Molecular-weight distribution of polypropylenes by dynamic mechanical analysis

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ABSTRACT: One of the most important factors in determining the properties of polypropylenes is their molecular-weight distribution (MWD). The most popular method for determining MWD is size-exclusion chromatography (SEC); however, SEC on polyolefins can involve a number of potential problems. In contrast, a dynamic mechanical test (DMA), when done properly, alleviates these shortcomings without sacrificing a great deal of information. This paper reviews the two techniques and presents work that correlates DMA results with MWD of polypropylene homo- and copolymers.

KEYWORDS: Addition polymers, chemical analysis, chromatography, copolymers, dynamic tests, molecular weight distribution, polyhydrocarbons, polyolefins, polypropylene, test methods.

One of the key structural characteristics affecting the performance of polypropylenes is their molecular-weight distribution (MWD). During manufacture, the MWD can affect production rates and pellet size and shape. During processing, MWD will affect extruder torque or ram pressure, miscibility of additives, melt strength, and performance in finishing operations (draw ratio, neck-in, orientation, etc.). Finally, end-product performance, including flexibility from low to high temperatures, impact resistance, tensile properties, and even aging or weatherability, are a significant function of the MWD.

The current preferred method for estimating the MWD of polypropylenes is size-exclusion chromatography (SEC), using a high-temperature gel-permeation-chromatography (GPC) unit. Of course, there are a number of other polymer characteristics which can affect any or all of these performance areas, including:

- Tacticity (methyl sequencing)
- Functionality (grafting, oxidation, blending, copolymerization)
- Additives (stabilizers, processing aids).

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Although the SEC method is a powerful analytical tool, it is generally insensitive to these characteristics because it is purely a relative measure of molecular size distribution.

An alternative means of estimating MWD is melt rheology measurements. Certainly determination of the entire MWD curve from rheological measurements is a complex theoretical and mathematical exercise. However, through a basic understanding of the relationships between the MWD and resulting rheological behavior, considerable (and often sufficient) information about the MWD can be easily derived. In addition, because the rheology of a polymer system is a response not only of the MWD but also of the tacticity, functionality, and additive package, it can, in many cases, offer insights not apparent from an SEC test.

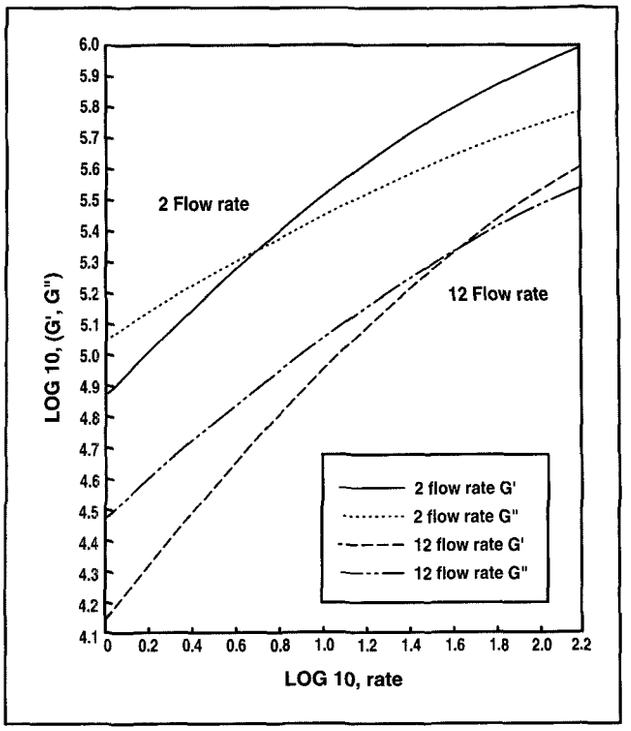
In this paper, I expand on a theory offering a simple relationship between melt rheology and molecular-weight averages *(1)* and compare the advantages and disadvantages of SEC versus rheology for measuring this property of polypropylenes.

