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## Size Exclusion Chromatography of Branched Polyethylenes to Predict Rheological Properties

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**Abstract:** Three methods of predicting dynamic viscosity of branched polyethylenes from size exclusion chromatography (SEC), refractive index/light-scattering detection data were examined: relating parameters in the Cross viscosity equation to molecular weight averages, use of a mixing rule, and a method based on the similarity of the cumulative molecular property distributions to a dimensionless viscosity versus frequency plot. The use of accurate SEC data was emphasized. The third “curve similarity” method provided the most promising results. The use of cumulative  $g'$  (the molecular contraction factor based on intrinsic viscosity) distributions, in addition to cumulative molecular weight distributions, enable very useful sample comparisons.

**Keywords:** Polyethylene; Branching; Size exclusion chromatography; Viscosity; Structure-property characterization

Prediction of rheological properties from molecular properties has a long history in polymer science.<sup>[1–3]</sup> The most reliable methods are for linear polymers, monodisperse in molecular weight. Branched polydisperse polymers, such as low-density polyethylene, are less understood. Furthermore,

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theoretical models often require quantities that are not particularly accurate or reproducibly obtained through experiment. Root-mean-square radius and the molecular contraction factor,  $g$ , are two notable examples. The former is often of low reproducibility and available only over a narrow range of molecular sizes when obtained by size exclusion chromatography (SEC) light-scattering detection. The latter is either calculated from the root-mean-square radius or is related with uncertainty to  $g'$ , the molecular contraction factor based on intrinsic viscosity.

The objective of this work is to develop robust predictions of rheological properties for branched polyethylenes by utilizing the best possible data obtainable from SEC with differential refractive index (DRI) and dual-angle light-scattering detection. With this instrumentation, the primary information available is a differential refractive index chromatogram and two light-scattering chromatograms (one corresponding to the  $15^\circ$  and the other to the  $90^\circ$  scattering angle). A polystyrene calibration curve and Mark-Houwink constants for polystyrene and for linear polyethylene complete the obtainable data.

Oscillatory shear rheology measurements provide various moduli and the phase angle. Dynamic viscosity (the magnitude of the complex viscosity), at different frequencies, is obtained from this information.

## THEORY

### Size Exclusion Chromatography Interpretation

The application of a molecular weight calibration curve to a chromatogram obtained from a DRI detector continues to be one of the most reproducible mathematical operations in SEC interpretation. Universal calibration can be used to convert a polystyrene calibration curve to a linear polyethylene calibration curve. Thus, the molecular weight averages ( $M_{N,LIN}$ ,  $M_{W,LIN}$ ) and molecular weight distribution for a linear polyethylene sample with the same DRI chromatogram (i.e., same size distribution) as a branched polyethylene sample can readily be obtained. Also, the area under the  $15^\circ$  light-scattering chromatogram provides an accurate weight-average molecular weight ( $M_{W,LS}$ ) that reflects branching. (In this work, we actually calculated the scattering function,  $P(\theta)$ , at each retention volume from the  $15^\circ$  and  $90^\circ$  detector outputs and divided each  $15^\circ$  height by  $P(15)$  before integrating (see Equation (16) in Mourey and Balke.<sup>[4]</sup> However, this more rigorous procedure causes a barely significant change at the highest molecular weights.)

By using the local concentration values from the DRI chromatogram, that same light-scattering chromatogram can also provide local weight-average molecular weights at each retention volume. However, here is where

