Flow-Injection Polymer Analysis of Styrenic Block Copolymers. II

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ABSTRACT: A flow-injection polymer analysis (FIPA) method for the dilute solution characterization of unsaturated styrenic block copolymers was developed. The method is rapid, works with both butadiene and isoprene comonomers, and covers a range of 0–100% styrene content in the polymer. Solutions of the polymer were introduced into a flowing mobile phase and monitored by an array of three close-coupled detectors: a right-angle laser light-scattering unit, a differential refractive index detector (DRI), and a differential pressure viscometer. In addition, a separate, dual-detector instrument was set up specifically to evaluate the styrene content by the FIPA method. In that case, the detectors were a DRI and an ultraviolet detector. Within an analysis time of a few minutes, information on molecular weight, molecular size, and comonomer composition could be obtained directly. The data were compared to those obtained from a preexisting gel permeation chromatography analysis method. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2190–2201, 2002

Key words: styrenic block copolymers; styrene; butadiene; isoprene; flow-injection polymer analysis

INTRODUCTION

A variety of methods for characterizing styrenic block copolymers (SBCs) have been practiced for many years and the measured structure–property relationships are generally well understood. Riess et al.[1] presented a generic overview on the properties and characterization of block copolymers several years ago. Likewise, Bywater[2] presented a literature review on the subject of anionic polymerization, the chemistry used to produce the polymers used in this study. The reader is referred to these studies for an excellent overview of SBC properties and analyses.

This work focuses on issues of interest, taking advantage of the latest advances in molecular size-specific detectors to provide high precision with rapid, low-cost characterization for process control and product specifications. With rapid turnaround on molar mass and styrene, necessary adjustments can be made to the reactor targets of subsequent batches such that production of off-grade resin can be minimized or eliminated.

SBC polymerizations use organic solvents well suited to solution characterization techniques, even if the analysis solvent specified differs from the reaction solvent. The reactor liquor may be quickly diluted and dissolved for characterization

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by classical techniques (GPC, light scattering, viscometry, or a combination thereof). For example, solution properties such as Mark–Houwink relationships[2] and correlations[1] of solution viscosity measurements to melt viscosity have been evaluated for many commercial grades of SBCs.

We report here our experiences with the dilute solution characterization of styrenic block copolymers, containing either butadiene or isoprene blocks, using a commercially available detector array employed as a bench-top flow-injection monitor. Issues involving speed, precision, long-term reproducibility, and suitability for a plant environment are assessed.

EXPERIMENTAL

Materials

The SBC samples studied were either commercially available products or reactor samples. The tetrahydrofuran (THF) used for the analysis was HPLC or equivalent grade purchased from VWR (Chicago, IL). It was stabilized with 250 ppm ionol as purchased.

The flow-injection polymer analysis (FIPA) instrumentation consisted of an Isco 500-mL syringe pump (Model 500D; Isco, Lincoln, NE), an HP auto-injector (Model 1050; Hewlett–Packard, Palo Alto, CA), and a Viscotek TDA instrument (Model 300; Viscotek, Houston, TX). This latter instrument consisted of a right-angle laser light-scattering (RALLS) detector, a differential refractive index (DRI) detector, and a differential pressure viscometer (IV) mounted in series on a bench residing in a thermostated oven. A Viscogel 100-Å guard column was positioned prior to the detectors, merely to separate the polymeric sample from low molecular weight components (i.e., reactor solvent, additives, etc.). Data were collected and analyzed by Viscotek's TriSEC GPC software package. Analyses were carried out at 30°C at a flow rate of 1.5 mL/min, for a total run time of 5 min per analysis. Concentrations in the range 0.5–1.0 mg/mL were used.

A polystyrene standard [M_w = 50,000 g/mol, [η] = 0.265 dL/g, with specific refractive index increment (dn/dc) = 0.185 mL/g] was used to calibrate the detector array. A 0.5 mg/mL solution in THF, prepared accurately, was injected five times for calibration. The area of each detector response combined with known values for M_w, [η], and concentration were used to obtain instrument cal-

ibration constants for each detector. These constants were used to convert the detector response of unknowns into values for M_w, [η], concentration, percentage styrene, and dn/dc. Because the detector response attributed to the polymer is found at identical retention times with a constant flow rate, the integration limits and baseline limits were maintained as univariant by the software, thus removing analyst subjectivity for these selections.

The dn/dc values were measured either by using the calibrated DRI detector of the TDA or calculated from process knowledge of percentage styrene. Values of dn/dc for the SBC samples ranged from 0.135 to 0.166 mL/g. The precision error on the dn/dc values, when calculated from the DRI detector response, is about ±0.002 mL/g. Precision error, reported as percentage relative standard deviation (% RSD) at 2σ on both the M_w and [η], was typically 1.0–1.5%.

GPC analyses were performed a Hewlett–Packard 1090 LC, run at 40°C with a THF mobile phase. Four Polymer Labs (Amherst, MA) PLGel GPC columns (300 × 7.5 mm; 5 micron particle size) were used: one Mixed C, two 10^5 Å, and one 10^4 Å. The columns were calibrated with Polymer Labs polystyrene standards in the molar mass range of 1.3K–3.15 MM g/mol. The analysis time per sample was 45 min at a mobile phase flow rate of 1 mL/min. A 100-μL aliquot of a 0.4 mg/mL solution was injected. A Hewlett–Packard Model 1047A refractive index instrument, installed externally, was used as the detector. Data acquisition and reduction used Polymer Labs GPC software version 4.04.

Melt flow rate (MFR) analyses were done according to ASTM D-1238 (200°C, 5 kg).

FIPA data for percentage styrene were collected on a modular HPLC system consisting of a Hewlett–Packard 1050 pump, autosampler, and diode array detector, with a Waters model 410 differential refractometer (Waters Associates, Milford, MA) connected through an HP 35900 C analog-to-digital converter. Instrument control and data analyses were performed with HP Chemstation software version A.06.03. Initial runs were made with the FIPA column at ambient temperature. Later runs employed a Waters column heater box controlled at 35°C. The system was calibrated with nearly monodisperse samples of polystyrene, polyisoprene, and polybutadiene synthesized by a lab reactor using anionic chemistry.

