Application of advanced gel permeation chromatography to the characterization of styrenic copolymers

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Products produced by anionic polymerization of nonpolar monomers, such as polybutadienes (BR), polyisoprenes (IR), solution styrene butadiene rubbers (SSBR) and styrenic block copolymers (SBC), already dominate important positions in industries. Examples include thermoplastic elastomers, adhesives, impact modifiers, lubricant modifiers, vulcanized compounds, asphalt modification and others. SBCs combine the properties of a thermoplastic resin, polystyrene and those of an elastomer, polybutadiene, polyisoprene or poly(ethylene-co-butylene). SBCs derive their useful properties from their ability to form distinct styrene (hard phase) and diene (rubber phase) domains (ref. 1).

Living anionic polymerization technology can produce polymers with a narrow molecular weight distribution, a block copolymer structure and a controlled microstructure suitable for a wide variety of applications (refs. 1 and 2). Leveraging these advantages, Dynasol Group produces a broad range of polybutadienes, SSBRs and SBCs for several applications. Polymer microstructure and macrostructure will determine if a given material is suitable for a particular application. Macrostructure corresponds to the molecular weight, molecular weight distribution and long-chain branching concentration, and the microstructure describes the monomer sequence distribution and the content of butadiene 1,4 and 1,2 addition. Depending on the polymerization conditions (solvent, temperature and added polar modifier), the microstructure of polybutadienes and styrenic copolymers can vary in a wide range. The microstructure of polybutadienes and styrenic copolymers (SSBR and SBC) can be determined by attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), Raman spectroscopy, proton nuclear magnetic resonance (^{1}H-NMR) and ^{13}C-NMR spectroscopy (ref. 2).

Macrostructure is considered to be a fundamental parameter affecting the mechanical properties and the ability of polymers to be mixed, processed and fabricated into finished products. Gel permeation/size exclusion chromatography (GPC/SEC) is one of the most important separation analytical techniques to determine polymer macrostructure (refs. 3 and 4). A conventional GPC/SEC equipped with only a refraction index detector is calibrated with polystyrene standards, and the relative polymer molecular weight and molecular weight distribution are obtained. In order to estimate the absolute molecular weight from relative molecular weight, the universal calibration curve principle or the individual hydrodynamic equivalence ratio can be used. The universal calibration curve method requires the knowledge of the intrinsic viscosity (η) for the polymer to be analyzed and for the polystyrene calibration standards. Individual hydrodynamic ratios are obtained by calibrating the GPC with homopolymers of polystyrene and polybutadiene blocks, and then use a combining rule (based on an independent measurement of the copolymer's composition) to interpolate between the polystyrene and polybutadiene calibration curves. Another option is to directly determine the absolute molecular weight with a multi-detector GPC/SEC system equipped with refractive index and light scattering detectors. The advanced multi-detector GPC/SEC system offers absolute molecular weight and branching analysis through intrinsic viscosity (IV). A combination of concentration detectors offers the ability to determine copolymer composition (refs. 5 and 6).

