., shifting to lower molar mass) were observed at high sample concentrations due to the column overloading (i.e., the columns are no longer separating the sample based on molar mass). With a fixed injection volume of 300 μ L, it is found that adequate chromatographic resolution is maintained using concentrations less than 4.7 mg/mL for this polystyrene sample under the tested concentration range of the present work. This agrees well with the published work^[22] in which adequate chromatographic resolution was maintained on a system of two PLgel Mixed B columns with an injection volume of 500 μ L and a concentration of 1.6 mg/mL for a broad molar mass polyethylene resin. For the SEC-FT-IR-viscometry analyses of styrene copolymers, sample

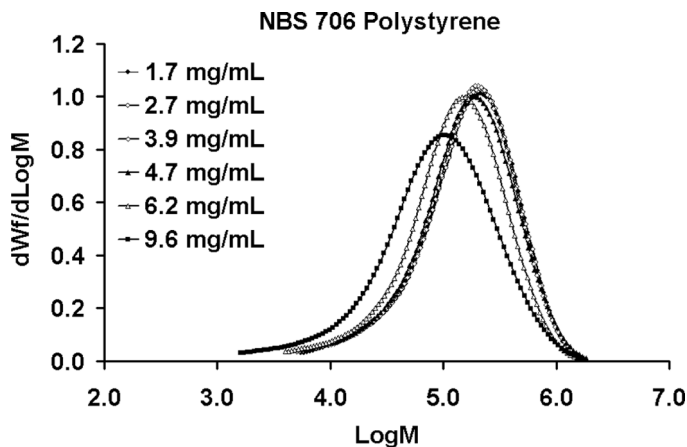


Figure 4. Distortions of molar mass distribution curves due to column overloading.

concentrations are usually kept in the range of 2.5 to 4.5 mg/mL in this work.

The accuracy of the SEC-FT-IR-viscometry method for measuring molar mass distribution and average molar masses can be checked by comparing the results of homopolymers (e.g., polystyrene) to those obtained using the SEC-DRI method. The differential molar mass distribution of NBS 706 obtained using the SEC-FT-IR-viscometry method is shown in Figure 5. For comparison, this sample was also subjected to

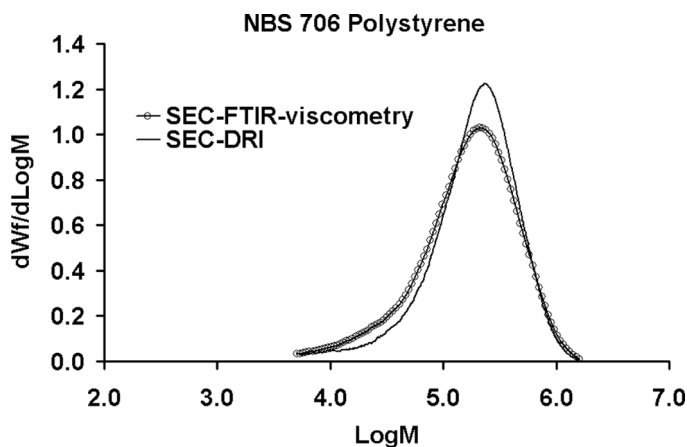


Figure 5. Differential molar mass distribution of NBS 706 sample obtained with two different detector systems.

SEC-DRI analysis using an SEC instrument with a DRI concentration detector. The two methods provided practically identical results in terms of the weight-average molar masses (243000 and 256000 for SEC-FT-IR-viscometry and SEC-DRI, respectively), which are very close to the value (250000) reported in literature.^[3] However, as shown in Figure 5, the SEC-FT-IR-viscometry method gives a broader molar mass distribution compared to the result obtained from the SEC-DRI method. This is most likely a result of different detector volumes for the two systems. The FT-IR cell is 70 μL , which is significantly larger than the 10 μL DRI cell.

Styrene and butadiene are defined as the two components for the FT-IR detection in the SEC-FT-IR-viscometry analysis of styrene-butadiene copolymers. Shown in Figure 6 is an example of SEC-FT-IR-viscometry analysis for this type of sample. One of advantages of SEC-FT-IR-viscometry is its capability for composition distribution analysis. Traditional SEC analysis determines molar mass distribution of macromolecules and provides average molar masses. Since FT-IR is able to measure polymer composition along with polymer concentration, SEC-FT-IR-viscometry analysis provides the composition distribution of styrene copolymer in addition to the molar mass distribution and average molar masses. As shown in Figure 6, one curve represents molar mass distribution and the other represents composition distribution (i.e., styrene content as a function of molar mass).