BACKGROUND

The reader is referred to the companion study[3] for details on the instrument capabilities and the assumptions and limitations of the software when analyzing lighting and viscometry signals. Details on the use of the DRI detector signal are given below.

Differential Refractive Index Detector

The concentration-sensitive detector in the TDA is a differential refractive index detector. In principle, for a FIPA measurement, there is no need even to operate this detector if the analyst has accurate knowledge of the concentration of the polymer solution to be measured. Often, and especially for samples taken from a reactor, this is not the case. Therefore, the DRI serves as an accurate, on-line measurement of solution concentration when calibrated with a solution of known concentration and specific refractive index increment, dn/dc. Knowledge of the dn/dc value of the polymer–solvent combination is a prerequisite.

Conversely, the DRI detector can be used to measure dn/dc from gravimetrically prepared polymer solutions. This is an indirect but accurate measurement of comonomer composition if the comonomers exhibit differences in dn/dc in the solvent of choice. The value of dn/dc, therefore, is linked to the comonomer composition of the polymer. Accurate knowledge of this value is crucial to the FIPA measurement in two important ways: (1) to return an absolute M_w from light-scattering data; and (2) for the DRI detector to return accurate values of polymer concentration. [Concentration is a critical parameter for calculating M_w and $[\eta]$ from the light-scattering and viscometry data, respectively. See eqs. (1)–(4) in the companion study.[3]] In copolymers synthesized from two monomers, it is known[4] that the dn/dc value correlates linearly with comonomer composition. The relationship is shown in the following equation:

$$\left(\frac{dn}{dc}\right)_{\text{SBS}} = \%S\left(\frac{dn}{dc}\right)_{\text{S}} + \%B\left(\frac{dn}{dc}\right)_{\text{B}} \qquad (1)$$

Equation (1) provides a means other than calculation from the DRI detector signal from which dn/dc may be obtained.

Table I   Percentage Styrene for SIS Copolymer Using *dn/dc* from Calibrated DRI and Corresponding Value of Percent Styrene[a]

	dn/dc (mL/g)	Percentage Styrene
	0.145	27.8
	0.142	23.5
	0.143	24.2
	0.143	25.7
	0.144	26.7
Average	0.143	25.6
SD	0.001	1.8
Relative SD (1σ)	0.7%	6.9

[a] Where *dn/dc* is the same, but percentage styrene varies, is because of the rounding off of the *dn/dc* value.

RESULTS AND DISCUSSION

The FIPA Method

For an overview of the FIPA method, the reader is again referred to the companion study[3] involving the characterization of EPDM.

How to Manage dn/dc *and Its Relationship to Percentage Styrene*

The critical *dn/dc* parameter can be obtained during analysis by DRI or calculated based on process knowledge of polymer percentage styrene. In the first case, very accurate knowledge of the polymer solution concentration is required. The analyst must pull a carefully measured quantity from the liquor before dilution and analysis. A potential advantage, however, is that by measuring *dn/dc* with the DRI detector, we are in essence measuring copolymer composition (e.g., percentage styrene). In the second case, we calculate *dn/dc* based on process knowledge of percentage styrene and use of eq. (1). Reactor liquors can be more easily and rapidly analyzed. Here the calibrated DRI detector returns percentage solids as an experimental result.

We found in repeat runs of the same solution that the *dn/dc* values obtained from the DRI detector signal varied, run to run, as much as ±0.003 mL/g. In turn, calculated percentage styrene varied as much as 3–4%. Table I shows an example of these data for styrene–isoprene–styrene (SIS) triblock. The current standard method[5] used to obtain percentage styrene involves pressing the sample into a film and mea-

Table II   Percentage Styrene Comparison for SIS Copolyer Samples[a]

Sample	dn/dc (mL/g)	Percentage Styrene by FIPA-DRI	Percentage Styrene Film RI
SIS-A	0.135	11.5	15.8
SIS-B-1	0.137	13.9	15.2
SIS-B-2	0.139	17.9	15.2
SIS-C	0.156	48.5	44.7
SIS-R	0.141	22.1	20.6
SIS-D-1	0.137	14.4	15.5
SIS-D-2	0.137	14.2	14.7
SIS-D-3	0.138	16.5	15.1
SIS-E-1	0.139	18.0	18.1
SIS-F-1	0.138	16.8	18.5
SIS-B-3	0.138	15.4	15.3
SIS-F-2	0.139	18.5	18.2
SIS-E-2	0.139	17.1	18.3
SIS-G	0.141	21.7	25.0
SIS-H	0.146	31.0	29.9
SIS-I	0.143	25.6	28.9

[a] Where dn/dc is the same, but percentage styrene varies, is because of the rounding off of the dn/dc value.

suring its refractive index (RI), and it has a precision of under 1.0% at the 95% confidence interval (15–50% styrene range). The FIPA method, although more convenient and rapid, offers no advantage in precision over the current standard method. In Table II, a comparison of percentage styrene determined from dn/dc obtained from the calibrated DRI detector is compared to percentage styrene from the established film RI method. Comparisons were favorable and suggested that the FIPA method, suitably modified, is promising for the determination of percentage styrene, although precision using DRI alone is not expected to be better than that of the current film method.

We observed that experimental values for percentage styrene vary little from the measured styrene feed into the reactor. Process knowledge for percentage styrene (meter values) has proven to be very robust for obtaining dn/dc [again, from eq. (1)] based on our experience thus far. This also eliminates variation in the dn/dc value, thus increasing the precision of the values obtained for both M_w and $[\eta]$. It also eliminates the need for gravimetrically prepared samples, in that the concentration can "float" and be determined from the DRI response. Most of the M_w and $[\eta]$ data reported herein, particularly those measured for block copolymer reactor liquors, were based on process knowledge for dn/dc.