Comparison of methods

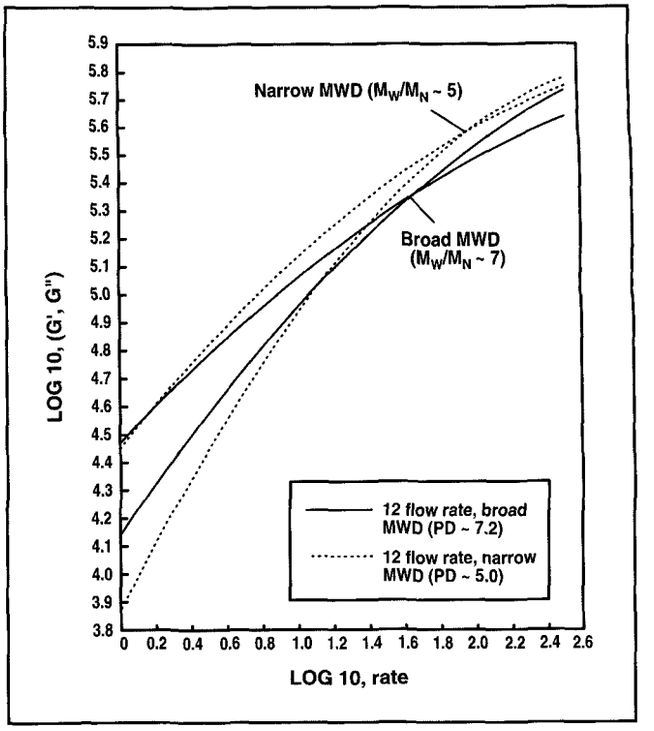
SEC

Size-exclusion chromatography is a special form of gel-permeation chromatography useful for estimating polymer molecular weights. Currently, the main commercially available GPC ap-

1. DMA frequency sweeps of polypropylene homopolymers



2. DMA frequency sweeps of 12-flow-rate samples



paratus capable of operating at the temperatures necessary to keep polymers in solution is the Waters 150C unit. The polymers are dissolved in a hot solvent, such as trichlorobenzene or o-dichlorobenzene at relatively low concentrations (approximately 0.1% weight per volume). For polypropylenes, the unit is generally maintained near its upper temperature specification of 150°C. The solutions are loaded into the machine as vials on a carousel, then an auto-injector system takes up a sample, which is pumped through the heart of the chromatography part of the system—the columns.

The columns used are packed gels of styrene-di-vinyl benzene, which are semiporous beads of varying nominal pore sizes ranging from several hundred to one million angstroms. Thus, the columns act as molecular sieves, and the smaller molecules are held up longer in the pores while the larger ones elute more quickly.

The final stage of the SEC apparatus is one or more detectors that respond to concentration changes (differential refractometer), viscosity changes (differential viscometer), or particle size (light scattering). Through calibration of the retention times and detector response using polymers of "known" MWD, the MWD of unknowns, relative to these standards, is obtained. With the combination of the concentration detector and either a viscometer or light-scattering detector, it also is possible to gather some information concerning the degree of branching and radius of gyration of the sample.

Thus, SEC is a very powerful analytical tool, and offers a means of directly assessing differences in molecular structure. These differences then can be related to performance differences. However, as with any analytical method, there are a number of potential pitfalls to be considered when assessing the utility of SEC as a laboratory method, particularly if it is to be used for quality assurance:

1. The equipment is expensive (about US$ 100,000 for a unit with data processing capabilities).
2. Operation at high temperatures for extended periods involves considerable maintenance costs for rebuilding pumps, valves, and injector parts.
3. The solvents used (chlorinated benzenes) are not suspected carcinogens, but they are considered toxic, with the potential for kidney and liver damage from long-term exposure. In addition, hot solvent burns are a possibility, since the solutions must be heated to about 150°C to effect dissolution of the polymer.
4. Continuous analysis of polypropylenes is hard on the columns, requiring frequent column re-

I. Comparison of test costs (based on 100 samples/month)

Expense	Annual Cost, US$ SEC	DMA
Maintenance and repairs	15,000	3,000
Columns	10,000	0
Solvent	3,000	0
Total	28,000	3,000

placement at a typical cost of approximately US$ 2000 per set.

5. The resulting MWD curves are highly dependent on the column configuration used; therefore, the results are best used in a comparative manner rather than as long-term, universally comparable data.
6. The molecular-weight averages are highly dependent on the choice of calibration standards.
7. Frequent calibration checks are required due to continual deterioration of the columns.
8. Samples that contain inorganic fillers or a high ash content should not be analyzed by SEC because these "contaminants" will quickly clog the column pores, resulting in partial or total loss of column effectiveness.
9. Analysis of the chromatograms requires operator selection of the appropriate baseline, which is often somewhat subjective, particularly in the low-molecular-weight region.

DMA

Dynamic mechanical analysis is a branch of rheology in which a sample is physically strained in a dynamic sine-wave fashion, and the resulting stress and phase angle are monitored. The results are mathematically transformed into storage or elastic modulus (G'), loss, or viscous modulus (G"), and loss tangent or tanΔ (G"/G') using a computer. The theory is beyond the scope of this paper *(2)*. There are a number of manufacturers of DMA equipment (Rheometrics, DuPont, Bolin, Monsanto, Polymer Laboratories, Seiko, to mention a few), and prices range from about US$ 50,000 up to US$ 250,000, depending on the capabilities and options. The unit used in this study is an older model Rheometrics RMS-7200 which has been upgraded to use a personal computer to control the instrument, acquire the data, perform the calculations, and generate the results in tabular or graphic formats.

