Flow-Injection Polymer Analysis of Ethylene Propylene Diene Monomer Elastomers. I

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ABSTRACT: A rapid, flow-injection polymer analysis (FIPA) method for the solution characterization of EPDM elastomers, with a wide range of ethylene comonomer content, was developed. Solutions of the polymer were introduced into a flowing mobile phase which was monitored by an array of three detectors: a right-angle laser light-scattering unit, a differential refractive index detector, and a differential pressure viscometer. To adequately characterize a wide range of comonomer composition, it was found that a nominal temperature of 90°C and a solvent (e.g., 1,2,4-trichlorobenzene) capable of high-temperature sample dissolution was needed for the analysis. Polymer association or aggregation was observed in cyclohexane at lower analysis temperatures. With an analysis time of a few minutes, information on molecular weight, molecular size, and comonomer composition can be obtained directly. Information regarding polydispersity and properties such as melt viscosity may be obtained indirectly or through correlation to other, independent property measurements. The data were also compared to a high-temperature GPC analysis method already in use. The combination of rapid analysis time and measurement of fundamental molecular properties suggests the usefulness of the instrumentation and method to plant process control. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2178–2189, 2002

Key words: ethylene–propylene rubber; ethylene propylene diene monomer; flow-injection polymer analysis; high-temperature GPC

INTRODUCTION

A variety of methods for characterizing ethylene–propylene–diene terpolymers (EPDM) have been practiced for many years and the measured structure–property relationships are generally well understood, as one may expect for a mature, commodity polymer. Ver Strate[1] gave a very good, if necessarily generic, overview on the subject several years ago. Even earlier, Baldwin and Ver Strate[2] presented a literature review with well over 1300 references on the subject of EPDM rubber chemistry and characterization. The reader is referred to these studies for an excellent overview of EPDM analysis. Presently, interest revolves around how to take advantage of the latest advances in molecular size-specific detectors to provide high-precision, rapid, low-cost characterization for process control, product specifications, and correlation to other parameters that are less precise or more time-consuming to measure.

Commercial-scale polymerizations that utilize a solvent are clearly well suited to solution characterization techniques, even if the analysis sol-

vent specified differs from the reaction solvent. The process to produce EPDM is a good example. Such processes produce a liquor that may be quickly diluted and molecularly dissolved for characterization by classical techniques like GPC, light scattering (LS), viscometry [intrinsic viscosity (IV)], or a combination thereof. Indeed, solution properties such as Mark–Houwink (M-H) relationships,[2] and correlations[1] of solution viscosity measurements to melt or Mooney viscosity have been determined for many commercial grades of EPR and EPDM. The influence of branching, ethylene content, and polydispersity on these measurements are also known. Traditional GPC measurement, though invaluable for insight into size distribution and molecular architecture when used with LS and IV detection, is a slow technique for process control, and an expensive, high-maintenance technique to use routinely for all but finished product lot analysis. However, Polymer Labs, Inc. (Amherst, MA)[3] recently introduced columns for fast GPC analysis with the purpose of aiding the high-throughput screening of materials developed in a combinatorial chemistry approach for the synthesis of new polymers. It is uncertain at this time how suitable this method is for a plant environment. Either way, the data interpretation requires a certain level of competence as well. The expense and maintenance problems are generally compounded by the lack of in-plant expertise and in cases where high-temperature measurements are required.

We report here a flow-injection polymer analysis (FIPA) method that is similar in spirit to a GPC–LS–IV measurement but is greatly simplified in terms of data interpretation and analysis time by removing the columns from the measurement. These types of measurements have been performed at Dow for many years by deGroot[4] and the authors (D.S.P., R.J.B.) using ambient and high-temperature GPC systems with the columns removed. Hall et al.[5] reported a method for characterizing chitosan using so-called standalone light-scattering and viscometry measurements. Viscotek, Inc. (Houston, TX), now offers an instrument and software specifically designed for the triple-detection, flow-injection analysis of polymer solutions. FIPA simplification carries the price of losing detailed information on the molecular size distribution. However, the speed of the analysis coupled with the bulk molecular properties obtained make the technique particularly suitable for monitoring a solution polymerization process. As shown herein, other information, in-

cluding a polydispersity index (albeit less informative than a size-distribution profile) reported as the ratio of M_w and M_v, may be obtained as well.

EXPERIMENTAL

The EPDM samples studied were commercially available ethylene–propylene–diene terpolymers or process samples. The solvents, 1,2,4-trichlorobenzene (TCB) and cyclohexane (CH) were HPLC or equivalent grade purchased from VWR (Chicago, IL). They were charged with 250 ppm ionol prior to use as the mobile phase or polymer solvent.

The FIPA instrumentation consisted of an LKB Model 2150 HPLC isocratic pump (LKB, Bromma, Sweden), a Viscotek Model DG-800 membrane solvent degasser, a Pierce Reacti-Therm III stirring hot plate (Pierce, Rockford, IL), and a Viscotek Model 300 TDA instrument. This instrument consisted of a right-angle laser light-scattering (RALLS) detector, a differential refractive index (DRI) detector, and a differential pressure viscometer mounted in series on a bench residing in a thermostated oven. For 90°C measurements, a 2-ft. length of tubing was introduced inside of the TDA between the entrance port and the manual injector to allow the mobile phase to reach temperature. A Viscogel 100-Å guard column was positioned prior to the detectors merely to separate the polymeric sample from the "matrix" (i.e., process solvent, additives, etc.). The TDA was equipped with a manual injection port. Data were collected and analyzed by Viscotek's TriSEC GPC software package.

High-temperature GPC analysis were accomplished on a Waters Model 150C (Waters, Milford, MA) at 145°C using 3 Polymer Labs Mixed B columns with a TCB mobile phase (Amherst, MA). The columns were calibrated with narrow PS standards in the molecular weight range of 7.5 mM to 0.58K g/mol. The molecular weight averages for the EPDM samples were reported as polyethylene equivalents using $\mathbf{a}$ = 0.725, K = 4.064 × 10^{-4} for the samples, $\mathbf{a}$ = 0.725, K = 9.528 × 10^{-5} for the standards. FIPA work at 145°C in TCB was performed on a Polymer Labs Model 210 GPC equipped with a *Precision Detector* (Franklin, MA) Model 2040 dual-angle LS detector and a Viscotek 210R viscometer.