As mentioned in a previous section, the use of multiple concentration detection methods is generally inevitable in the analysis of copolymers and dual-concentration detection has been described.^[6-8] The principle

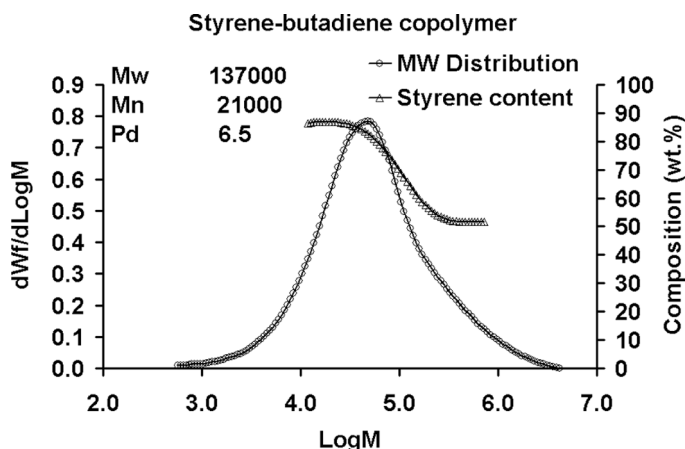


Figure 6. SEC-FT-IR-viscometry analysis of styrene-butadiene copolymer.

of dual detection is rather simple: when a copolymer that contains the monomers A with a concentration of C_A and the monomers B with a concentration of C_B is eluted in the slice i of the peak, it will cause signals R_1 and R_2 in detectors 1 and 2, respectively. The signal magnitudes depend on the corresponding response factors f_{1A} and f_{1B} for detector 1 and f_{2A} and f_{2B} for detector 2. From the relationships $R_1 = f_{1A}C_A + f_{1B}C_B$ and $R_2 = f_{2A}C_A + f_{2B}C_B$, the monomer concentrations can be calculated by: $C_A = (R_1f_{2B} - R_2f_{1B}) / (f_{1A}f_{2B} - f_{2A}f_{1B})$, $C_B = (R_1f_{2A} - R_2f_{1A}) / (f_{1B}f_{2A} - f_{2B}f_{1A})$. Therefore, the copolymer concentration C can be calculated by $C = C_A + C_B$ as well as the copolymer composition (i.e., the weight fractions w_A and w_B of the monomers A and B) by $w_A = C_A/C$ and $w_B = C_B/C$. It is obvious that dual-concentration detection is applicable only for copolymers with two monomers or for binary polymer mixtures. The advantage of SEC-FT-IR-viscometry is its capability to characterize styrene copolymers with three or more components (i.e., monomers). Shown in Figure 7 are the molar mass distribution and composition distributions of a styrene-methylmethacrylate-butadiene copolymer. Styrene, methylmethacrylate, and butadiene are defined as the three components for FT-IR detection in the SEC-FT-IR-viscometry analysis for this type of copolymer. The molar mass distribution and composition distributions for a more complex copolymer system, styrene-methylmethacrylate-butylacrylate-butadiene copolymer, are shown in Figure 8. Styrene, methylmethacrylate, butylacrylate, and butadiene are defined as the four components for FT-IR detection in the SEC-FT-IR-viscometry analysis for this type of copolymer.

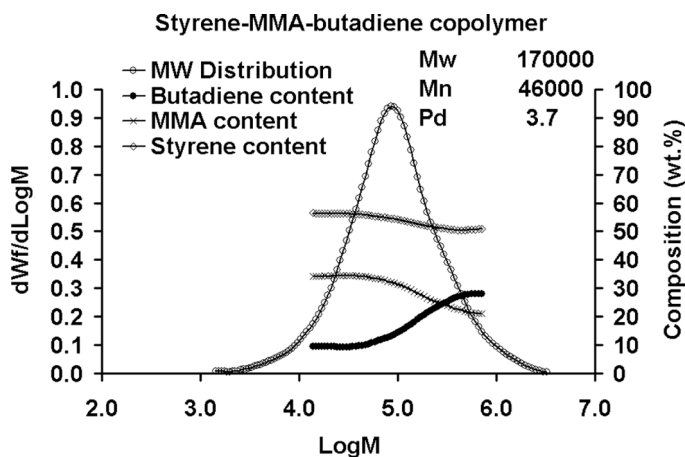


Figure 7. SEC-FT-IR-viscometry analysis of styrene-methylmethacrylate-butadiene copolymer.