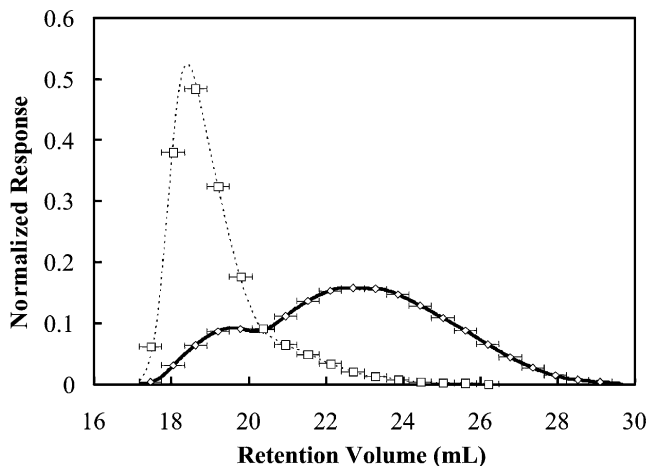
we encounter two major problems. The first is specifying the interdetector volume between the DRI and light-scattering detectors. Here, a previously published method involving overlaying calibration curves derived from light-scattering detection and injection of narrow polystyrene standards was used.<sup>[5]</sup> The second major problem is more difficult to overcome: the different relative sensitivities of the light-scattering and DRI detectors.

As shown in Figure 1, at the lower retention volumes, there is a comparatively large light-scattering detector response and a low or nonexistent DRI response. At high retention volumes the situation is reversed. The result is regions where the two detectors cannot be combined to obtain local  $M_W$  values. Conventionally, this problem is overcome by somehow obtaining extrapolated values.<sup>[6]</sup> Extrapolation is almost always a very uncertain procedure. In this work, data binning is used in place of extrapolation into high noise regions: height data are averaged over 50 data points using the following equation for the DRI output:

$$[W_N(v)]_{binned} = \frac{\int_i^{i+49} W_N(v) dv}{v_{i+49} - v_i} \quad (1)$$

The binned value of the height,  $[W_N(v)]_{binned}$ , is assigned to the retention volume at the midpoint of the range  $v_i$  to  $v_{i+49}$  where  $i = 1, 50, 100, 150, \dots$ . The same procedure was used for the light-scattering chromatograms, with  $R(\theta)$  substituted for  $W_N(v)$ . The trapezoidal rule was used for the integration.

Thus, the chromatograms are essentially converted into histograms. An example of the chromatogram heights used, along with the range of



**Figure 1.** Chromatograms and binned heights (dashed: 15° light scattering, solid: differential refractometer).

retention volumes (a horizontal bar through the point) encompassed by each average height, is shown in Figure 1. In the remainder of this paper the subscript “*binned*” is omitted because binned heights are used throughout.

### Relating Molecular Properties to Viscosity

Three methods of relating molecular properties to viscosity were used, as described below.

#### Model 1: Multiple Linear Regression

The Cross viscosity equation can be written as:<sup>[7]</sup>

$$\eta^*(\omega) = \frac{\eta_0}{1 + K^*\omega^a} \quad (2)$$

where  $\eta^*$  is the dynamic viscosity,  $\omega$  is frequency, and the three fitting parameters are zero shear viscosity ( $\eta_0$ ),  $K^*$ , and  $a$ . When the viscosity data for all samples are fit to this equation, each sample provides these three parameter values.

Now, we can define a measure of polydispersity as  $P$  from the ratio of quantities obtained, assuming linear molecules:

$$P = \frac{M_{W,LIN}}{M_{N,LIN}} \quad (3)$$

and a measure of branching as  $G$  from the ratio of a quantity incorporating branching to one calculated, assuming linear molecules:

$$G = \frac{M_{W,LS}}{M_{W,LIN}} \quad (4)$$

Finally, we can express each parameter of the Cross viscosity equation as functions of  $M_w$ ,  $P$ , and  $G$  by using multiple linear regression.

#### Model 2: The Method of Pedersen and Ram<sup>[8]</sup>

The primary equations in this method use one relating viscosity to a lumped structure parameter  $(gM)_w^*$  where  $A$  and  $B$  are constants:

$$\log \eta(\omega) = A + B \log (gM)_w^* \quad (5)$$

One defines  $(gM)_w^*$ :

$$(gM)_w^* = \sum_{i=1}^{c-1} w_i g_i M_i + (gM)_c q_c \quad (6)$$

where  $w_i$  are weight fractions, and  $q_c$  is the height of the cumulative  $gM$  distribution (i.e., “wt. fraction greater than”) at a particular value of  $gM$ ,  $(gM)_c$ .