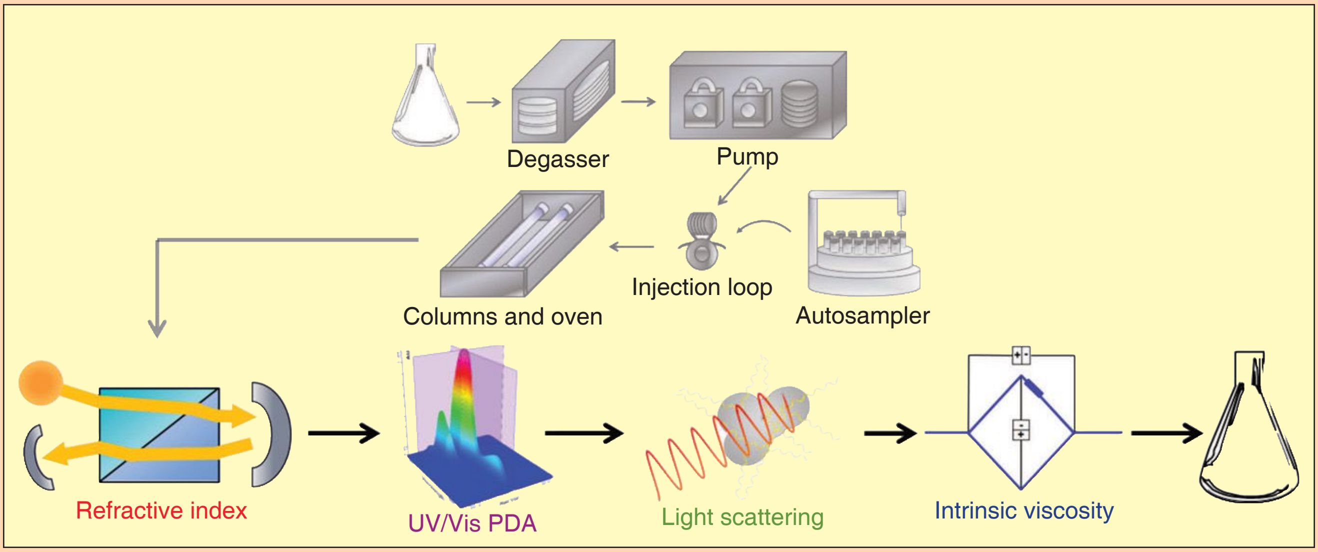
In this article, two methods are described, using a conventional GPC/SEC, to estimate the absolute molecular weight of model polybutadienes and styrenic copolymers. Results are obtained with an advanced multi-detector GPC/SEC system equipped with a light scattering detector. In the second part, a GPC/SEC method was implemented to estimate the total styrene concentration of the styrenic copolymers. Ultraviolet (UV) and refractive index (RI) detectors were used to estimate the styrene concentration, and results were compared with ^{1}H-NMR and ATR-FTIR.

Experimental

Model polymers, polybutadienes and styrene/butadiene copolymers with controlled microstructure were synthetized by a living anionic polymerization technique. Cyclohexane (Dynasol Group) with purity higher than 98%, butadiene with purity of 99% (Repsol) and styrene with purity higher than 99% (Repsol) were used in the synthesis of the model polybutadienes and styrenic copolymers. Monomers and solvent were purified further by passing them through drying columns packed with alumina. Initiator n-butyllithium dissolved in cyclohexane, 24% w/w (Albemarle), was stored under nitrogen atmosphere until it was used. Then 2,6-dibutyl-para-cresol (BHT) was added as a shortstop for the living anionic polymerization, and at the same time acted as an antioxidant.

The polymerization reactor was equipped with a system that enables precise control of temperature: ±3°C. The solution polymerization of butadiene or styrene butadiene mixture in cyclohexane was carried out in a two-liter batch reactor under nitrogen atmosphere. The initial polymerization temperature was 60°C and was performed under quasi-adiabatic conditions. The addition of butadiene, styrene and solvent to the reactor was carried out using volumetric columns. The required amount of n-butyllithium was added into the reactor at the desired temperature. The initial concentration of butadiene or styrene butadiene mixture in the reaction mixture was 12% w/w. A polar modifier in a given concentration was added to control the microstructure of the polybutadienes or styrenic copolymers.

Figure 1 - schematic diagram of the multi-detector GPC/SEC system



Polymer macrostructure

Model polymers were characterized by gel permeation/size exclusion chromatography (GPC/SEC). Polymer molecular weight distributions were determined by a multi-detector GPC/SEC system equipped with a four-column PLgel 5 µm Mixed-C. A multi-detector GPC/SEC (Omnisec) from Malvern Panalytical Ltd. (Worcestershire, U.K.) equipped with refractive index, UV/visible PDA, viscosimetric and light scattering detectors was employed. Tetrahydrofurane (THF) was the mobile phase (T = 35°C), and its flow rate was 0.9 mL/minute. Light scattering (LS) and refraction index (RI) detectors were used to determine the molecular weight distribution of the model polymers. Figure 1 shows a schematic diagram of the multi-detector GPC/SEC system used in this study. Figure 2 describes the polymer parameters determined from information obtained from the multi-detector GPC/SEC system. The multi-detector GPC/SEC system is equipped with ultraviolet (UV), refractive index (RI), light scattering (LS) and viscosimetric detectors. Figure 3 shows a typical chromatogram obtained with a multi-detector GPC/SEC system. The chromatogram shows the signals obtained with the UV, RI and LS detectors (refs. 4 and 5).