Analyses using CH as both the mobile phase and the solvent were carried out at 70°C and a

flow rate of 1.5 mL/min for a total run time of 5 min per analysis. Concentrations of approximately 1 mg/mL were used. Analyses using TCB as both the mobile phase and the solvent were carried out using a flow rate of 0.7 mL/min, run time of 7 min, and a 90°C instrument temperature, the current maximum attainable temperature on the TDA. Sample dissolution, however, was done at 145°C. This ensured both rapid dissolution and a nonassociated polymer prior to introduction into the TDA instrument. Concentrations of approximately 0.5 mg/mL were used. Process liquors were prepared for analysis by injecting the warmed, viscous solution into the stirring solvent controlled at the temperature of choice. Complete dissolution occurred in a few minutes. The hot polymer solutions were drawn into a 100-μL injection loop with a 10-mL glass syringe. The analysis was run nominally in triplicate for each sample. Precision, as percentage relative standard deviation at 1σ, was about 2–2.5% for M_w and 0.7–1.5% for $[\eta]$. We believe that the precision would increase several-fold by employing a high-temperature autosampler in lieu of the manual injection method employed for this work. For a discussion of precision, see the companion study, Flow-Injection Polymer Analysis (FIPA) of Styrenic Block Copolymers. II.[6]

The specific refractive index increments dn/dc were measured using the calibrated DRI detector of the TDA. For the measurements in CH at 70°C, a 50K g/mol polystyrene standard, assigned a dn/dc value of 0.172 mL/g, was used to calibrate the detector. Values of dn/dc for the EPDM samples ranged from 0.075 to 0.083 mL/g. For the measurements in TCB at 90°C, an Engage ethylene–octene copolymer, assigned a dn/dc value of -0.104 mL/g, was used to calibrate the detector. Values of dn/dc for the EPDM samples ranged from -0.091 to -0.105 mL/g. The precision error on the dn/dc values is about ± 0.002 mL/g.

The RALLS instrument was calibrated using the same samples mentioned above for the DRI calibration. The Engage sample was assigned a value of 150,000 g/mol for the calibration, based on high-temperature GPC characterization.

BACKGROUND

In this section we briefly review the principles and theory of the operation of the detectors in the TDA. This information has been presented before,[7] but it is useful to have the information available herein as a reference. It also helps to illustrate limitations in the measurement capabilities of the instruments and the assumptions used in the calculations.

The TDA utilizes a right-angle (90°C) laser light-scattering detector operating at $\lambda_0 = 670$ nm. As such, the particle form factor $P(qR_g)$, in the light-scattering equation presented in eq. (1) cannot be taken as 1 as in low-angle measurements[8] if the macromolecular chain size exceeds about $(\lambda_0/50)n$.

$$Kc/\mathscr{R} = 1/MP(qR_g) + 2A_2c \qquad (1)$$

where K is an optical constant containing $(dn/dc)^2$, c is the concentration of the polymer solution in g/mL; R is the reduced Rayleigh scattering; M_w is the weight average molecular weight; P is the particle form factor, a function of q and R_g; q is the magnitude of the scattering vector $4\pi n\lambda_0^{-1}\sin\theta/2$, where n is the refractive index of the solution and λ_0 is the *in vacuo* wavelength of the laser light; R_g is the polymer radius of gyration, size parameter; and A_2 is the second virial coefficient, the magnitude of which quantifies two-body interactions in the solution.

The particle form factor quantifies the reduction scattered light intensity that the detector sees as a result of destructive interference of the light scattered from different segments of the polymer chain, in this case at 90°, and must be measured or approximated if multiangle measurements are not made. The Viscotek software accomplishes this by estimating R_g from the Flory–Fox[9] and Ptitsyn–Eisner[10] equations, shown in eq. (2) below.

$$R_g = (1/6)^{1/2}([\eta]M/\Phi)^{1/3} \qquad (2)$$

where $[\eta]$ is the solution intrinsic viscosity, M is an estimated molecular weight, $\Phi = 2.86 \times 10^{21}[1 - 2.63(2\mathbf{a} - 1)/3 + 2.86(2\mathbf{a} - \frac{1}{3})^2]$, and $\mathbf{a}$ is the exponent from the M-H relationship.

First, the molecular weight is estimated assuming $P(qR_g) = 1$. Then R_g is estimated from eq. (2) and the result used to calculate $P(qR_g)$, using the Debye[11] equation that relates the random coil shape to the particle form factor, is

$$P(qR_g) = P(90°) = 2[e^{-x} - (1 - x)]/x^2 \qquad (3)$$

where $x = q^2R_g{}^2$.

Next, the new particle form factor is inserted into eq. (1) to recalculate M_w. This process is repeated until the value becomes constant. For the work presented here, there was approximately an 11% "correction" for the biggest polymers ($M_w \sim 350K$ g/mol). If the polymer chains are large enough that a form factor correction is needed, then the accuracy of the number is only as good as the applicability of eq. (2) and the value of the M-H **a** value in eq. (2), which is not a user-supplied value. Evaluating R_g [and, ultimately, $P(90°)$] using eq. (2) is not valid for branched polymers.[12] This presents a major limitation in using a RALLS–IV combination for absolute molecular architecture studies. We have found in practice that the calculation method described above works adequately for polymer samples consisting of random coil chain architecture dissolved in organic solvents. Using a single scattering angle, M_w is correctly obtained from eq. (1) by measuring the scattering of several solutions with different concentrations and the reduced scattering extrapolated to zero concentration. The y-intercept is $1/M_w$, the slope, $2A_2$. Measurements are often routinely made using a single, low-concentration solution (e.g., 0.5 mg/mL or less) and assuming the A_2 term is negligible. This assumption generally works satisfactorily. As shown in this report, the importance of collecting LS data by measuring the scattering intensity over a range of concentration should not be discounted. The trend in this relationship reveals much about how the polymer chains behave in the solvent at the temperature of choice.

The viscometer in the TDA is a four-capillary Wheatstone bridge arrangement. The polymer property actually measured is η_{sp}, the specific viscosity, and η_{rel}, the relative viscosity ($\eta_{sp} + 1$). These values are then used to calculate $[\eta]$ using the Solomon–Gottesman[13] relationship shown in eq. (4):

$$[\eta] = 2^{1/2}(\eta_{sp} - \ln(\eta_{\mathrm{rel}})^{1/2}/c \qquad (4)$$

Equation (4) is used in the Viscotek software to calculate a property from a finite concentration that is properly obtained from an extrapolation to zero concentration. The Solomon–Gottesman study suggested that eq. (4) is limited to low concentrations (linear region of a Huggins-type plot). Thus, it is not likely to work if the polymer exhibits "unusual" solution behavior (e.g., aggregation) that would introduce curvature or other abnormal concentration dependencies into a Huggins-type solution viscosity plot.