### Model 3: Curve Similarity

As early as 1962, it was noted that the shape of the cumulative molecular weight distributions and the plot of viscosity versus frequency were similar.<sup>[9-11]</sup> The key problem in this approach is to superimpose the curves by transforming molecular weight into frequency (or shear rate). There is little guidance on how to accomplish this for polydisperse, branched, entangled polymers.<sup>[12]</sup> Even for linear polymers, the theoretical approaches providing the transformations are not satisfactory.<sup>[10]</sup> In this work we use both the cumulative molecular weight distribution and the cumulative  $g'$  distribution. The former is well known and readily obtained accurately using a light-scattering detector in combination with a DRI detector.

To calculate a cumulative  $g'$  distribution, we employ the usual calculation for obtaining  $g'$ :

$$g'_i = \left( \frac{M_{i,LIN}}{M_{i,LS}} \right)_{v=v_i}^{a+1} \quad (7)$$

so that:

$$\log g'_i = (a + 1)(\log M_{i,LIN} - \log M_{i,LS}) \quad (8)$$

A plot of the cumulative area under the DRI chromatogram to  $v_i$  versus  $\log g'_i$  is the required distribution. Note that the same cumulative area versus  $\log M_{i,LS}$  results in the cumulative molar mass distribution.

To transform the  $\log g'$  and  $\log M$  cumulative distributions to superimpose on  $\eta/\eta_0$  versus  $\log \omega$  a transformation is required. The one proposed here is:

$$\log \omega = \beta_0 + \beta_1 \log M_{i,LS} + \beta_2 \log g'_i \quad (9)$$

where the  $\beta$  values are three unknown parameters determined by superimposing cumulative heights (common to both  $g'$  and  $M_{i,LS}$ ) on  $\eta/\eta_0$  versus  $\log \omega$ .

There are two major uncertainties: (i) whether or not the superposition can be obtained and (ii) whether the unknown parameters can be determined in advance from only the molecular property information. Associated with (i) is the uncertainty as to whether or not the  $g'$  distribution can account for the effect of branching on the viscosity curve. Of course, even if both of these uncertainties are overcome, there will still remain the problem of determining zero shear viscosity so that absolute viscosity values can be obtained from  $\eta/\eta_0$ .<sup>[13]</sup> In the absence of data from creep experiments, one must extract it from a fit of the viscosity versus frequency data to a model – we select the Cross model because it provides excellent fits with a minimum number of parameters.

## EXPERIMENTAL

### Materials

Samples: low-density and high-density polyethylenes are commercial extrusion-grade resins (Table I).

Calibration standards: SRM 1484 and SRM 1483 linear polyethylenes (NIST) for the LS detector; narrow polystyrene standards from Polymer Labs for SEC calibration. Mark-Houwink constants<sup>[14]</sup> (where the intrinsic viscosity is expressed in dL/g) were polystyrene:  $K = 1.26 \times 10^{-4}$ ,  $a = 0.702$ ; polyethylene:  $K = 5.10 \times 10^{-4}$ ,  $a = 0.706$ . As shown in Table I, sample numbers indicate the weight-average molecular weight from light scattering, the quantity  $G$  (Equation (4)), and polydispersity,  $P$  (Equation (3)).

### Size-Exclusion Chromatography

A Waters Corporation GPC 2000 chromatograph using 1,2,4-trichlorobenzene at 140°C was equipped with a PD2040 two-angle light-scattering detector (Precision Detectors). SEC separations were on three TosoHaas GMHXL-HT 7.8 mm  $\times$  300 mm mixed-bed columns, with a nominal flow rate of 0.7 mL/min. Samples were dissolved at a concentration of 1.0 mg/mL at 160°C for 4 h (actual concentrations were calculated using the solvent densities reported by deGroot<sup>[15]</sup>). The sample solvent contained 0.25% butylated hydroxy toluene (BHT) as a thermal stabilizer and flow rate marker. Sample injection volume was 206.5  $\mu$ L.