The relative molecular weights of the model polymers were measured with a conventional GPC/SEC (Waters) equipped with a refraction index detector. Linear polystyrenes were used to

Figure 2 - polymer parameters measured by the multi-detector GPC/SEC system

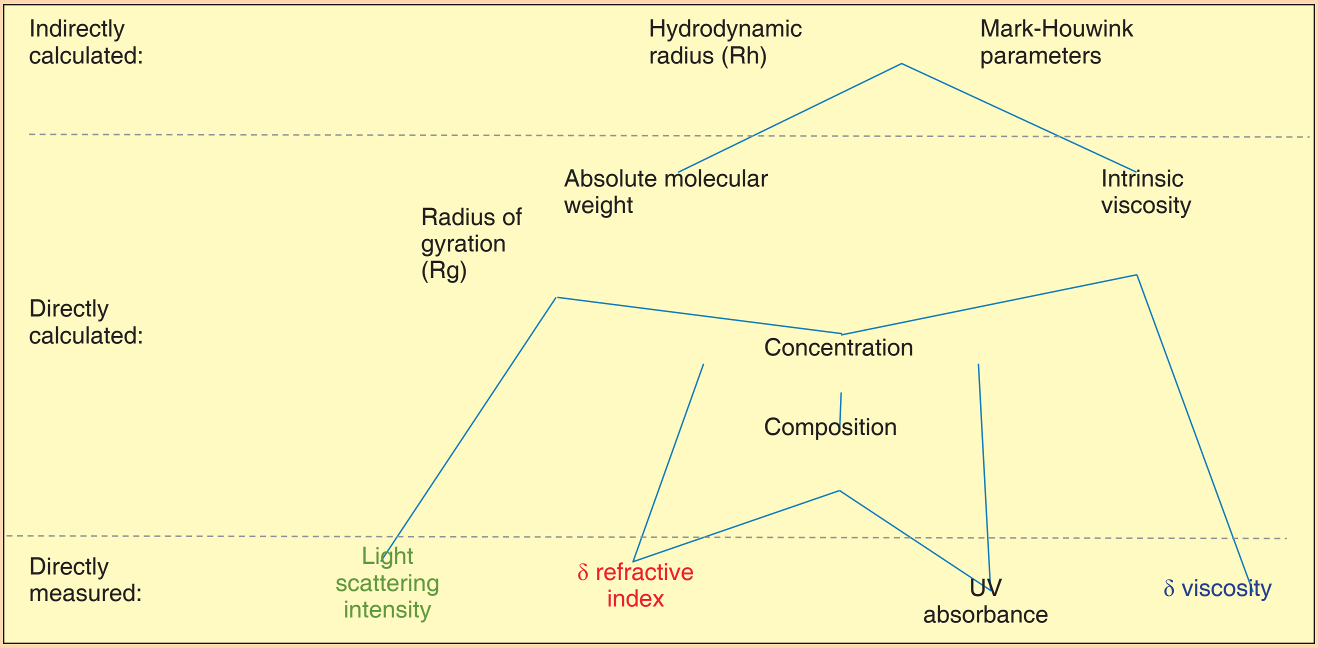
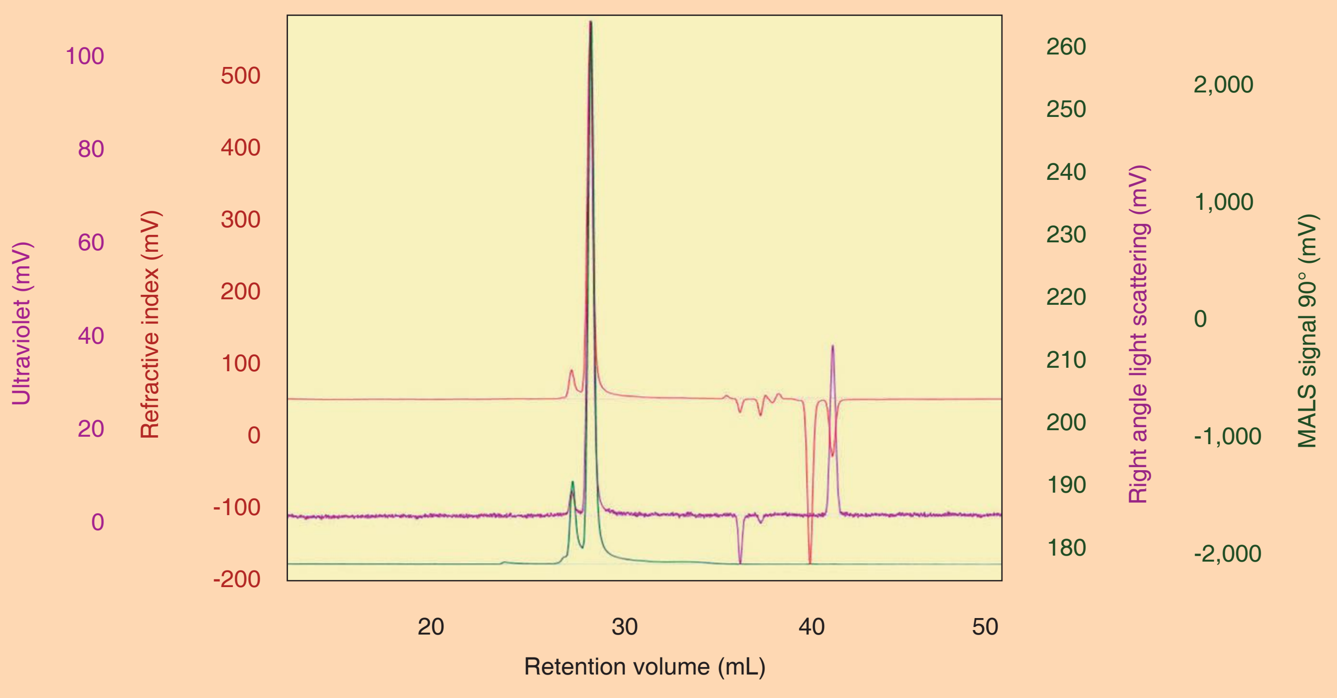