The concentration-sensitive detector in the TDA is a DRI detector. In principle, in a FIPA measurement, there is no need to even 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 the process, this is not the case. Therefore, the DRI, when calibrated with a standard of known concentration and dn/dc, serves as an accurate, "on-line" measurement of solution concentration. The dn/dc value of the polymer–solvent combination must be known, however. Alternatively, the DRI detector can be used to measure dn/dc from carefully prepared polymer solutions. This, in turn, is an indirect but accurate measurement of comonomer composition, provided the comonomers in question exhibit differences in dn/dc in the solvent of choice.

RESULTS AND DISCUSSION

The FIPA Method

Shown in Figure 1 is an example of the raw data obtained from the FIPA analysis. The sample is introduced into a flowing mobile phase where it encounters a small GPC column prior to the detectors. The breadth and retention volume of the detector responses reveal no molecular property information in this method. It is the area under the traces that provide the desired bulk property values (M_w, $[\eta]$, concentration, or dn/dc). Referring to Figure 1, the signal in the DRI trace starting at about 3 mL retention volume is "the matrix," small molecules that reflect differences in the composition of the mobile phase and the solution solvent. Any additives or residual solvent peculiar to the polymer sample appear here. The FIPA column merely serves to isolate the polymeric species and to spread the sample to give a detector response that can be predictably (using automatic baseline and integration limits in the software) integrated and processed. The speed of the analysis results from removal of a full GPC column set. In principle, the column is not necessary in the measurement if the mobile phase and dissolution solvent are compositionally closely matched. A loop of tubing that serves the purpose of allowing sample diffusion could replace the column. In cases where the dissolution solvent differs from the mobile phase, or where additives are
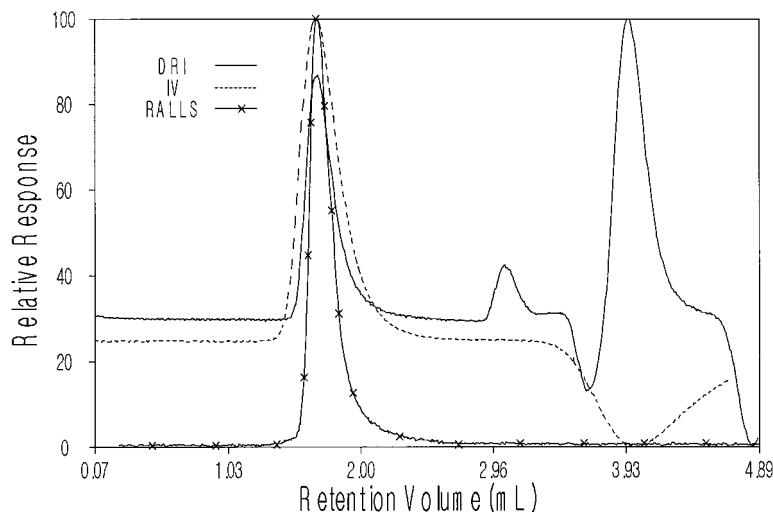
Figure 1   Raw detector traces collected in the FIPA method.

present in the polymer, a separation column is necessary to avoid spurious LS and DRI results.

Measurements in CH

The measurements were first undertaken using cyclohexane as the mobile phase and the solvent at 70°C. We were aware of the possibility of polymer chain aggregation at this analysis temperature. The very low (or absent) crystallinity of many of the samples suggested that lower-temperature characterization would be adequate. Also, the lower temperature and CH were attractive for several reasons. For example, because the method was to be developed for routine plant lab analysis, we wished to avoid the inherent hassle of a high-temperature characterization, if possible. Initially, use of TCB at higher temperatures was considered a fallback option. We have an abundance of experience in handling TCB in Dow, but its use is unnecessary at an analysis temperature of 70°C. Ying et al.[14,15] reported a GPC analysis of isotactic polypropylene in cyclohexane after dissolution in hot decalin. Similar methods were also reported by Ibhadon[16] but the analysis was done at 60°C. Rao et al.[17] also discussed similar methods for the moderate-temperature GPC analysis of polyolefins. In that study he describes dissolution of polyolefins in a high-temperature solvent followed by analysis at 70 or 90°C (depending on molecular weight) in a mobile phase such as methylcyclohexane. These studies suggested, at the very least, that cyclohexane at 70°C was worthy of additional evaluation, partic-

ularly for EPDM samples with low or absent crystallinity.

For many of the samples, the method was deemed adequate. In fact, LS M_w values com-

Table I   FIPA Data from Analysis in CH at 70°C

Sample	$M_w{}^{\text{a}}$ (g/mol)	$[\eta]^{\text{b}}$ (mL/g)	GPC $M_w{}^{\text{c}}$ (g/mol)
EPDM E-1	152,366	1.572	184,900
EPDM R-1	149,852	1.725	195,600
EPDM R-2	192,153	1.923	271,900
EPDM R-4	162,610	1.711	193,300
EPDM H-1	107,337	1.382	125,800
EPDM B-1	99,857	1.292	98,800
EPDM I-1	97,502	1.290	93,800
EPDM A-1	146,617	1.716	141,600
EPDM A-3	144,878	1.719	142,500
EPDM A-2	140,740	1.739	143,600
EPDM A-4	135,554	1.746	143,000
EPDM R-5	223,467	2.180	290,800
EPDM F-1	160,020	1.789	199,000
EPDM D-1	102,952	1.317	120,800
EPDM C-1	111,052	1.268	110,100
EPDM G-1	143,847	1.560	130,100
EPDM X-1	98,787	1.304	93,100
EPDM X-3	105,016	1.310	102,200
EPDM X-2	150,393	1.681	177,200
EPDM X-4	108,256	1.334	91,500
PEO-B-1	135,266	1.615	150,000
PEO A-1	60,366	0.812	47,100

^a Relative SD, 1σ: 1.5–2.5%.
^b Relative SD, 1σ: 0.6–1.5%.
^c Relative SD, 1σ: 3–5%.

$$y = -1.119 \times 10^{-3}x + 5.604 \times 10^{-6}$$

(a)