### Rheology

Polyethylenes were characterized with a Rheometrics RMS 800 rheometer in the 25 mm parallel-plate testing geometry. Frequency sweeps at 10% strain were carried out at test temperatures of 200°C, 230°C, and 260°C under a dry nitrogen atmosphere. Time-temperature superposition was used to produce master curves of the storage and loss moduli with a reference temperature of 200°C, and the dynamic viscosity curves were calculated at 200°C for all samples from the moduli.

## RESULTS AND DISCUSSION

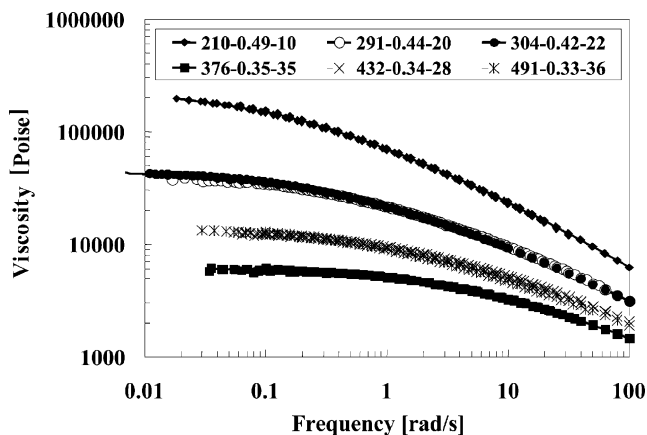
### Model 1

Figures 2(a) and 2(b) show the viscosity data fit by the Cross viscosity equation. Table II shows the parameter values used in this equation.

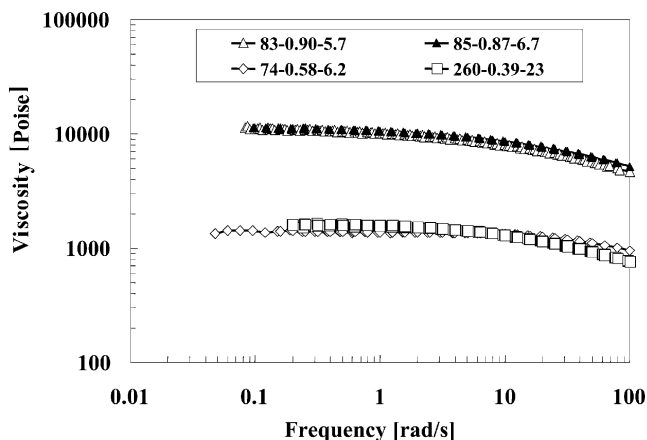
**Table I.** SEC data for polyethylene samples

Sample number	Type (density) (gm/mL)	MFI	$M_{W,LS}$	$M_{W,LIN}$	$M_{W,LIN}/M_{W,LS}$	$M_{N,LIN}$	$M_{W,LS}/M_{N,LIN}$
83-0.90-5.7	HDPE (0.963)	8	83,300	75,200	0.903	14,600	5.71
85-0.87-6.7	HDPE (0.962)	8	84,900	73,800	0.869	12,600	6.74
74-0.58-6.2	LDPE (0.925)	50	73,800	43,100	0.584	11,900	6.20
210-0.49-10	LDPE (0.923)	0.75	210,000	103,000	0.490	20,500	10.24
291-0.44-20	LDPE (0.924)	4.15	291,000	128,000	0.440	14,700	19.80
304-0.42-22	LDPE (0.923)	4.2	304,000	129,000	0.424	14,100	21.56
260-0.39-23	LDPE (0.913)	70	260,000	100,000	0.385	11,500	22.61
376-0.35-35	LDPE (0.916)	20	376,000	131,000	0.348	10,900	34.50
432-0.34-28	LDPE (0.917)	10	432,000	148,000	0.343	15,700	27.52
491-0.33-36	LDPE (0.918)	10	491,000	161,000	0.328	13,800	35.58





(a)



(b)

**Figure 2.** (a) Viscosity vs. frequency, showing fits of the Cross viscosity equation (see Table I for sample descriptions); (b) Viscosity vs. frequency, showing fits of the Cross viscosity equation (see Table I for sample descriptions).