Figure 3 - chromatogram of SSBR-03 sample obtained with a multi-detector GPC/SEC system



calibrate the conventional GPC/SEC equipment. Two different methods were used to estimate the absolute molecular weight from relative molecular weight, including the universal calibration curve principle and hydrodynamic equivalence factor.

Polymer microstructure

Polymer microstructure was determined by ^{1}H-NMR and attenuated total reflectance (ATR-FTIR). Model polymers were dissolved in $CDCl_3$ and analyzed by liquid ^{1}H-NMR according to ISO 21561:2005 in an NMR spectrometer, 400 MHz, from Bruker (Fällanden, Switzerland). Fourier transform infrared spectroscopy was carried out using the ATR-FTIR mode on a Nicolet Avator 360 FTIR with a 32-scan per sample cycle and a resolution of 4. The polymers were scanned between 400 and 4,000 cm^{-1}. ATR-FTIR was calibrated with samples previously analyzed by ^{1}H-NMR. Polymer microstructure parameters determined by ATR-FTIR were vinyl content (relative to butadiene) and total styrene concentration (ISO 21561-2:2016).

Results

Polybutadienes (BR) and styrenic copolymers (SSBR, SB and SBS) with controlled microstructure and varying molecular weights were synthesized by living anionic polymerization. Table 1 shows the microstructure of the model polymers, polybutadienes and styrenic copolymers synthetized in bench reactors. The microstructure of the model polymers was determined by ^{1}H-NMR. The molecular weight and molecular weight distribution of the polymers were determined with a multi-detector GPC/SEC system, as well as by means of a conventional GPC/SEC calibrated with polystyrene standards.