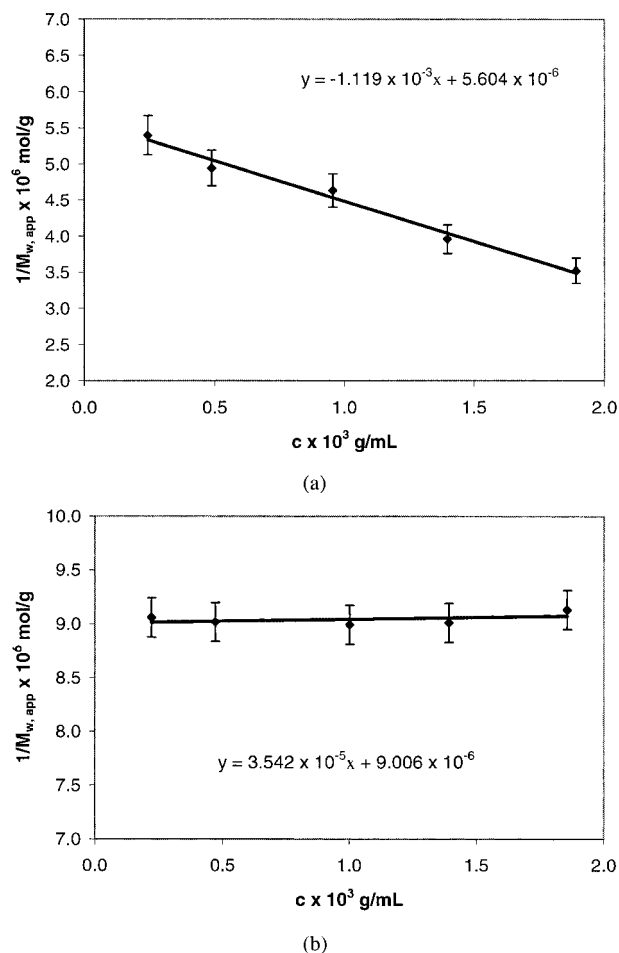$$y = 3.542 \times 10^{-5}x + 9.006 \times 10^{-6}$$

(b)

Figure 2 (a) $1/M_{w,\mathrm{app}}$ versus c plot for a high molecular weight, 70% ethylene EPDM process sample characterized in CH at 70°C. The negative slope of this plot strongly suggests aggregated polymer chains in solution. (b) $1/M_{w,\mathrm{app}}$ versus c plot for a low molecular weight, 50% ethylene EPDM finished lot sample characterized in CH at 70°C. The near independence of $1/M_{w,\mathrm{app}}$ on c suggests a system close to theta conditions.

pared favorably to PE equivalent M_w values measured by high-temperature GPC, as shown in Table I. The LS M_w values were obtained without a second virial coefficient correction. Samples exceeding about 150,000 g/mol, however, appeared severely underestimated when compared to the GPC values. We also noted shifts in the values calculated for M_w and $[\eta]$ when identical samples with reasonably small differences in solution concentration were analyzed. This prompted us to investigate the changes in apparent weight-average molecular weight, $M_{w,\mathrm{app}}$, with concentration. Figure 2(a) and (b) show the results for two sam-

ples. One is a high molecular weight process sample with about 70% ethylene, the other a lower molecular weight finished product with about 50% ethylene. The finished product plot [Fig. 2(b)] exhibits almost no slope. The value of A_2, then, must be close to zero, theta solution conditions. The process sample, by contrast, gave a large negative slope, strongly suggesting aggregation or association. Given a wide range of concentration, one may be able to classify the type of association from a $1/M_{w,\mathrm{app}}$ versus c plot. All types exhibit a negative value for the second virial coefficient but in so-called closed-and-open type association,[18] the plot generally displays some curvature. According to the definition proposed by Elias,[18] whether association is classified "open" or "closed" has to do with whether a continuous size distribution of aggregated species is present ("open") or only one is present and in equilibrium with the nonaggregated chain ("closed").
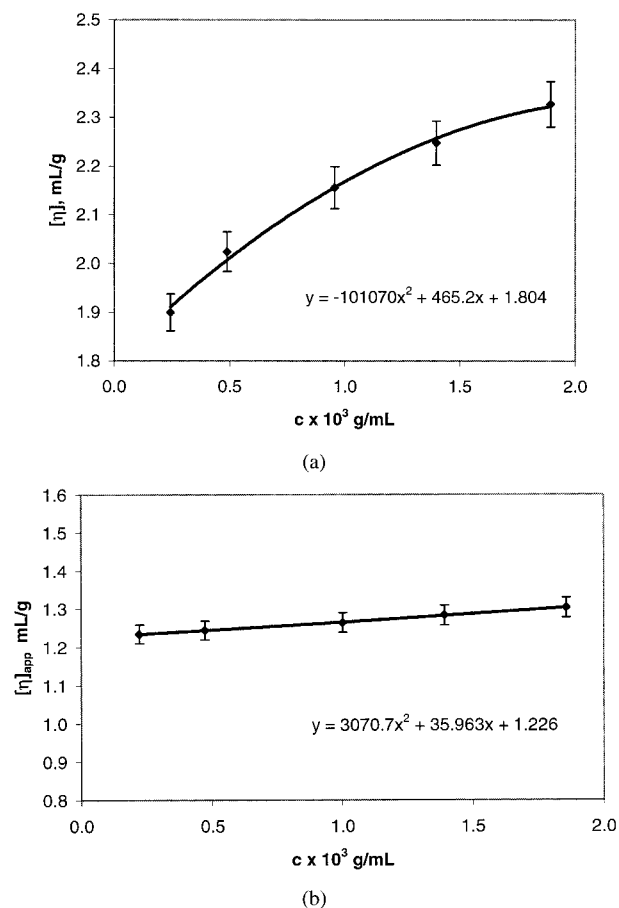

$$y = -101070x^2 + 465.2x + 1.804$$

(a)

$$y = 3070.7x^2 + 35.963x + 1.226$$

(b)

Figure 3 (a) $[\eta]_{\mathrm{app}}$ versus c for the sample in Figure 2(a) under the same analysis conditions. (b) $[\eta]_{\mathrm{app}}$ versus c for the sample in Figure 2(b) under the same analysis conditions.
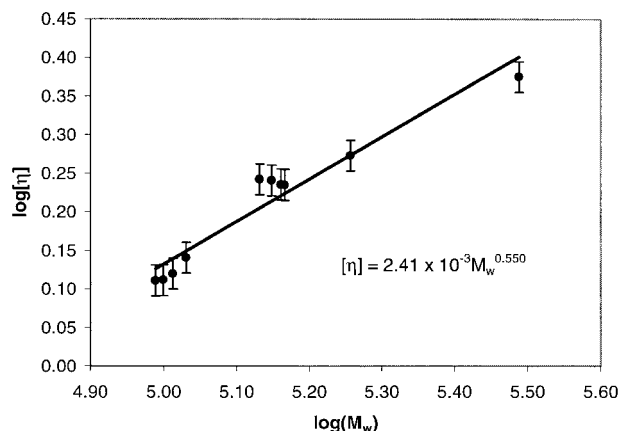
Figure 4 Mark–Houwink plot of 70% ethylene EPDM samples in CH at 70°C, ignoring effects of polydispersity.