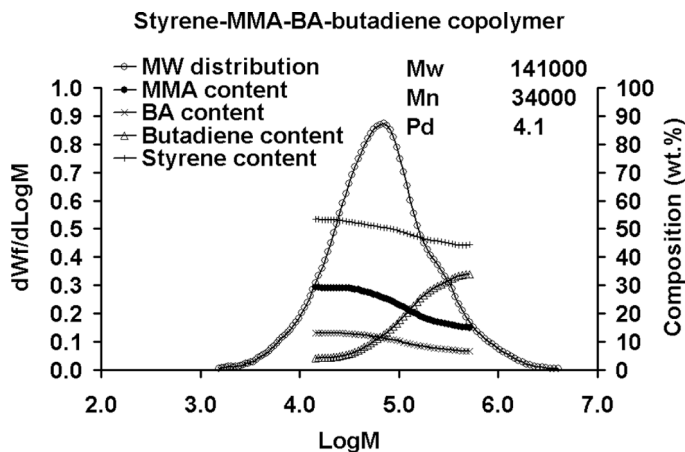


Figure 8. SEC-FT-IR-viscometry analysis of styrene-methylmethacrylate-butylacrylate-butadiene copolymer.

CONCLUSIONS

A SEC-FT-IR-viscometry method has been developed to allow for the determination of molar mass averages, molar mass distribution, and composition distributions (i.e., comonomer contents as a function of molar mass) of styrene copolymers. The current method couples an on-line FT-IR detector and a differential viscometer with SEC. Using a chemometric technique, partial least squares, to analyze the FT-IR spectra allows for determining the concentration and composition (i.e., the weight fractions of monomers) of the eluting copolymer at each slice. The combination of FT-IR concentration detector and differential viscometer allows the universal calibration approach to be applied for the determination of molar mass of the eluting copolymer at each slice. Chromatographic conditions were optimized to maximize sample concentration at the detectors while maintaining acceptable chromatographic resolution. As examples for the application of this method, molar mass distribution and comonomer content as a function of molar mass were described for styrene-butadiene, styrene-methylmethacrylate-butadiene, and styrene-methylmethacrylate-butylacrylate-butadiene copolymers.

REFERENCES

- [1] Moore, J. C. (1964). Gel permeation chromatography. I: A new method for molecular weight distribution of high polymers. *J. Polym. Sci. Part A Gen. Pap.* **2**, 835-843.

- [2] Grubisic, Z., P. Rempp, and H. Benoit. (1967). A universal calibration for gel permeation chromatography. *J. Polym. Sci. Part B Polym. Lett.* **5**, 753–759.
- [3] Haney, M. A. (1985). The differential viscometer. II. On-line viscosity detector for size-exclusion chromatography. *J. Appl. Polym. Sci.* **30**, 3037–3049.
- [4] Ekmanis, J. L. and R. A. Skinner. (1991). Gel permeation chromatographic analysis of polymers with an online viscometer detector. *J. Appl. Polym. Sci. Appl. Polym. Symp.* **48**, 57–73.
- [5] Yau, W. W. and S. W. Rementer. (1990). Polymer characterization by SEC-viscometry: Molecular weight (MW), size (Rg) and intrinsic viscosity (IV) distribution. *J. Liq. Chromatogr.* **13**, 627–675.
- [6] Lee, H. C., M. Ree, and T. Y. Chang. (1995). Characterization of binary polymer mixtures by size-exclusion chromatography with multiple detection. *Polymer* **36**, 2215–2218.
- [7] Trathnigg, B., S. Feichtenhofer, and M. Kollroser. (1997). Quantitation in liquid-chromatography of polymers: Size-exclusion chromatography with dual detection. *J. Chromatogr. A* **786**, 75–84.
- [8] Grubisic-Gallot, Z., J. P. Lingelser, and Y. Gallot. (1990). Characterization of block copolymers by size exclusion chromatography. *Polym. Bull.* **23**, 389–395.
- [9] Cheung, P., S. T. Balke, T. Schunk, and T. H. Mourey. (1993). Assessment and development of evaporative interfaces for size-exclusion chromatography/Fourier-transform infrared spectrometry. *J. Appl. Polym. Sci. Appl. Polym. Symp.* **52**, 105–124.
- [10] Willis, J. N., J. L. Dwyer, and M. X. Liu. (1997). Polymer characterization using SEC-FTIR. *Int. J. Polym. Anal. Charact.* **4**, 21–29.
- [11] Cheung, P. C., S. T. Balke, and T. C. Schunk. (1995). Size-exclusion chromatography-Fourier transform IR spectrometry using a solvent-evaporative interface. *Adv. Chem. Ser.* **247**, 265–279.
- [12] Ludlow, M., D. Loudon, S. Taylor, A. Handley, B. Wright, and I. D. Wilson. (1999). Size exclusion chromatography with UV detection coupled to online $^1\text{H-NMR}$ and online collection via a dedicated interface for subsequent off-line FT-IR. *Anal. Commun.* **36**, 85–87.
- [13] Willis, J. N., J. L. Dwyer, X. Liu, and W. A. Dark. (1999). Size exclusion chromatography-FTIR analysis of polyethylene. In *Chromatography of Polymers: Hyphenated and Multidimensional Techniques*, ed. T. Provder. Washington, D.C.: American Chemical Society, pp. 226–231.
- [14] Ludlow, M., D. Loudon, A. Handley, S. Taylor, B. Wright, and I. D. Wilson. (1999). Size-exclusion chromatography with on-line ultraviolet, proton nuclear magnetic resonance and mass spectrometric detection and on-line collection off-line Fourier transform infrared spectroscopy. *J. Chromatogr.* **857**, 89–96.
- [15] Tackx, P., S. Bremmers, and E. Gelade. (2000). Chemical composition distribution of linear-low density polyethylenes by SEC-FT-IR. *Int. J. Polym. Anal. Charact.* **6**, 147–154.
- [16] Torabi, K., A. Karami, S. T. Balke, and T. C. Schunk. (2001). Quantitative FTIR detection in size-exclusion chromatography. *J. Chromatogr. A* **910**, 19–30.