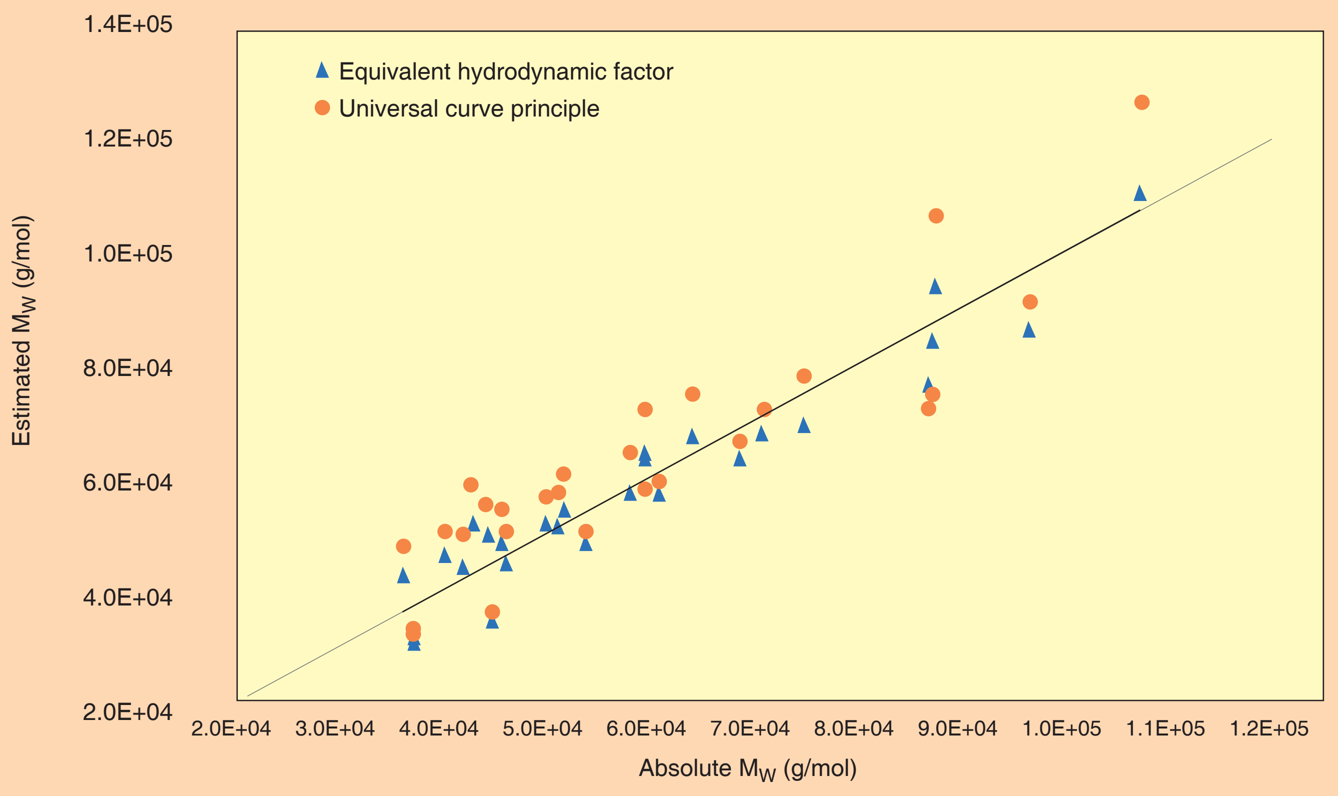
In the case of the GPC/SEC multi-detector system, the constants of the refractive index, UV and light scattering detectors, K_{RI}, K_{UV} and K_{LS}, were determined using a polystyrene standard with broad molecular weight distribution. In order to deter-

Table 1 - microstructure of model polybutadienes and styrenic copolymers determined by ^{1}H-NMR

	Polymer type	*Total styrene content (%)*	*Vinyl content* (%)*
BR-01	Polybutadiene	0.0	85.0
BR-02	Polybutadiene	0.0	93.7
BR-03	Polybutadiene	0.0	29.5
BR-04	Polybutadiene	0.0	43.7
BR-05	Polybutadiene	0.0	57.2
BR-06	Polybutadiene	0.0	64.9
BR-07	Polybutadiene	0.0	69.1
SB-01	SB	49.5	29.5
SB-02	SB	31.0	34.9
SB-03	SB	9.7	17.7
SB-04	SB	19.3	17.1
SB-05	SB	28.5	15.6
SB-06	SB	40.1	16.9
SB-07	SB	50.5	17.5
SB-08	SB	30.3	38.2
SB-09	SB	50.5	44.7
SB-10	SB	29.6	59.6
SB-11	SB	29.4	13.2
SB-12	SB	24.0	12.4
SBS-01	SBS	40.4	38.6
SBS-02	SBS	39.8	56.2
SBS-03	SBS	40.8	44.4
SBR-01	SSBR	20.1	12.9
SBR-02	SSBR	26.8	18.5
SBR-03	SSBR	40.2	52.6
SBR-04	SSBR	28.3	27.5

*Vinyl content referred to butadiene

Figure 4 - absolute molecular weights of model polymers estimated with equivalent hydrodynamic factor and universal curve principle



mine the absolute molecular weight of a polymer with the light scattering detector, its dn/dc (difference in refractive index between the sample and the solvent) was estimated from the refractive index detector signal. Given that the concentration of the injected polymer is known and it was assumed that the entire injected sample elutes outside of the GPC/SEC columns:

- The refractive index (RI) detector signal is $K_{RI} \cdot dn/dc \cdot$ (concentration)
- The ultraviolet (UV) detector signal is $K_{UV} \cdot (dA/dc) \cdot$ (concentration)
- The light scattering detector (LS) signal is $K_{LS} \cdot$ molecular weight $\cdot (dn/dc)^2 \cdot$ (concentration)

The absolute molecular weight of the model polymers was estimated from the relative molecular weights using two approaches: hydrodynamic equivalence factor and the universal curve calibration principle. The hydrodynamic equivalence factor was estimated using Chang's combining rule (refs. 7 and 8): $r_c = 1 + 0.96^* (1 - w_{sty})$, where w_{sty} is the weight fraction of styrene in the polymer. Absolute molecular weights were estimated dividing the relative molecular weights by the corresponding equivalence factor (ref. 7).

In the universal calibration method, the following Mark-Houwink constants were used: a = 0.717 and k = 1.251 x 10^{-4} dL/g for polystyrene; for the polybutadienes, a = 0.693 and k = 4.57 x 10^{-4} dL/g; and for the styrene/butadiene copolymers, a = 0.693 and k was estimated using an internal correlation that depends only on the total styrene concentration. The absolute molecular weight of a given polymer was estimated using the following equation (ref. 3):

$$\mathrm{In}\ M_2 = \frac{1 + a_1}{1 + a_2}\ \mathrm{In}\ M_1 + \frac{1}{1 + a_2}\ \mathrm{In}\ \frac{k_1}{k_2} \qquad (1)$$

where M_2 is the absolute molecular weight, M_1 is the relative molecular weight, a_1 and k_1 are the constants of polystyrene, and a_2 and k_2 are the constants of the polymer.

Figure 4 shows the absolute weight average molecular weights, M_w, estimated by the hydrodynamic equivalence factor and universal curve calibration principle as a function of the absolute M_w obtained by the multi-detector GPC/SEC system. Note that both methods give molecular weight values close to those obtained by the light scattering detector. The mean error in the estimation of absolute M_w was determined for each method. Table 2 shows the error obtained for each method. The method that gave the least error was the hydrodynamic equivalence factor, with an error of about half that obtained with the universal

Table 2 - average error in estimating absolute molecular weights (M_w) with a conventional GPC/SEC

Method	*Average error (g/mol)*	*Average percentage error (%)*
Hydrodynamic equivalence factor	±4,766	±9
Universal curve principle	±8,350	±15

curve calibration principle. It was observed in both methods that when the vinyl content was greater than 60%, the error increased significantly. It is concluded that both methods allow estimating the molecular masses with an error of less than 20%, being more precise when the vinyl content is less than 60%.

The total styrene concentration in the copolymers was determined using the GPC/SEC multi-detector system (refs. 6 and 9). Combining the information obtained with concentration detectors (refractive index and ultraviolet detectors), the total styrene concentration in the copolymers was determined. In order to determine the composition of an A-B copolymer, it is necessary to use the signals from the RI and UV detectors. The detector signals are described by the following equations:

$$RI_{signal} \propto C_A \left(\frac{dn}{dc}\right)_A + C_B \left(\frac{dn}{dc}\right)_B \tag{2}$$

$$UV_{signal} \propto C_A \left(\frac{dA}{dc}\right)_A + C_B \left(\frac{dA}{dc}\right)_B \tag{3}$$

Therefore, the result is two equations and two unknowns (CA and CB). To determine the copolymer composition, it is necessary to know the dn/dc values of each of the blocks that make up the copolymer; and one of the blocks must be a chromophore (dA/dc > 0). Combining equations 2 and 3 further assuming that at the selected wavelength $(dA/dc)_B = 0$, the result is:

$$\frac{UV_{signal}}{RI_{signal}} = \frac{C_A\left(\frac{dA}{dc}\right)_A + C_B\left(\frac{dA}{dc}\right)_B}{C_A\left(\frac{dn}{dc}\right)_A + C_B\left(\frac{dn}{dc}\right)_B} = \frac{W_A\left(\frac{dA}{dc}\right)_A}{W_A\left(\frac{dn}{dc}\right)_A + (1 - w_A)\left(\frac{dn}{dc}\right)_B} \tag{4}$$