In contrast to SEC, there is very little routine maintenance due to wear of parts, so maintenance and upkeep costs are considerably lower. In addition, the modulus results are an absolute, not a relative value, they do not require operator intervention, and the only machine calibration required is an occasional check to ensure the transducer and temperature controllers are in good working condition. A comparison of advantages and disadvantages from upkeep and cost perspectives is made in **Table I**.

Relationship between MWD and DMA curves

There are a number of references relating the rheological response of polymers to their molecular-weight distributions *(3–8)*, and they generally employ rather elegant mathematical models and theoretical considerations of polymer geometry. However, in this work, the complications of a universally applicable mathematical model were not an issue since our purpose was to correlate rheology with MWD for a homogenous polymer family: polypropylenes.

Reference 1 presents a rather simple relationship relating MWD to the results from a single DMA experiment, specifically the crossover point. The crossover point is where the two moduli (G' and G") cross each other when a DMA frequency sweep is performed at constant temperature. If we examine the differences in the G' and G" curves for several different MWD polypropylene samples, we can understand how the magnitude of the moduli and the frequency at which the crossover point occurs should be a relatively unique combination for polypropylene samples of varying MWD.

Figure 1 compares these plots for a higher-molecular-weight (2 flow rate) versus lower-molecular-weight (12 flow rate) polypropylene sample, while **Fig. 2** compares two 12-flow-rate samples that were made differently, resulting in different polydispersity. Therefore, the approach was taken to evaluate a number of varying MWD polypropylene homopolymers and to use computer modeling techniques to empirically develop a mathematical model to relate the crossover points to the MWD values.

Experimental

The MWD was obtained using the SEC method described above, at the following experimental conditions: 30 mg of the pelletized polypropylene samples were dissolved in 40 mL of o-dichlorobenzene by refluxing (at approximately 180°C) for 15 minutes. The solutions then were prefiltered through a hot, glass filter pad to reduce possible contaminants.

The SEC runs were done on a Waters 150C unit at 145°C, an injection volume of 250 mL, and a flow rate of 1.2 mL/min. The column set consisted of three Waters Microstyragel HT-Linear mixed bed columns, and the standard differential refractometer detector was used. A single broad polypropylene standard (obtained from American Polymer Standards), with M_w = 267,000 and M_n = 43,000, was used for calibration. The data acquisition, calibration routine, and MWD calculations were done using Waters' Expert-Ease 845 software system on a VaxStation 2000.

Two injections of each sample were taken, and the raw chromatogram data was averaged for the two injections prior to analysis. Results are reported as the M_n (number-average molecular weight), M_w (weight-average molecular weight), M_z (z-average molecular weight), and M_w/M_n (polydispersity index).

DMA testing was done on a Rheometrics rotational mechanical spectrometer, model RMS-7200, in the frequency sweep mode, with a cone and plate fixture at 180°C and 15% strain. The machine control and data acquisition and calculations were done using a PC-retrofit from Advanced Instrumentation Concepts. The resulting G' and G" curves were transferred into a VAX mainframe and the Log (modulus) versus Log (frequency) plots were fit with quadratic equations using a RS-1 sci-

II. DMA and SEC results on polypropylene homopolymers

Flow rate	Log10 XFREQ	Log10 XMOD	SEC M_w	SEC M_n	SEC M_z	SEC M_w/M_n	Predicted from RMS M_w	Predicted from RMS M_n	Predicted from RMS M_z	Predicted from RMS M_w/M_n
6.2	1.2350	5.3561	309,600	48,900	857,600	6.3	307,871	50,150	868,498	6.1
19.6	2.3560	5.6952	217,200	48,600	509,900	4.5	205,556	55,643	445,722	3.7
35.1	2.4044	5.7034	191,400	56,500	400,800	3.4	201,361	55,867	437,527	3.6
33.9	2.3623	5.6248	210,600	45,400	530,400	4.6	204,456	44,578	488,073	4.6
1.37	0.4643	5.3335	487,400	95,000	1,201,000	5.1	440,310	61,531	118,9213	7.2
32.6	2.4644	5.6773	195,900	47,400	431,300	4.1	197,475	50,139	450,107	3.9
1.11	0.3147	5.3226	470,500	79,400	1,250,000	5.9	466,504	62,558	1,270,396	7.5
19.7	2.0524	5.5405	226,500	40,600	585,200	5.6	228,339	42,069	571,512	5.4
13.1	1.9172	5.5775	252,300	49,800	592,700	5.1	247,802	49,722	569,560	5.0
2.35	0.6933	5.3329	395,400	61,600	1,066,000	6.4	398,748	59,837	1,084,902	6.7
19.2	2.3095	5.7409	211,700	63,500	426,500	3.3	203,540	63,464	421,454	3.2

entific software package. The values of the frequency and modulus at the crossover points then were determined by successive approximations using the quadratic equations.