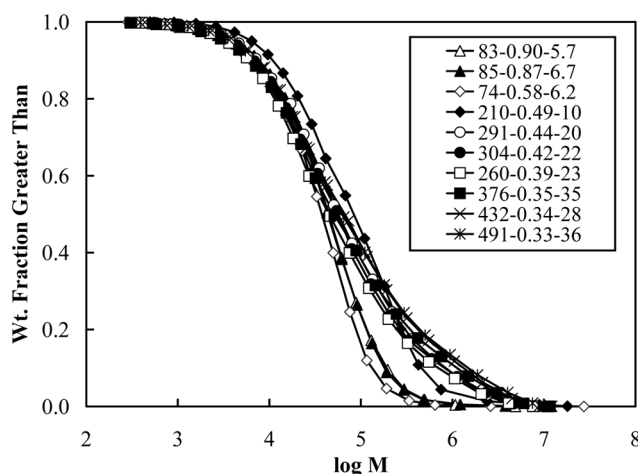
Excellent fits were obtained. Furthermore, multiple linear regression was able to relate each term in the Cross viscosity equation to  $M_{W,LS}$ ,  $P$ , and  $G$ . However, the fits showed extremely high correlation among these terms, and each equation used many terms. The origin of the correlation was the interdependence of the molecular weight averages that were used. This would mean, for example, that Model 1 could not distinguish the effect of an increase in  $P$  from the effect of an increase in  $G$ . The multiple terms indicated the possibility of “overfitting,” where

**Table II.** Parameter values

Sample	$\eta_0$	$a$	$K^*$	$\delta_0$	$\delta_1$	$\delta_2$	$\delta_3$
83-0.90-5.7	11500	0.519	0.133	0.667	-2.61	2.57	0
85-0.87-6.7	11500	0.550	0.0980				
210-0.49-10	245000	0.586	2.50	12.6	-5.48	2.14	1.17
291-0.44-20	43900	0.546	1.04				
304-0.42-22	47600	0.537	1.21				
376-0.35-35	6400	0.563	0.258	11.9	-5.35	2.32	1.89
432-0.34-28	14100	0.532	0.504				
491-0.33-36	15200	0.504	0.692				
74-0.58-6.2	1400	0.888	0.00811	-202.8	48.3	1.87	1.04
260-0.39-23	1700	0.581	0.0817				

the model is not capable of reliably predicting from new data. Thus, even with excellent fits, Model 1 was useless for prediction.

To emphasize the differences between samples and to reduce the correlation problems, we decided to utilize distributions rather than averages. Figure 3 shows the cumulative molecular weight distributions, and Figure 4 shows the cumulative  $g'$  distributions. We defined three "families" of polymers based upon the value of branching (i.e., the value of  $G$ ): (1) mostly linear polymers ( $G > 0.8$ ); (2) branched polymers ( $0.4 < G \leq 0.8$ ); and highly branched polymers ( $G \leq 0.4$ ). In Table I, the samples are arranged in order of increasing  $M_{W,LS}$ , which is also in order of decreasing  $G$ .