Percentage Styrene by Dual-Detector FIPA: Preliminary Evaluation

In this section we report preliminary results on a dual-detector FIPA method designed specifically to measure percentage styrene. The instrumentation was assembled from stand-alone equipment, including an HPLC pump, auto-injector, ultraviolet (UV), and DRI detection. (At this writing, Viscotek, Inc. has only recently begun to offer instrumentation with a UV detector on board.) However, utilizing UV detection for the analysis of comonomer composition in polymers has been done previously. Yau[6] summarized the use of dual detection in GPC analysis to give both size and compositional distributions.

Both DRI and UV detectors are sensitive to styrene composition, although results are also both affected by sample concentration at the point of analysis. When both are used together, however, the *ratio* of the DRI and UV detector signals effectively cancels the concentration dependence on the measurement. By calibrating the detector responses to polystyrene, polybutadiene, and polyisoprene homopolymers, the percentage styrene can be calculated directly from eq. (2) without knowledge of the solution concentration for copolymers with these blocks. This feature becomes quite advantageous when sampling reactor liquors.

$$\%S = \frac{A_{\mathrm{DRI},B}k_{\mathrm{UV},B} - A_{\mathrm{UV},B}k_{\mathrm{DRI},B}}{A_{\mathrm{UV},S}k_{\mathrm{DRI},S} - A_{\mathrm{UV},B}k_{\mathrm{DRI},B} - A_{\mathrm{DRI},S}k_{\mathrm{UV},S} - A_{\mathrm{DRI},B}k_{\mathrm{UV},B}} \quad (2)$$

where A is the area under either the DRI or UV signal and k is the calibration response factor for either the DRI or UV detector.

In Table III a precision comparison is presented between the established film RI method and the dual-detector FIPA method. The sample was a styrene–butadiene–styrene (SBS) triblock. Although the film RI method was still more precise by a factor of 2, the FIPA method dramatically improved from use of a DRI detector alone, as described in the previous section. Several possible problems were noted in this exploratory work that, upon correction, should improve the precision of the FIPA method.

In short, we believe that a UV detector mounted on board with the other detectors in the TDA 300, in the same oven-controlled environment, may offer improved precision over that of current methods. Also, the percentage styrene

Table III   SBS Copolymer: Percentage Styrene by Dual Detector, DRI/UV FIPA Versus Film RI Method

Number	Film RI Percentage Styrene	Day Run	FIPA Percentage Styrene
1	29.5	1	29.33
2	29.5	1	29.26
3	29.7	1	29.12
4	29.5	1	29.50
5	29.5	1	29.36
6	29.7	2	29.23
7	29.5	2	29.61
8	29.7	2	29.92
9	29.5	2	29.07
10	29.5	2	29.00
Average	29.6		29.3
SD	0.10		0.28
Relative SD	0.33%		0.94%
Relative precision at 95% confidence	0.74%		2.12%

values need not be measured in an independent run: all measured parameters will be derived from the same injection with the introduction of UV detection into the current commercially available instrument.

Another advantage to measuring percentage styrene by FIPA is increased dynamic range of the detection: from 0 to 100% styrene versus the 10–50% styrene of the current, validated film RI method. For high styrene samples, although the film preparation is not any different from that for low styrene samples, the analysis becomes impractical.

Consideration of the Concentration Effect on M_w and $[\eta]$

It is known[7] that in GPC measurements, peak retention volume is influenced by sample concentration (see Fig. 1). Above a certain concentration, which varies depending on the sample's molecular weight, column overloading and a "viscous fingering" effect are noted. The values for M_w and $[\eta]$, derived from light scattering and differential pressure viscometry, may likewise be influenced by concentration. This effect manifests itself in light-scattering data through the magnitude of the second virial coefficient A_2. For the viscometry data, the Solomon–Gottesman equation[3] attempts to return a value of $[\eta]$ at a finite concentration. At issue, then, is whether we need to apply an A_2 correction to our data and whether

the Solomon–Gottesman relationship adequately returns $[\eta]$.

The FIPA measurements were made at several concentrations on a single polymer sample and the concentration was plotted against apparent M_w and $[\eta]$, as shown in Figures 2 and 3. The data for the particular example shown here were derived from the analysis of an SBS reactor liquor. Aliquots of liquor were removed at several different volumes and diluted to the same final volume. As expected, there was a small increase in molar mass with decreasing concentration. However, at about 100 μL of reactor liquor volume and below, the change in molar mass became small enough
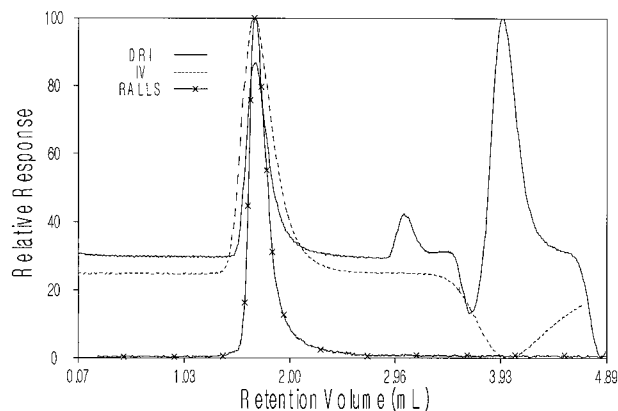

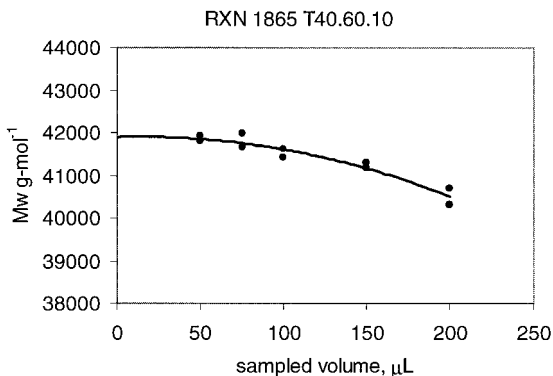**Figure 1**   Raw detector traces collected in the FIPA method.