The plot in Figure 2(a) appears indicative of a polymer dispersed in a thermodynamically poor solvent. Baldwin and Verstrate[2] mentioned that even amorphous EP copolymers display an "agglomeration" phenomenon in solvents at 23°C but offered no explanation for the behavior. Ver Strate[1] also mentioned the observation of association in dilute solution for many EPDM products below 80°C. Clearly, the degree of association must be dictated by both molecular weight and ethylene content and the association we observed was probably attributable to poor solvation of the crystalline portions of the sample. We also found negative second virial coefficients for samples of lower molecular weight but high ethylene content (exceeding 70%). In Figure 3(a) and (b), apparent intrinsic viscosity $[\eta]_{app}$ versus concentration is plotted for the same two samples. These relationships, where the $[\eta]_{app}$ is calculated from eq. (4), should have slopes close to zero. In Figure 3(b) there is approximately a 6% difference between the values of $[\eta]_{app}$ calculated at the highest and lowest concentrations (4× difference in concentration). In Figure 3(a), however, the strong concentration dependency on the values reinforces the notion of a poorly behaving polymer sample in CH. The curvature in Figure 3(a) again suggested an association phenomenon.[19] For our purposes, a large dependency in the measurement of M_w and $[\eta]$ on concentration was unacceptable, especially in the measurement of process samples where the concentration of the solution prepared for analysis is more difficult to control.

Figure 4 shows Mark–Houwink plots constructed for 70% ethylene content samples mea-

sured in CH at 70°C using only M_w and $[\eta]$ obtained from the FIPA method. In the plots, the samples have about the same ethylene content but their polydispersity varies by several percent. From Figure 4, **a** = 0.550. For linear chain architecture, these values clearly indicate "nonexpanded" coils in CH, with the **a** value essentially indicating theta conditions. Although true theta solvent conditions would be useful for eliminating the concentration effect on measured M_w, realistically CH at 70°C yields thermodynamically poor solvent conditions for high molecular weight process samples and finished products, and was unsuitable for an analysis method universally applicable to our process and product polymers.

The measurements of apparent M_w versus concentration were repeated in TCB at 145°C for the difficult process sample [Figs. 2(a) and 3(a)]. The results are shown in Figure 5(a) and (b). Both figures are indicative of a nonaggregating polymer–solvent–temperature system. The molecular
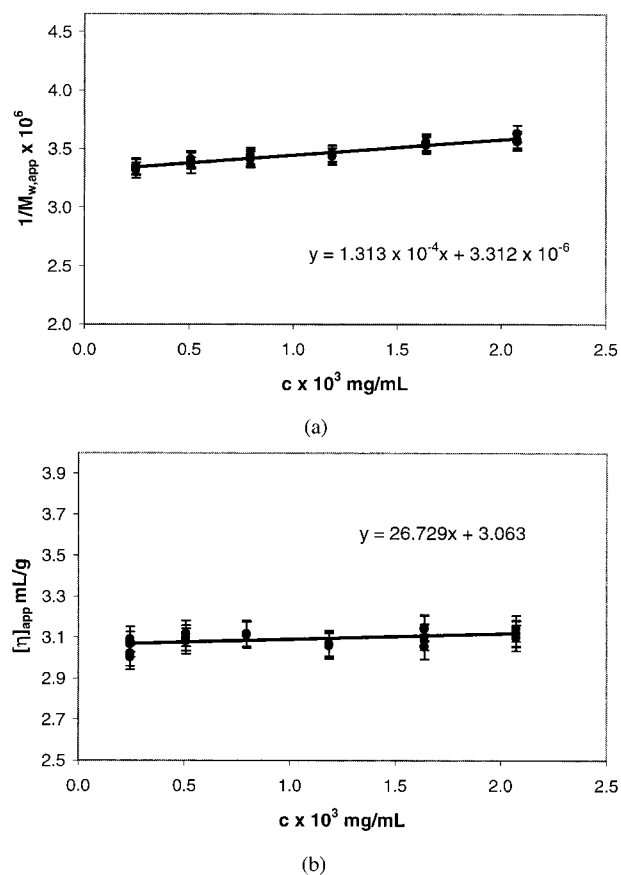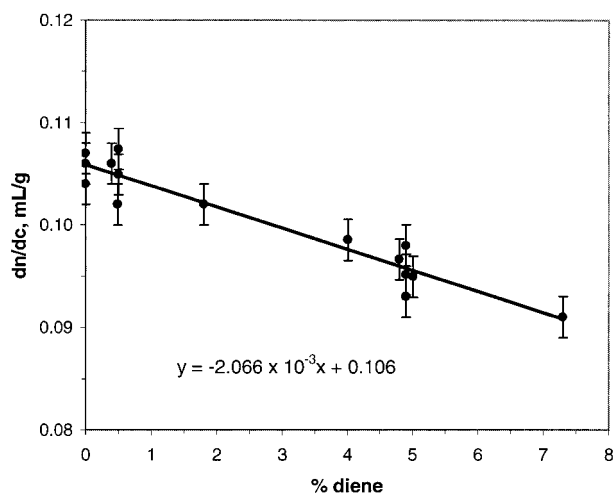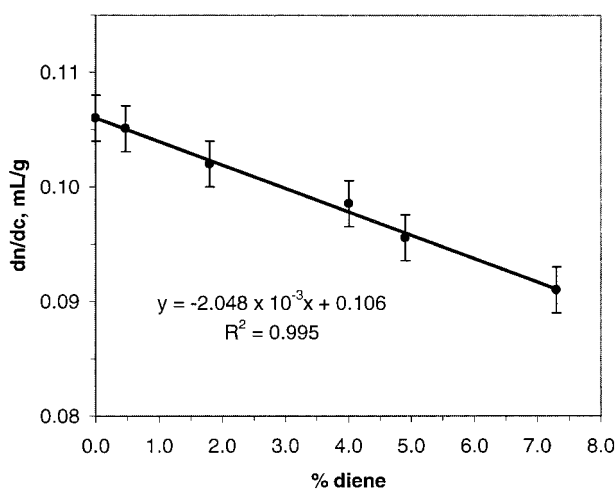

(a)

(b)

Figure 5 (a) $1/M_{w,app}$ versus c plot for the sample in Figure 2(a) in TCB at 145°C. (b) $[\eta]_{app}$ versus c for the sample in Figure 2(a) in TCB at 145°C.

weight dependency on concentration in Figure 4(a) is so small that at concentrations of about 1 mg/mL or less, an A_2 correction is not necessary. The plot in Figure 5(b) shows the expected result for the calculation of $[\eta]$ if the relationship given in eq. (4) is valid.