Flow-rate testing was done following American Society for Testing and Materials Procedure D-1238, condition "L" (230°C, 2.16 kg load).

Results

Table II lists the samples evaluated, as well as the resulting SEC, DMA, and flow-rate data. This data was analyzed using the RS-1's multiple regression modeling routines, and the number of parameters was minimized through statistical analysis of variance methods. The resulting models and correlation coefficients are shown in **Table III**. The goodness of fit for the M_n, M_w, M_z, M_w/M_n, and flow rate (predicted from the DMA crossover point versus the observed values) is good.

A second data set, which included random ethylene copolymers, was analyzed in a similar fashion. In this case, the percent ethylene was determined by a proprietary Fourier transform infrared technique, and the percent ethylene was included in the model as an independent variable. Again, the goodness of fit was quite good for the M_w, M_z, and flow rate, and acceptable for the M_n and polydispersity index. Several samples with very high (greater than 5%) levels of ethylene had to be dropped to achieve a good fit.

III. Statistical models

Model	Term	Coefficient	R^2
M_w	1	–2.777 E+7	0.9989
	XF	–1.716 E+6	
	XM	1.063 E+7	
	XF X XM	2.878 E+5	
	XM^2	–9.983 E+5	
M_n	1	6.107 E+5	0.9315
	XF	–5.737 E+5	
	XM	–1.032 E+5	
	XF X XM	1.094 E+5	
	XF^2	–1.514 E+4	
M_z	1	4.681 E+6	0.9941
	XF	–5.827 E+5	
	XM	–6.083 E+5	
	XF^2	1.085 E+5	
Flow rate	1	3.661 E+2	0.9646
	XF	–1.871 E+1	
	XM	–6.744 E+1	
	XF^2	1.592 E+1	

Table IV compares the statistical deviation of the MWD numbers based on a long-term comparison of the SEC versus the DMA method for a single sample. This illustrates that the DMA technique is at least as accurate as the SEC method.

Conclusions

The DMA method offers a quick and reliable alternative for estimating the M_n, M_w, M_z, polydispersity, and flow rate of polypropylenes. We have found this model to be useful for estimating

IV. Statistical comparison of SEC versus DMA

Method SPC standard	SEC 267,000 PP LCL	SEC 267,000 PP UCL	DMA, 12-Flow-rate PP LCL	DMA, 12-Flow-rate PP UCL
M_w/1000	239	305	244	261
M_n/1000	37.4	50.6	39.5	44.3
M_z/1000	NA	NA	678	804
M_w/M_n	5.4	7.2	5.9	6.2
Flow rate	NA	NA	11.8	15.6

PP = polypropylene

these properties of filled samples, which one would be reluctant to deposit on the SEC columns. It offers advantages over SEC with respect to elimination of solvents, less maintenance and upkeep expense, and results that are not dependent on operator baseline selection or choice of columns. In addition, this method offers the potential for on-line analysis, and there are already several on-line rheological analyzers on the market. To the best of my knowledge, there is not yet an on-line method capable of doing SEC on polypropylenes.

Thus, although size-exclusion chromatography is a very powerful method for observing subtle differences in molecular size distribution, it appears that dynamic mechanical analysis is a suitable alternative with significant practical advantages.

Literature cited

1. Zeichner, G. R. and Patel, P. D., *Proceedings of the 2nd World Congress on Chemical Engineering*, Vol. 6, 1981, p. 333.
2. Ferry, J. D., *Viscoelastic Properties of Polymers*, 3rd edn., John Wiley & Sons, New York, 1980.
3. Rahalkar, R. R., *Rheological Acta.* 28(2): 166–175(1989).
4. Tuminello, W. H., Cudre-Mauroux, N., and McGrory, W. J., *SPC-Antec Proceedings*, 1990.
5. Wu, S., *Polymer Engineering & Sci.* 25(2):(1985).
6. McGrory, W. J. and Tuminello, W. H., *J. of Rheology* 34(6): 867(1990).
7. Pearson, G. H. and Garfield, L. J., *Polymer Engineering & Sci.* 18(5): 583(1978).
8. Minoshima, W., White, J. L., and Spruiell, J. E., *Polymer Engineering & Sci.* 20(17):(1980).

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