Figure 2 Concentration effect on apparent M_w from RALLS detection.

that it fell within the precision of the measurement. There is only a 0.7% difference between the apparent M_w measured at 100 μL reactor liquor volume versus the M_w value found by extrapolation to zero concentration. Likewise, there was only a modest decrease in [η] with decreasing concentration. From Figure 3, there is only a 1% difference in the value of apparent [η] at 100 μL of reactor liquor volume and the value of [η] found by extrapolation to zero concentration. Generally, analyses performed on solutions within several percent of 0.5 mg/mL should provide high signal to noise in all detectors, corresponding to high precision, and very close agreement to values found by extrapolation to zero concentration, corresponding to high accuracy. At this concentration, we concluded that an A_2 correction on the light-scattering data and any further correction of the viscometry data beyond what the Solomon–Gottesman relationship already provided was unwarranted.

Precision of M_w and [η]

One issue with using a FIPA method as a routine characterization tool was the precision in the M_w and [η] values returned by the method. For the commercial process, the precision of the data needs to exceed commonly employed quality control techniques such as current melt flow rate (MFR) or GPC measurements to offer control improvement. The MFR measurement[8] has a % RSD in the range of 1.1–3.5% (sample and operator dependent). The precision of the routine GPC measurement is about 1.5% at 2σ.

Table IV shows the results of a simple intravial reproducibility study on several SIS copolymers. The samples were injected multiple times from

the same vial. The RSD at 2σ is no higher than 1% for either M_w or [η]. An SBS sample, examined in the same manner, revealed similar results. These data are shown in Table V.

A longer-term precision study was also undertaken. A polystyrene standard (the same one used to calibrate the TDA instrument) and SIS sample were analyzed over about a month-long period and control charts were constructed, as shown in Figure 4. The erratic appearance of the last several runs in each chart was traced to a plugged filter on-line before the RALLS detector in the TDA. Even with these data included, the RSD at 2σ for the SIS sample was 2.0%; for the polystyrene standard, 1.2%.

Finally, a comparison of M_w and [η] values of several reactor runs measured first on the day of the synthesis, and again after an elapsed time of several weeks, is shown in Table VI. In all cases, the difference in the average values falls comfortably within the stated precision of the measurement. Strikingly, the [η] values are essentially identical.

All of the data presented in this section suggest a highly reproducible, robust method. Because the final, desired molecular property data are derived from the total area under the detector traces, the precision of the method is more resistant to many analysis parameters that affect traditional GPC results that rely heavily on determination of retention volume.

Correlation of FIPA Data to Melt Flow Rate of SIS Copolymers

Thus far, properties we measured such as M_w, [η], percentage styrene, and the reproducibility of the
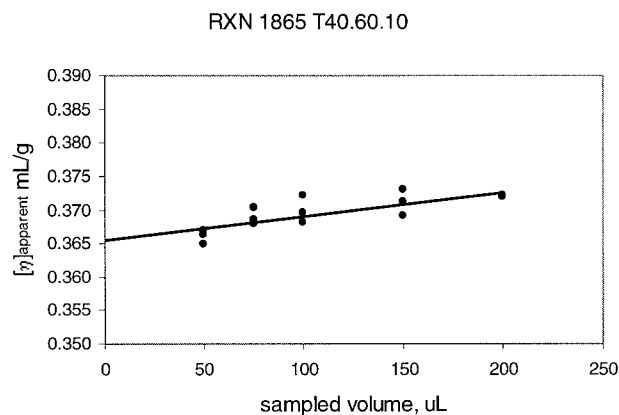

Figure 3 Concentration effect on apparent [η] from differential pressure viscometry detection.

measurements have not required a careful examination of structural differences in the samples. The SIS samples in this study were all triblock copolymers that contained styrene and either isoprene or butadiene. In addition to differences in comonomer content and molar mass, the samples may also contain varying quantities of diblock, a copolymer that lacks the final styrene block found in triblock copolymers. All of these structural differences influence the melt flow properties of the

Table IV   Intravial Precision of Selected SIS Copolymer Samples[a]

Sample	M_w	$[\eta]$
SIS-F-3	130,900	0.923
	131,900	0.924
	132,100	0.923
	131,400	0.922
	130,500	0.920
Average	131,360	0.922
SD	669	0.002
Relative SD (1σ)	0.5%	0.2%
SIS-B-1	146,300	1.013
	145,400	1.003
	145,800	1.010
	146,300	1.012
	144,900	1.003
Average	145,740	1.008
SD	602	0.005
Relative SD (1σ)	0.4%	0.5%
SIS-H	98,300	0.703
	98,200	0.700
	99,300	0.701
	99,700	0.701
	97,900	0.699
Average	98,680	0.701
SD	776	0.002
Relative SD (1σ)	0.8%	0.2%
SIS-C	78,100	0.545
	78,500	0.548
	79,100	0.550
	78,500	0.550
	78,100	0.545
Average	78,460	0.548
SD	410	0.003
Relative SD (1σ)	0.5%	0.5%

[a] Ten pellets dissolved in 20 mL THF then diluted 1:10. Concentration range 0.7–1.0 mg/mL.

Table V   Intravial Precision for SBS Copolymer[a]

Sample	M_w	$[\eta]$
SBS-1		
Average	79,533	0.801
SD	358	0.001
Relative SD (1σ)	0.5%	0.2%
SBS-2		
Average	73,440	0.779
SD	193	0.001
Relative SD (1σ)	0.3%	0.1%
SBS-3		
Average	69,966	0.769
SD	21	0.001
Relative SD (1σ)	0.0%	0.1%
SBS-4		
Average	69,612	0.769
SD	100	0.001
Relative SD (1σ)	0.1%	0.1%
SBS-5		
Average	70,190	0.774
SD	147	0.001
Relative SD (1σ)	0.2%	0.1%
SBS-6		
Average	69,934	0.789
SD	70	0.001
Relative SD (1σ)	0.1%	0.2%
SBS-7		
Average	68,354	0.775
SD	126	0.001
Relative SD (1σ)	0.2%	0.1%

[a] Nominally six repeat runs for each.

finished product and also influence how molecular size parameters like M_w and $[\eta]$ correlate to the observed behavior. Correlating FIPA data to MFR would reduce the time lag and effort between synthesis and reactor retargeting.