The values of dn/dc measured using the DRI detector in the TDA fell in the range of 0.075–0.083 mL/g. There was no obvious dependency of dn/dc on ethylene (or propylene) content, although the values did appear to track with diene content, albeit somewhat noisily. Perhaps some of the scatter in the data was the result of the aggregation noted in some of the samples that may affect dn/dc. Or, it could simply be that the mea-

Figure 7 dn/dc versus percentage diene in TCB at 145°C.

surements were of poorer quality because of low dn/dc values. This trend was unexpected, especially because of the small quantities of diene in the samples, but was also apparent (and much less noisy) when TCB was used as the solvent, as presented in the next section.

Measurements in TCB

It is possible that the above method was inadequate for some samples because the dissolution was not accomplished at the modest 70°C temperature. The papers by Rao, Ying, and Ibhadon cited above suggest that dissolution in a high-temperature solvent followed by elution with a lower-temperature mobile phase should yield an adequate characterization. In the end, we saw little advantage to purchasing, using, and disposing of two (or more) solvents for the same analysis when one was adequate for the task. Therefore, given that a higher temperature was needed for a universally applicable analysis method, we settled on TCB for the solvent and mobile phase. Although Rao et al.[17] and Ying et al.[14,15] suggest that the dn/dc values are greater (and hence offer better detector sensitivity) for polypropylene in solvents like cyclohexane than those in chlorinated solvents, we observed the opposite for the samples in this work. Perusal of extensive tables of dn/dc values for polyethylene and polypropylene in studies like those of Huglin[20] indicate that hydrocarbon solvents offer very little or no advantage in terms of higher dn/dc values for polyolefin analysis, at least at the temperatures reported.

Figure 6   (a) dn/dc versus percentage diene in TCB at 90°C. (b) dn/dc versus percentage diene. Same as (a), but data of similar percentage diene are averaged.
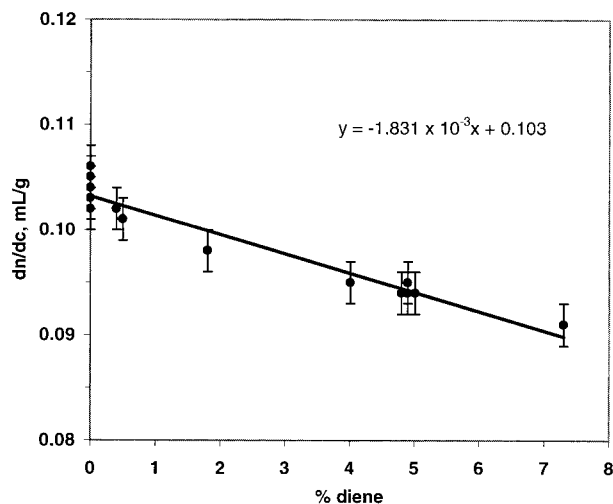
Higher signal to noise of the DRI detector in TCB allowed us to reduce the concentration of the analysis solution from 1.0 to 0.5 mg/mL, which extended the life of the small GPC column installed in the TDA. Our dissolution was carried out in TCB at 145°C, as the other GPC methods cited above recommend, but injected into a TCB mobile phase at 90°C.

The values for dn/dc were determined on-line, in a manner similar to those measured in CH. The DRI detector was calibrated this time, however, with an Engage ethylene–octene copolymer, using the value of dn/dc at 145°C, -0.104 mL/g. Samples with differences of about 1–1.5% in diene content displayed significant differences in dn/dc values. Figure 6(a) and (b) show plots of percentage diene versus dn/dc. The absolute value of dn/dc becomes smaller with increasing diene. The plot in Figure 6(b) was produced from Figure 6(a) by averaging values of similar ($\pm 0.5\%$) diene content. The data point at 0% diene was determined by measuring an atactic polypropylene ($dn/dc = -0.107$ mL/g) and averaging it with the value
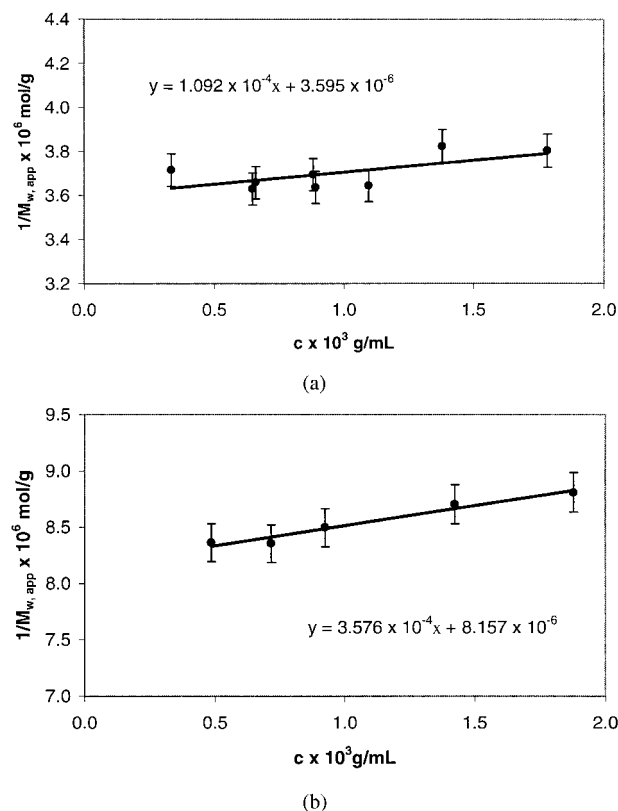

(a)

(b)

Figure 9 (a) $[\eta]_{app}$ versus c for the sample in Figure 2(a) in TCB at 90°C. (b) $[\eta]_{app}$ versus c for the sample in Figure 2(b) in TCB at 90°C.