**Figure 3.** Cumulative molecular weight distributions for the polyethylene samples.

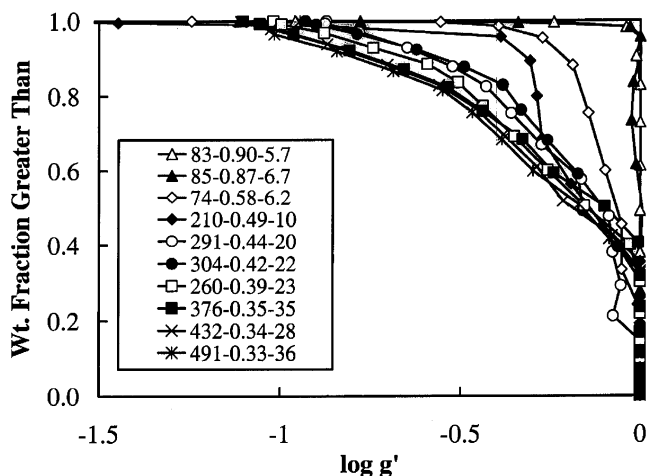


Figure 4.  $g'$  distributions for the polyethylene samples.

## Model 2

The Pedersen and Ram<sup>[8]</sup> model (Figure 5) shows that at any specified value of  $g'M$ , the height of the cumulative distribution is nearly the same for seven of the ten samples. The similarity of the lower part of the molecular weight distribution of these samples combined with this fact meant that the method could not adequately distinguish these viscosity curves.

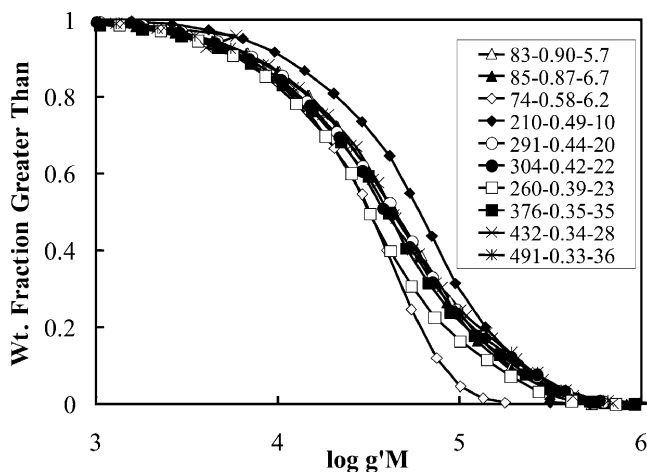


Figure 5.  $g'M$  distributions for the polyethylene samples.

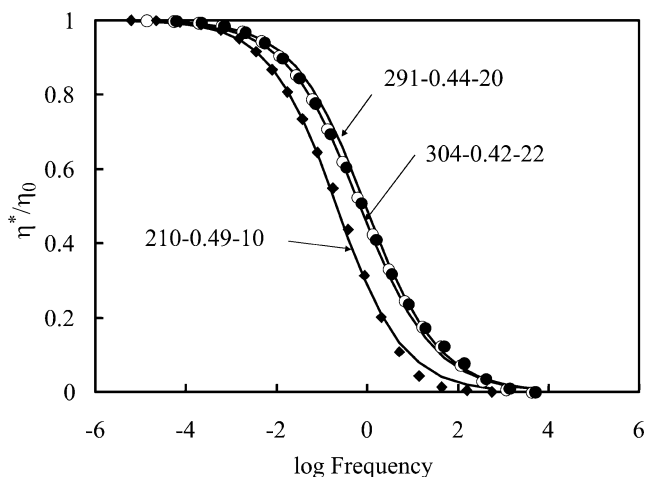
### Model 3

The transformation (Equation (9)) readily superimposed the cumulative distribution heights on the viscosity ratio versus frequency data. Fits were very good, and the contribution of the  $g'$  term in the transformation was found to nicely account for the effect of branching on the viscosity ratio. However, to obtain this level of accuracy, each sample was allocated its own separate set of three fitting parameters. Various strategies were employed to obtain more universal parameters. The best involves allowing  $\beta_0$  to be a linear function of the logarithm of the whole polymer number-average molecular weight, ( $M_{N,LIN}$ ) obtained using the linear polyethylene calibration curve. Now Equation (9) becomes Equation (10) where the  $\delta$  values are new constants:

$$\log \omega = \delta_0 + \delta_1 \log M_{N,LIN} + \delta_2 \log M_{i,LS} + \delta_3 \log g'_i \quad (10)$$