The goal was to correlate $[\eta]$ to MFR. The "master curve" approach, plotting all SIS samples, regardless of comonomer quantity, molar mass, and diblock content, on a single plot was not very valuable. As shown in the first plot in Figure 5, the correlation of dilute solution viscosity to MFR was rather poor. In the second plot, a simple "correction" was applied to all samples with M_w exceeding 100K g/mol. This correction was developed by recognizing that $[\eta] \propto M_w^{\mathbf{a}}$, where **a** is the Mark–Houwink coefficient, and that η (melt viscosity) $\propto M_w^{3.4}$. One can then show that $[\eta] \propto (1/\eta)^{3.4}$. By raising the MFR value of all samples exceeding 100K g/mol to the 1/3.4 power, a more linear correlation resulted, as the second plot in Figure 5 shows.
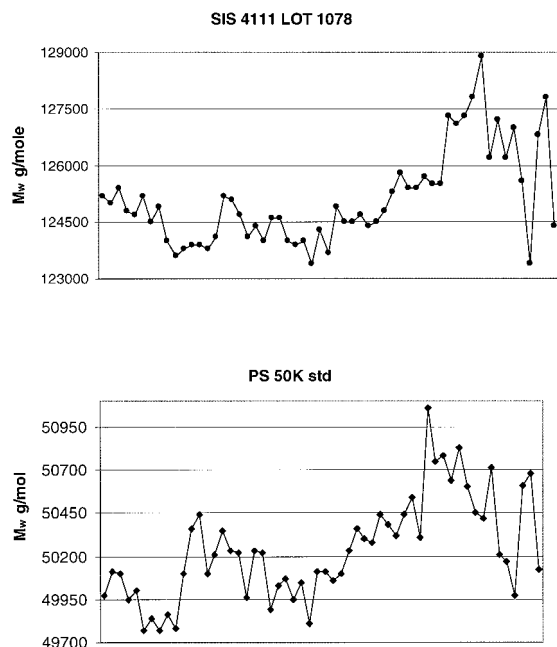
SIS 4111 LOT 1078

PS 50K std

Figure 4 Control charts of "long-term" reproducibility.

MFR vs [h]

"Corrected" MFR vs [η]

Figure 5 MFR versus [η], all SIS samples.

When samples containing diblock were removed from the plot, the correlation coefficient of the plot improved to $R^2 = 0.99$. We do not imply that this correction is theoretically valid nor pragmatically useful in plant operation. We merely note that it tends to rectify the data set. There are other reasons why a "master curve" approach to the correlation is difficult (e.g., the MFR measurements may be significantly below the order–disorder transition temperature of the polymers in question), but they are beyond the scope of this report.
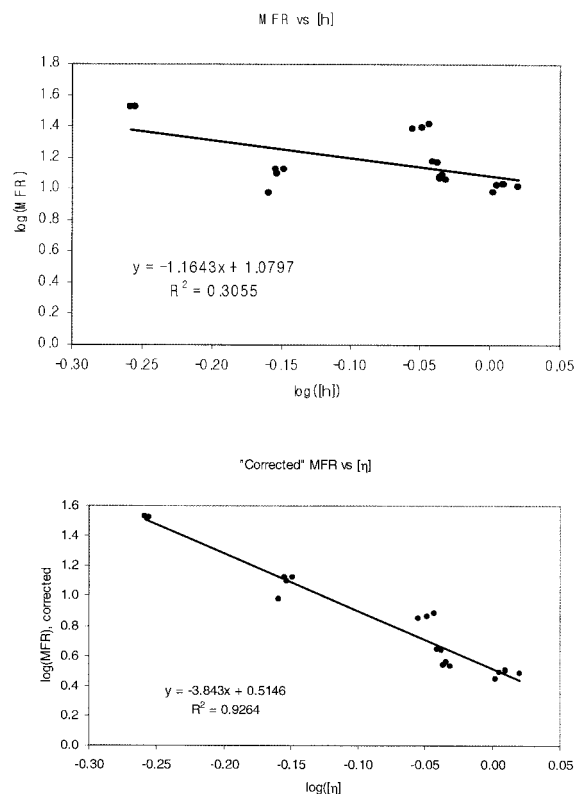
Simplifying the problem by limiting the correlation to a *single* SIS triblock product, and varying only the diblock content, provided a [η]–MFR correlation that was exceptionally linear. Figure 6 shows this plot and Table VII summarizes the MFR, FIPA data, and sample composition. If FIPA data (specifically [η]) were used to predict

Table VI Comparison of M_w and [η] Values Obtained Several Weeks Apart

| Sample | M_w (g/mol) | | | [η] (dL/g) | | |
	Sept. 2000[a]	Nov. 2000[b]	Absolute Difference (g/mol)	Sept. 2000[a]	Nov. 2000[b]	Absolute Difference (dL/g)
RX-42	57,400	58,100	700	0.511	0.509	0.002
RX-43	54,900	55,200	300	0.489	0.486	0.003
RX-44	55,950	56,300	350	0.492	0.493	0.001
RX-45	59,900	60,100	200	0.507	0.508	0.001
RX-49	59,000	58,200	800	0.365	0.365	0.000
RX-50	59,400	59,800	400	0.364	0.364	0.000
RX-51	64,500	64,500	0	0.377	0.377	0.000
RX-52	62,000	62,200	200	0.370	0.371	0.001

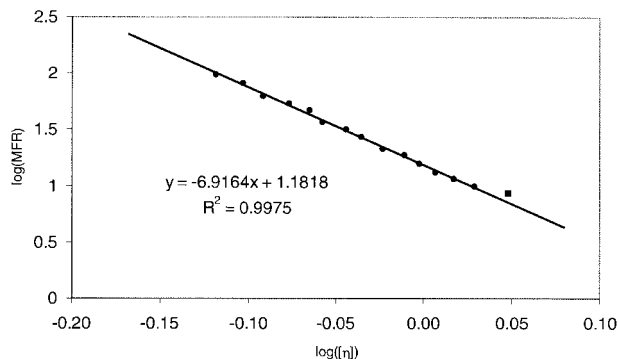[a] Average of two analyses.
[b] Average of five analyses.