(a)

(b)

Figure 8 (a) $1/M_{w,app}$ versus c plot for the sample in Figure 2(a) in TCB at 90°C. (b) $1/M_{w,app}$ versus c plot for the sample in Figure 2(b) in TCB at 90°C.
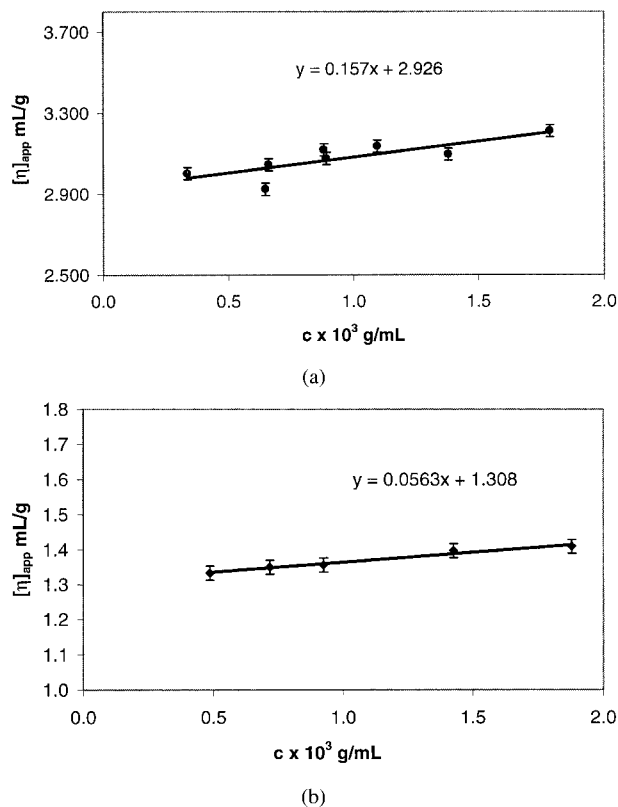
of the Engage sample. Similarly, the plot in Figure 7 was produced from data collected at 145°C, using a high-temperature GPC and the calibrated DRI method. The same trend was apparent under these analysis conditions. The advantage to this relationship, particularly when measuring process samples, is that the dn/dc can be predicted based on percentage diene in the sample without accurate knowledge of the sample concentration used for analysis. This makes sample preparation directly from process liquors easier and allows the analyst to get consistency in the M_w and $[\eta]$ measurements.

The influence of concentration on $M_{w,app}$ was investigated as before. Figure 8(a) and (b) show results for the same polymers analyzed in Figure 2(a) and (b). The apparent $[\eta]$ versus concentration trends are shown in Figure 9(a) and (b). The difference in behavior of the process sample in TCB at 90°C was obvious. The A_2 value (from the slope of the line) for this sample [Fig. 8(a)] was not negative, as before. The $[\eta]$ values differed by only 7% with a twofold difference in concentra-

Table II   FIPA Data from Analysis in TCB at 90°C

Sample	$M_w{}^a$ (g/mol)	$[\eta]^b$ (mL/g)	$M_{v,app}$ (g/mol)	M_w/M_v
EPDM A-1	138,600	1.839	126,550	1.10
EPDM A-2	134,233	1.878	130,268	1.03
EPDM B-1	96,555	1.318	79,893	1.21
EPDM C-1	118,000	1.328	80,754	1.46
EPDM D-1	115,733	1.520	97,286	1.19
EPDM E-1	219,333	1.928	135,153	1.62
EPDM F-1	187,317	2.085	150,494	1.24
EPDM X-1	89,317	1.363	83,706	1.07
EPDM R-1	183,200	2.020	144,069	1.27
EPDM R-2	275,033	2.572	201,164	1.37
PEO A-1	53,620	0.754	36,925	1.45
PEO B-1	150,933	1.625	106,692	1.41
EPDM G-1	140,833	1.515	96,861	1.45
EPDM R-3	306,667	2.823	228,776	1.34
EPDM R-4	211,120	1.974	139,621	1.51
EPDM X-2	184,400	2.141	156,186	1.18
EPDM R-5	267,067	2.733	218,773	1.22
EPDM R-6	236,900	2.392	181,966	1.30
EPDM R-7	186,400	1.968	138,960	1.34
EPDM R-8	236,600	2.300	172,388	1.37
EPDM R-9	172,100	2.177	159,751	1.08
EPDM R-10	144,967	1.654	109,370	1.33

[a] Relative SD, 1σ: 1.5–2.5%.
[b] Relative SD, 1σ: 0.6–1.5%.

tion. If the highest concentration (about 1.8 mg/ mL, significantly out of range of the concentration of interest) point was removed from the plot, the apparent $[\eta]$ was essentially invariant with concentration. The target concentration for the analysis is 0.5 mg/mL. If the process samples, after dilution, fall within 20% of this value, the values for M_w and $[\eta]$ will remain within the reported precision (1σ) of the measurements.

Table II summarizes the M_w and $[\eta]$ data for the measurements in TCB. Figure 10 shows the relationship between LS M_w and GPC M_w, derived as PE equivalents; M-H **a** = 0.725, K = 4.064×10^{-4}. These values were determined by Dickie[21] in Dow several years ago. Ver Strate[1] points out that in good solvents, the M-H relationship $[\eta] = 4 \times 10^{-4} M_w^{0.74}$ offers a reasonable estimate of M_w from $[\eta]$. These values were interpolated from M-H values for homogeneous polyethylene and polypropylene. The relationship $[\eta] = 2.92 \times 10^{-4} M_w^{0.726}$ was previously reported[1] for 50% ethylene EPDM in TCB at 135°C. We also prepared M-H plots from the FIPA measurements made in TCB. Figure 11(a) and (b) show the results. Despite polydispersity differences between

samples and the limited range of molecular weight, the M-H K and **a** values derived from these plots are in good agreement with the equation given by Ver Strate and other published M-H values.