- [17] Karami, A., S. T. Balke, and T. C. Schunk. (2001). Quantitative interpretation of Fourier-transform infrared spectroscopic data from a size-exclusion chromatography solvent-evaporation interface. *J. Chromatogr. A* **911**, 27–37.
- [18] Kok, S. J., N. C. Arentsen, P. J. C. H. Cools, Th. Hankemeier, and P. J. Schoenmakers. (2002). Fourier transform infrared spectroscopy with a sample deposition interface as a quantitative detector in size-exclusion chromatography. *J. Chromatogr. A* **948**, 257–265.
- [19] Brown, R. S., D. W. Hausler, L. T. Taylor, and R. C. Carter. (1981). Fourier transform infrared spectrometric detection in size-exclusion chromatographic separation of polar synfuel material. *Anal. Chem.* **53**, 197–201.
- [20] Voigt, D., K.-J. Eichhorn, K.-F. Arndt, and S. Prettin. (1997). Online size exclusion chromatography-Fourier transform infrared spectroscopy (FTIR): Investigation of preferential salvation effects. *Int. J. Polym. Anal. Charact.* **3**, 333–349.
- [21] <http://www.polymerlabs.com/gpc/ftircell.htm>
- [22] DesLauriers, P. J., D. C. Rohlfing, and E. T. Hsieh. (2002). Quantifying short chain branching microstructures in ethylene 1-olefin copolymers using size exclusion chromatography and Fourier transform infrared spectroscopy (SEC-FTIR). *Polymer* **43**, 159–170.
- [23] Kok, S. J., C. A. Wold, Th. Hankemeier, and P. J. Schoenmakers. (2003). Comparison of on-line flow-cell and off-line solvent-elimination interfaces for size-exclusion chromatography and Fourier-transform infrared spectroscopy in polymer analysis. *J. Chromatogr. A* **1017**, 83–96.
- [24] Chen, J. and H. Farag. (2004). Experimental set-up and literature review on bulk polymerization kinetics for the ter-polymer system: Styrene, methyl methacrylate and butyl acrylate. NOVA Chemicals Internal Technical Report TR1831. Calgary: NOVA Chemicals.
- [25] Geladi, P. and B. R. Kowalski. (1986). Partial least-squares regression: A tutorial. *Anal. Chim. Acta* **185**, 1–17.
- [26] Haney, M. A. (1985). The differential viscometer. I.: A new approach to the measurement of specific viscosities of polymer solutions. *J. Appl. Polym. Sci.* **30**, 3023–3036.
- [27] Thitiratsakul, R., S. T. Balke, and T. H. Mourey. (1996). Combining detectors in size exclusion chromatography. Part 1: Interdetector volume. *Int. J. Polym. Anal. Charact.* **2**, 345–357.
- [28] Thitiratsakul, R. and S. T. Balke. (1996). Combining detectors in size exclusion chromatography. Part 2: Peak shape changes. *Int. J. Polym. Anal. Charact.* **2**, 359–377.