Figure 6 MFR versus $[\eta]$, SIS-F-4 blended with diblock. ■, "pure" triblock sample.

MFR, the best approach is probably to have a product-specific correlation available for each product of interest. Although perhaps cumbersome for product release, the value of having the correlation is, again, for rapid feedback and predictions long before the sample is devolatilized. Moreover, as shown in Figure 7, a linear correlation between $[\eta]$ and percentage diblock also exists. This suggested that a measurement of $[\eta]$ from the FIPA method could be used as a predictor for percentage diblock in an unknown sample consisting of the same triblock and diblock polymers.

Table VII Diblock Blend Data for SIS-F-4[a]

M_w (g/mol)	$[\eta]$ (dL/g)	Percentage Diblock by GPC	MFR
159,667	1.119	1.0	8.5
152,000	1.070	4.7	9.7
148,767	1.041	9.8	11.3
146,033	1.017	14.6	13.0
141,667	0.996	19.9	15.4
137,967	0.976	25.0	18.5
133,600	0.949	30.0	21.1
130,100	0.922	35.1	26.9
124,267	0.904	39.9	31.3
119,700	0.876	45.3	36.6
117,800	0.861	50.6	46.3
112,433	0.838	55.4	52.9
107,833	0.811	60.6	62.3
103,767	0.789	65.7	80.2
98,867	0.762	71.4	95.5
94,833	0.739	76.6	—[b]
90,133	0.714	82.1	—[b]
83,200	0.676	92.8	—[b]
76,100	0.625	103.9	—[b]

[a] See Figures 6 and 7.
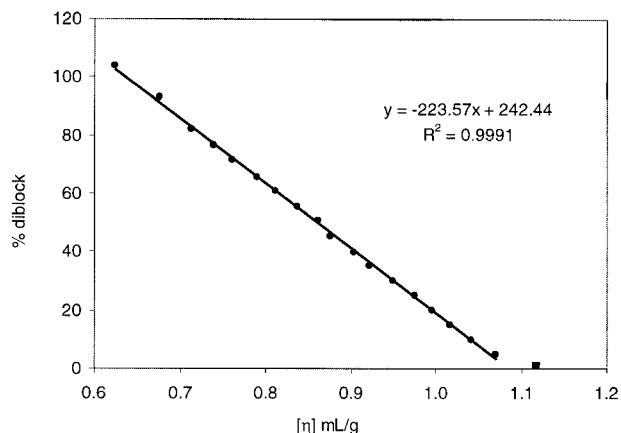[b] Not measurable by the employed MFR method.

Figure 7 $[\eta]$ versus percentage diblock, SIS-F-4 blended with diblock. ■, "pure" triblock sample.

The other noteworthy trend in the data of Table VII is the smooth trend of M_w and $[\eta]$ with increasing diblock. This is an excellent example of how, fundamentally, FIPA differs from GPC. In the FIPA method, there is *no* separation of the triblock from the smaller diblock. Therefore, as the percentage diblock increases, the average values the detectors "see" for the *bulk* sample correspondingly decrease.

FIPA for Process Control: Monitoring a Reactor

Another potential application of the FIPA method is its use as a monitor of polymerization reactions. A natural extrapolation of the method described herein would involve having the detector array "coupled" to the reactor to continuously monitor a reaction. Reed[9] has recently developed a detector array and sampling system, which he proposes for this type of on-line monitoring. Presently, the bench-top analyses provide rapid feedback on reaction progress. The obvious limitation is the need to "grab" and dilute samples. In this section we report the results of a reactor-monitoring campaign where batches of styrene–butadiene copolymers were produced over a period of about a month. Sample aliquots were taken only at the end of the reaction. For controlling a batch process these data are invaluable, given that immediate feedback allows adjustment of the molar mass target for subsequent batches. Traditionally, this feedback is provided by GPC. Therefore, the FIPA M_w from RALLS detection was compared to GPC M_p determined from a well-established correction method.[10] Figure 8 shows a control-type chart where molecular weight from both methods, as well as the target and requested
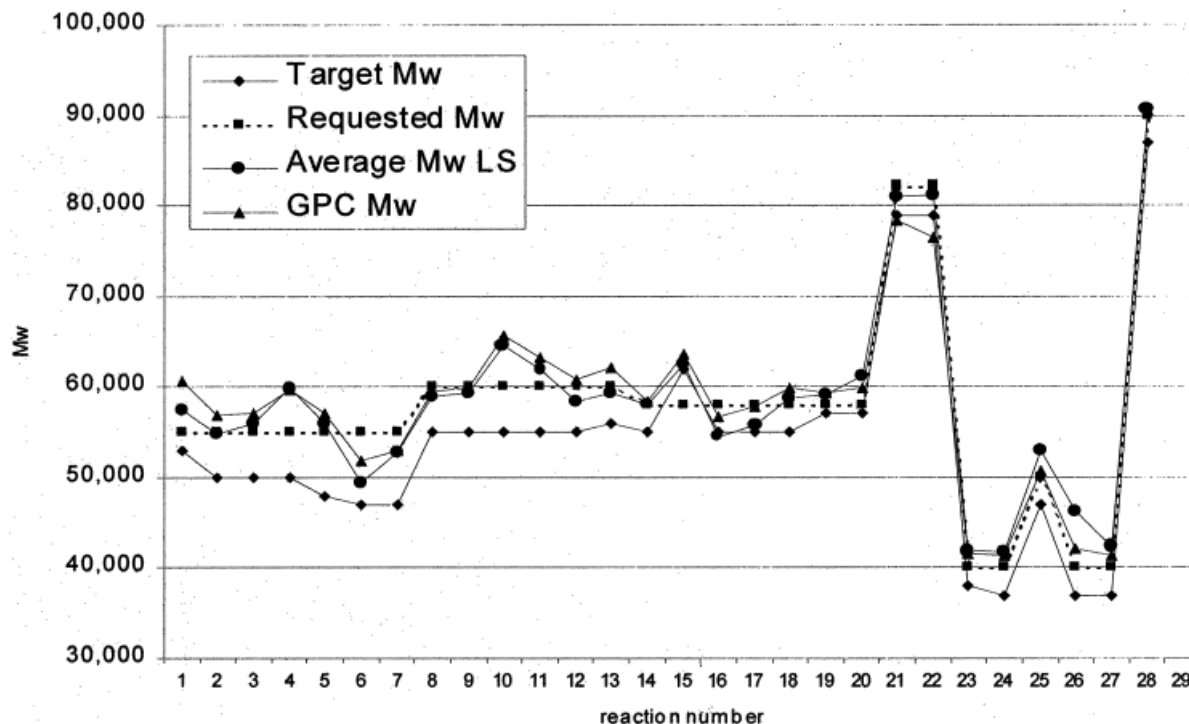
Figure 8   Comparison of FIPA, GPC, and target M_w for the reactor campaign.