Interest in estimating a meaningful polydispersity value from the FIPA data prompted us to
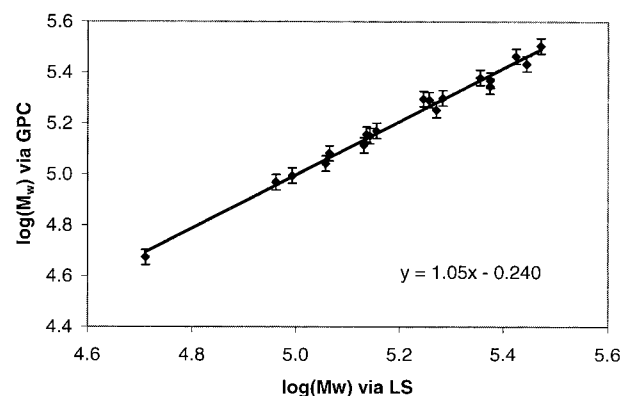
Figure 10   Relationship of GPC M_w to LS M_w. GPC M_w determined in TCB at 145°C; LS M_w in TCB at 90°C. See Experimental section for details.
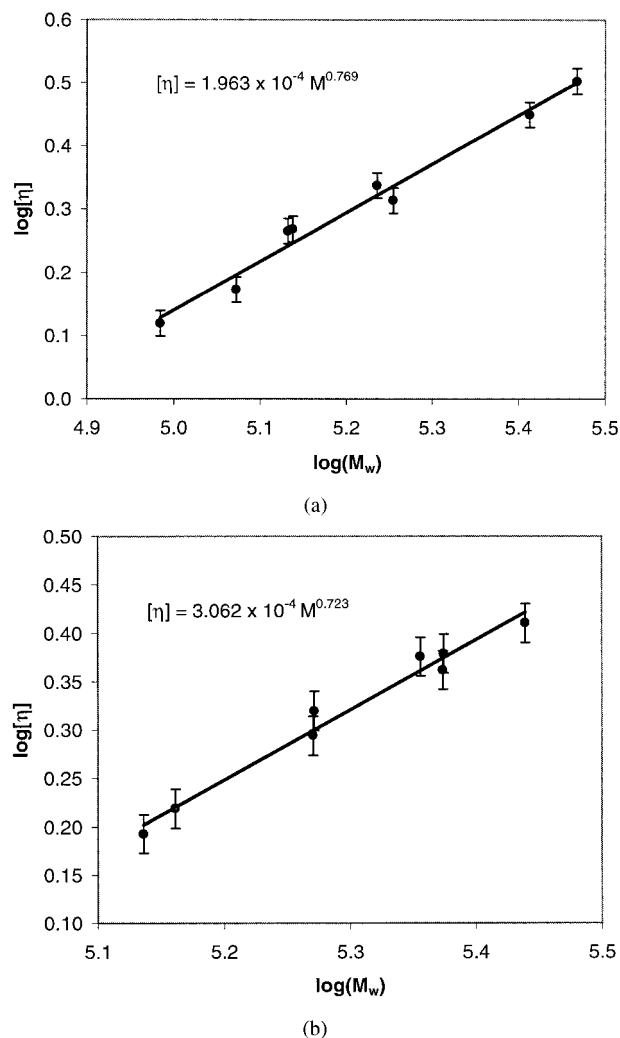
Figure 11   (a) Mark–Houwink plot of 70% ethylene EPDM samples in TCB at 90°C from FIPA data, ignoring effects of polydispersity. (b) Mark–Houwink plot of 42–66% ethylene EPDM samples from FIPA data, ignoring effects of polydispersity, in TCB at 90°C.

measure more accurate M-H values than those provided in Figure 11(a) and (b) so that the viscosity-average molecular weight M_v could be calculated. A polydispersity index M_w/M_v can then be measured for the samples using the FIPA method only. To measure the M-H values properly, samples of consistent polydispersity and comonomer composition are needed.[22] Therefore, we performed triple-detection GPC measurements at 90°C on samples with 50 and 70% ethylene to arrive at M-H value estimates. The relationships determined were: $[\eta] = 4.077 \times 10^{-4} M_w^{0.712}$ for 50% ethylene; $[\eta] = 3.027 \times 10^{-4} M_w^{0.735}$ for 70% ethylene. The precision error on K and **a**

was under 1.0% (1σ). As before, these relationships were consistent with older literature values.[2] In Table II the M_v values calculated from an average of the relationships given above are recorded with M_w/M_v.

The FIPA data were also used to develop a relationship with Mooney viscosity, a commonly measured property in the rubber industry. Viscosity measurements, in general, may vary with comonomer composition at constant molecular weight, given that monomer composition largely defines chain architecture. For example, a linear correlation of $[\eta]$ to Mooney will be realized with samples only of similar comonomer composition (and polydispersity). To remove the effect of varying comonomer composition, we instead plotted the apparent hydrodynamic size $R_{h,\,app}$ versus Mooney. Because[22,23] $R_h \propto M_w[\eta]$, the value of $R_{h,app}$ was taken as the product of the M_w and $[\eta]$ values measured in the FIPA method. Figure 12 shows the relationship. The usefulness of this plot is that the Mooney number of process samples can be estimated immediately, long before a sample is devolatilized and measured on a Mooney viscometer.

Finally, it was found that this method was adequate without modification for the rapid analysis of our Engage ethylene–octene copolymers.

CH Data versus TCB Data

Although the data generated in CH ultimately held no value for the routine characterization of these products, it was still interesting to compare the fundamental parameters obtained from both methods. The data in Tables I and II reveal that the M_w obtained from both methods compare fa-
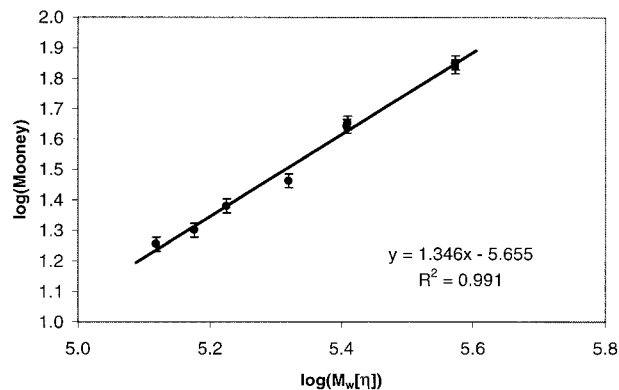

Figure 12   Relationship of Mooney to hydrodynamic volume, ignoring effects of polydispersity.

vorably, except in cases where the GPC M_w exceeds 150,000 g/mol. Interestingly, all of the LS M_w values that are underpredicted in the CH analysis method can be reasonably converted to HT-GPC values by the same multiplier. It is not prudent to implement the method with such a correction. There are still the problems of increased data variability coupled to solution concentration changes and the uncertainty of when it is appropriate to apply such a correction.

For all samples, $[\eta]$ is higher in TCB at 90°C than in CH at 70°C, indicating that the polymer chains are more expanded in TCB. Of course, this is consistent with the Mark–Houwink plots presented in Figures 4 and 11(a), where a dramatic change in the **a** value was apparent upon changing analysis conditions.

CONCLUSIONS

A flow-injection polymer analysis method was developed for the rapid measurement of the bulk molecular properties of EPDM commercial elastomers. The analysis is performed in TCB at 90°C and from a single measurement provides information on M_w, $[\eta]$, polydispersity, and Mooney number. The analysis can also be extended to the ethylene–octene copolymers. Analysis in cyclohexane at 70°C was inadequate for samples exceeding about 150,000 g/mol or ethylene content exceeding about 70%.

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