From equation 4, it is possible to determine, from the RI and UV detector signals, the copolymer composition expressed in weight fraction of component A. In order to determine the styrene concentration in the copolymers, Omnisec software, version 5.12, was used. In the case of the dA/dc values, a UV signal at wavelength 254 nm was selected. At this wavelength, only block A (styrene) absorbs; therefore, $(dA/dc)_B = 0$. Arbitrarily, it was assigned a value of $(dA/dc)_A = 1$. Individual dn/dc values of the blocks that make up the copolymer were 0.185 mL/g for polystyrene, and 0.112 mL/g and for polybutadiene. Figure 5 shows the total styrene concentration, expressed as a percentage by weight, of the styrenic copolymers estimated with the multi-detector GPC/SEC system, as well as that determined by ATR-FTIR as a function of the composition obtained by ^{1}H-NMR. Both methods predicted a styrene concentration very similar to that obtained by ^{1}H-NMR. Table 3 shows the errors in the determination of the total styrene concentration for both methods. The multi-detector GPC/SEC system estimated the total styrene concentration in the copolymer with an error of ±2.5 percentage units, which is slightly higher than that obtained by ATR-FTIR, which was ±1.3 percentage units.

On the other hand, the individual dn/dc for each polymer segment was estimated from the multi-detector GPC/SEC sys-

Figure 5 - total styrene concentration of styrenic copolymers determined by ATR-FTIR and the multi-detector GPC/SEC system