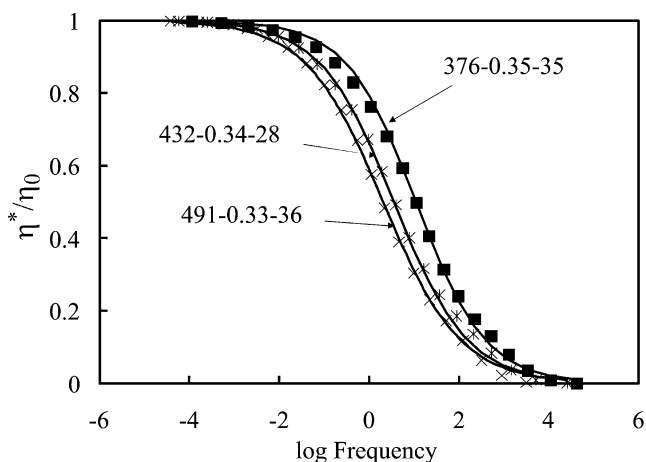
A two-step fitting process was used: first, a search for the values of  $\delta_0$ ,  $\delta_1$ , and  $\delta_2$  was done by minimizing a standard, unweighted least-squares objective function to match the cumulative molecular property distribution heights of the samples involved to the viscosity ratios. (Recall that the molecular property data for each sample consist of cumulative distribution heights where, for each height, the value of  $\log M$  and  $\log g'$  is known.) In this first step, only data corresponding to a  $g'$  of unity were used. In the second step, the value of  $\delta_3$  was obtained using all of the data for the samples involved.

The same Cross viscosity equation that fit the viscosity ratio versus frequency data also fit the cumulative height versus frequency data (where frequency was obtained from Equation (10)) with one set of four parameters for various combinations of samples. For example, Figure 6 shows that using Equation (10), good fits could be obtained for the "branched sample" family of three and one set of parameters (Table II). Figure 7 also appears to provide good fits using one set of parameters for the "highly branched" family of three. However, the predicted line for sample 491-0.33-36 passes nicely through the data for sample 432-0.34-28 and vice versa. The two predominantly linear polymer samples were also easily fit with one set of parameters. Samples 74-0.58-6.2 and 260-0.39-23 were also fit by one set of parameters. In using this method, the Cross viscosity equation is needed only to obtain the parameter values: it provides a convenient way of obtaining the experimental viscosity ratio values to compare the cumulative distribution heights when searching for the parameter ( $\delta$  values) to effect superposition. If the parameter values are known, then the Cross viscosity equation is not needed. The x-axis of the cumulative distribution obtained from the GPC chromatogram is converted to frequency by



**Figure 6.** Fits of viscosity data for branched polymers using the similarity model with one set of four parameters in Equation (10). Symbols show cumulative distribution heights and are the same as for Figure 5. The lines are the Cross viscosity equation fit to the viscosity ratio data.

using the molecular weight and  $g'$  values corresponding to each cumulative height via Equation (10). The method provides the beginning of an approach to obtaining  $\log M$  and  $g'$  from viscosity ratio versus frequency



**Figure 7.** Fits of viscosity data for highly branched polymers using the similarity model with one set of four parameters in Equation (10). Symbols show cumulative distribution heights and are the same as Figure 5. The lines are the Cross viscosity equation fit to the viscosity ratio data.

in a reverse of the two-step process. However, the whole polymer number-average molecular weight is also needed. Use of other rheological properties (notably phase angle) in addition to viscosity versus frequency would provide more information on the rheology side of the equations.