value, are compared. In this case, "target" refers to the value used by the plant operator to achieve the "requested" molar mass. As the data in Figure 8 illustrate, in most cases there was a very close correspondence of GPC M_p with FIPA M_w. For most batches produced, both GPC and FIPA values trended the same way; that is, they were either above or below the requested molecular weight by a similar magnitude. In all cases, the target molar mass value required to achieve the requested molar mass was lower than the other three values. For this application, the FIPA method provided the *same* information as provided by GPC, but nine times faster.

In Figure 9, GPC M_p is plotted against FIPA M_w. It was evident that there was a close correspondence between the two values. This adds to the confidence of the proposal that the GPC method be replaced by the faster FIPA method for reactor targeting.

Figures 10 and 11 are plots correlating $[\eta]$ and M_w from the FIPA data. The reactor campaign produced polymers with a wide range of styrene content and molar mass. All of the polymers, however, were similarly narrow with respect to distribution ($M_w/M_n < 1.05$). Polymers with identical molar mass yet different comonomer content can

display quite different dimensions in solution. In the FIPA data, this manifested itself through significant changes in $[\eta]$ at constant M_w. Figure 10 displays this property.

There is a linear relationship between $[\eta]$ and M_w at constant styrene content. The individual plots in Figure 10 fit a "master curve" if $[\eta]$ is
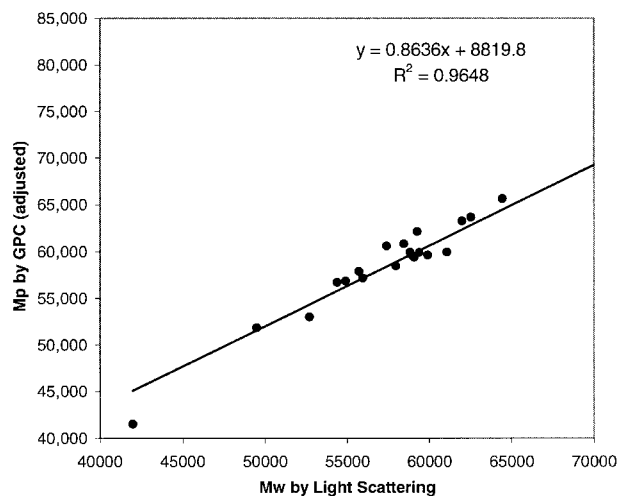

Figure 9   GPC M_p versus FIPA M_w (RALLS). Data from the reactor campaign.
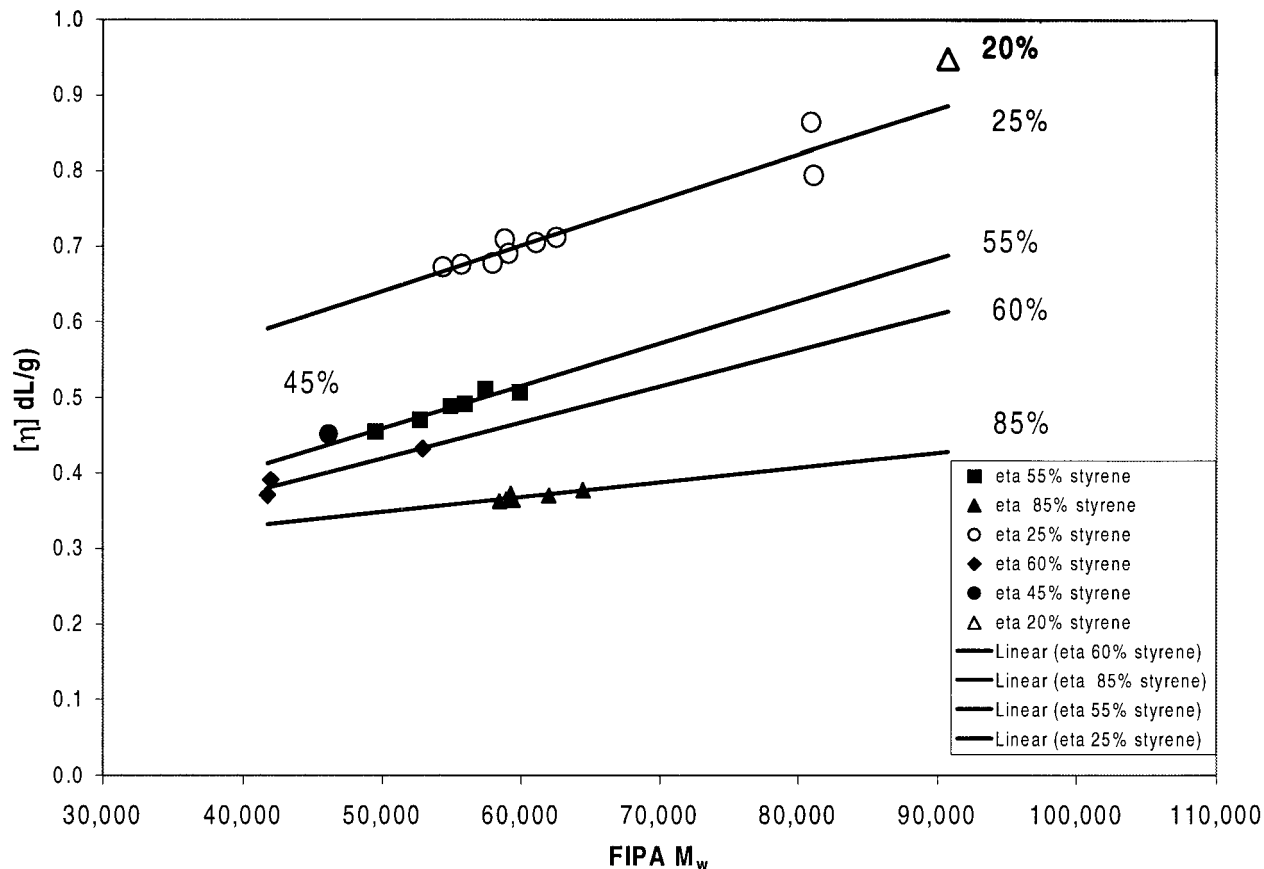
Figure 10 [η] versus FIPA M_w for the reactor campaign.