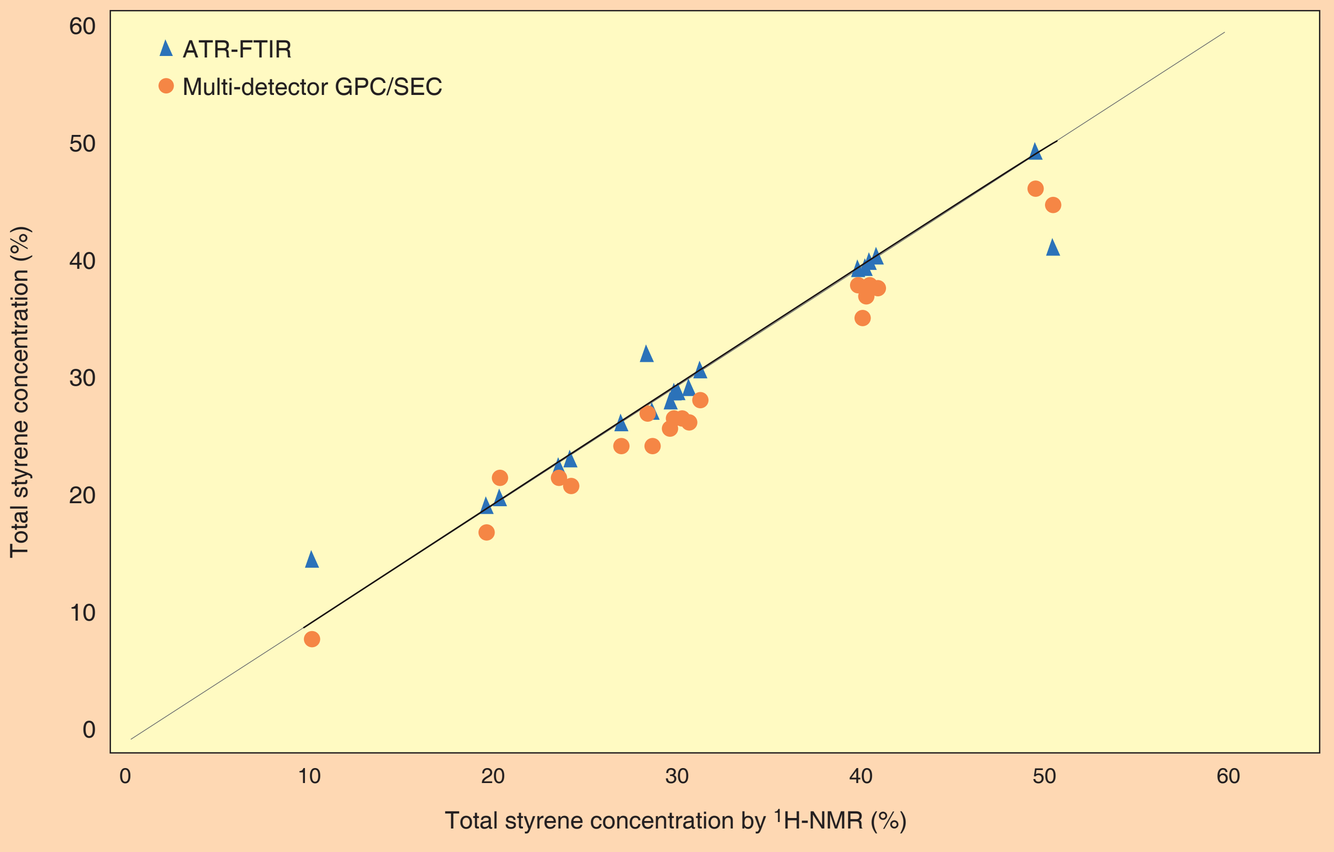


Table 3 - average error in total styrene concentration in copolymers

Method	*Average error (%)*	*Average percentage error (%)*
GPC/SEC multi-detector system	±2.5	±8.1
ATR-FTIR	±1.3	±5.9

tem. There is a way to use the multi-detector GPC/SEC to calculate an unknown dn/dc (refractive index increment) value. The multi-detector GPC/SEC will assume a 100% sample recovery, and by knowing the input concentration and injection volume, will relate the amount of mass injected into the system to the refractive index signal observed. The individual contributions (polybutadiene-1,2, polybutadiene-1,4 and polystyrene) from the dn/dc and ^{1}H-NMR copolymer microstructure were estimated. Individual contributions were carried out assuming that the following equation is valid:

$$\frac{dn}{dc} = w_{PB\_1,4}\left(\frac{dn}{dc}\right)_{PB\_1,4} + w_{PB\_1,2}\left(\frac{dn}{dc}\right)_{PB\_1,2} + w_{PS}\left(\frac{dn}{dc}\right)_{PS} \tag{5}$$

where $(dn/dc)_i$ is the variation of the refractive index with the concentration of homopolymer i, and w_i is the weight fraction of component i in the copolymer. Equation 5 was rearranged depending on two weight fractions. Figure 6 shows the experimental-observed dn/dc values as a function of those predicted with the correlation model described by equation 5. Table 4 shows the individual dn/dc values for polybutadiene-1,2, polybutadiene-1,4 and polystyrene. The squared correlation coefficient of the model was 89.5%. The values of dn/dc of the individual segments were similar to those reported in the literature (refs. 10-12).

Conclusions

The multi-detector GPC/SEC system provides a powerful analytical technique for comprehensively characterizing polybutadienes and styrenic copolymers. Beyond a simple relative molecular weight, the use of multiple detectors allows for more accurate results and a stronger understanding of how polymers such as these will behave in their respective applications. It has shown that accurate absolute molecular weights of polybutadienes and styrenic copolymers can be estimated by using a conventional GPC/SEC calibrated with polystyrene standards. Two different approaches were used: the hydrodynamic equivalence factor and the universal curve calibration principle. The hydrodynamic equivalence factor method provides a more accurate method to estimate the absolute molecular weight.

Figure 6 - correlation model for dn/dc for polybutadienes and styrenic copolymers, observed versus predicted

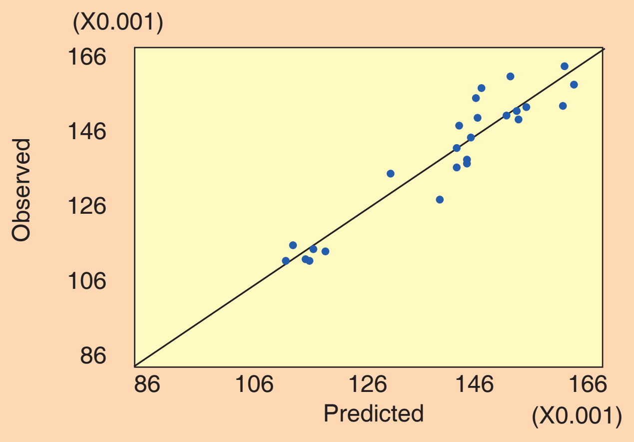


Table 4 - individual dn/dc for polybutadiene-1,2, polybutadiene-1,4 and polystyrene segments in THF at 35°C

	dn/dc (mL/g)
Polybutadiene-1,2	0.1985
Polybutadiene-1,4	0.1246
Polystyrene	0.1108

An analytical method has been proposed to determine the total styrene concentration in styrenic copolymers using a multi-detector GPC/SEC system by combining UV and refractive index (RI) detector signals. The results showed that a multi-detector GPC/SEC system could measure the total styrene concentration in styrenic copolymers with high accuracy. This analytical technique allows laboratories to determine the composition, distribution and the total styrene concentration in styrenic copolymers simultaneously.

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