## CONCLUSIONS

Of the three models tested, the “curve similarity” model, with a transformation including the effects of both molecular weight and branching, is the most promising. The method is mainly based upon distributions rather than averages and therefore uses the maximum possible amount of information. Furthermore, the information used is among the most reproducible and accurate information obtainable from the SEC. The method is easily implemented and sufficiently flexible to fit all of the data. However, the utility of the method will depend upon how successfully the parameters in the transformation can be predicted from molecular properties. There is some indication that polymer “families” that share the same parameter values can be defined when information regarding the general location of the molecular weights in the sample are supplied to the transformation via the value of  $M_{N,LIN}$ .

## REFERENCES

- [1] Guzman, J. D., J. D. Schieber, and R. Pollard. (2005). A regularization-free method for the calculation of molecular weight distributions from dynamic moduli data. *Rheol. Acta* **44**, 342–351.
- [2] Bubeck, R. A. (2002). Structure-property relationships in metallocene polyethylenes. *Mater. Sci. Eng. R Rep.* **39**, 1–28.
- [3] Gahleitner, M. (2001). Melt rheology of polyolefins. *Prog. Polym. Sci.* **26**, 895–944.
- [4] Mourey, T. H. and H. Coll. (1995). Size exclusion chromatography with light-scattering detection at two angles, polystyrene in tetrahydrofuran. In *Chromatographic Characterization of Polymers: Hyphenated and Multidimensional Techniques*, eds. T. Provder, H. G. Barth, and M. W. Urban. New York: Oxford University Press, pp. 123–140.
- [5] Mourey, T. H. and S. T. Balke. (1993). A strategy for interpreting multi-detector size-exclusion chromatography data. I: Development of a systematic approach. In *Chromatography of Polymers: Characterization by SEC and FFF*, ed. T. Provder. Washington, D.C.: American Chemical Society, pp. 180–198.
- [6] Brun, Y., M. Gorenstein, and N. Hay. (2000). New approach to model fitting in multi-detector GPC. *J. Liq. Chromatog.* **23**, 2615–2639.
- [7] Cross, M. M. (1965). Rheology of non-Newtonian fluids: A new flow equation for pseudoplastic systems. *J. Colloid Sci.* **20**, 417–437.

- [8] Pedersen, S. and A. Ram. (1978). Prediction of rheological properties of well-characterized branched polyethylenes from the distribution of molecular weight and long chain branches. *Polym. Eng. Sci.* **18**, 990–995.
- [9] Tuminello, W. H. (1986). Molecular weight and molecular weight distribution from dynamic measurements of polymer melts. *Polym. Eng. Sci.* **26**, 1339–1347.
- [10] Lavallee, C. and A. Berker. (1997). More on the prediction of molecular weight distributions of linear polymers from their rheology. *J. Rheol.* **41**, 851–871.
- [11] Seavey, K. C., Y. A. Liu, N. P. Khare, T. Bremner, and C. C. Chen. (2003). Quantifying relationships among the molecular weight distribution, non-Newtonian shear viscosity, and melt index for linear polymers. *Ind. Eng. Chem. Res.* **42**, 5354–5362.
- [12] Tuminello, W. H., W. H. Buck, and D. L. Kerbow. (1993). Rheological molecular-weight distribution determinations of ethylene tetrafluoroethylene copolymers—Implications for long-chain branching. *Macromolecules* **26**, 499–503.
- [13] Santamaria, A. (1985). Influence of long-chain branching in melt rheology and processing of low-density polyethylene. *Mater. Chem. Phys.* **12**, 1–28.
- [14] Otocka, E. P., R. J. Roe, M. Y. Hellman, and P. M. Muglia. (1971). Distribution of long and short branches in low-density polyethylenes. *Macromolecules* **4**, 507.
- [15] deGroot, W. A. (1989). Applications of gel permeation chromatography coupled with a low-angle laser light-scattering detector to industrial polyethylene research. *J. Appl. Polym. Sci. Appl. Polym. Symp.* **43**, 85.