plotted against butadiene molar mass only. This relationship is shown in Figure 11. Figures 10 and 11 graphically depict the essence of corrections made in GPC data to convert polystyrene equivalent molar mass to "absolute" molar mass for a block copolymer. Are these relationships applicable to FIPA? The relationships could be used to simplify the FIPA instrumentation by making viscosity detection all that is needed and M_w could be reliably estimated from [η]. Certainly, eliminating a detector has economic implications. However, if M_w is the fundamental parameter of interest for both targeting the reactor and for predicting product performance, a direct measurement is still the preferred route for obtaining the value.

CONCLUSIONS

This study is the second of a two-part series on the use of FIPA methodology for dilute solution polymer characterization. A FIPA method was developed that has proven thus far to be robust, fast, easy to use, and broadly applicable to styrenic block copolymer analysis. The precision was found to be significantly better than that of other methods currently used to characterize these polymers (e.g., MFR, GPC). An exception was found in the percentage styrene FIPA method, which needs further refinement to obtain the desired precision. Our experience with monitoring reactors suggested that the method would be valuable for reactor targeting, and that the ease of operation suggested a fairly unobtrusive method for analysts in a plant lab. We demonstrated that comonomer composition can be evaluated with the FIPA method. We found that a "master curve" approach to correlating [η] to MFR was not viable without significant correction for polymer structure variations. Single product correlation of [η] with MFR proved satisfactory. In the earlier companion study,[3] FIPA data have been shown to correlate linearly to Mooney viscosity for EPDM elastomers. Because it is known that M_w and [η] values for polymers indicate a
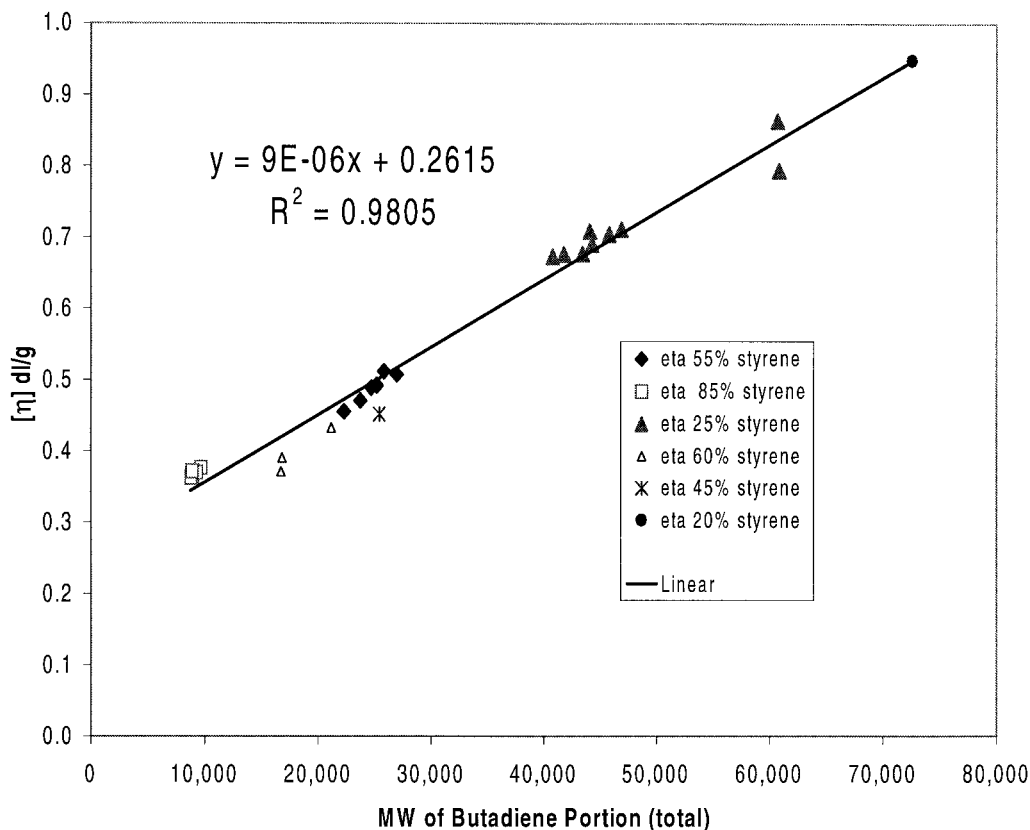
Figure 11 $[\eta]$ versus butadiene molar mass (derived from FIPA M_w) for the reactor campaign.

myriad of performance properties, it is likely that FIPA data would correlate to other important parameters.

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