

## Dynamic Mechanical Measurement of $\bar{M}_n$ \*

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### I. INTRODUCTION

The number-average molecular weight  $\bar{M}_n$  of a linear soluble polymer is normally estimated from the measurement of the colligative properties of its dilute solutions. The limitations of these methods have been thoroughly discussed.<sup>1</sup> For unfractionated materials, the osmotic methods are in general inapplicable because the lowest molecular weight species, which in large part determine the  $\bar{M}_n$ , diffuse through the membrane. As a result, the  $\bar{M}_n$  of unfractionated materials is usually overestimated.

The  $\bar{M}_n$  measured in dilute solution is also not necessarily the effective one in the bulk solid.<sup>2</sup> It is therefore desirable to have a means of measuring the  $\bar{M}_n$  in the solid state upon which the mechanical properties are also measured. In the present attempt to find a method for the simultaneous measurement of mechanical properties and  $\bar{M}_n$ , the dynamic torsion pendulum was the instrument of choice. This instrument has been previously described.<sup>3</sup>

### II. EXPERIMENTAL

Polystyrene fractions<sup>4</sup> and whole polymers of polystyrene prepared with a variety of catalysts were used as test materials. Characterization data are summarized in Table I. The  $\bar{M}_n$  were measured with an osmometer, or, for whole polymers, were calculated from the molecular weight distribution curves based on at least 15 fractions.

Materials 7, 8, and 9 in Table I were prepared by mixing a sharp fraction, ( $\bar{M}_v = 1,200,000$ ) with an equal weight of a fraction of lower molecular weight. The mixtures were made in dilute benzene solution and the mixed polymer recovered by freeze-drying.

The dynamic mechanical damping, as measured by the logarithmic decrement  $\delta$ , was obtained in the normal fashion.<sup>2,3</sup> With material 10, however, prolonged residence above the glass temperature permitted crystallization which would vitiate the measurements. A fresh sample was therefore measured at each test temperature, and the composite data used to construct the  $\delta$  vs.  $T$  curve.

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TABLE I  
Characterization Data on the Test Materials

Material	$\bar{M}_v \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_v/\bar{M}_n$	Dynamic $\bar{M}_n \times 10^{-3}$ (calc.)	Dynamic $\bar{M}_v/\bar{M}_n$ (calc.)
1	1,200	1,100	1.10	Used as standards	
2	306	278	1.10		
3	392	87	4.5		
4 <sup>a</sup>	223	243 <sup>b</sup>	1.02 <sup>b</sup>	220	1.2
5	364	304	1.20	400	1.7
6	350	100	3.50	90	3.20
7 <sup>c</sup>	262	199	1.32	141	1.65
8 <sup>c</sup>	633	418	1.51	340	1.0
9 <sup>c</sup>	539	138	3.90	215	3.35
10 <sup>d</sup>	620	129	4.8	149	4.2

<sup>a</sup> Data kindly supplied by Dr. A. S. Kenyon, Monsanto R & E Div.

<sup>b</sup>  $\bar{M}_w/\bar{M}_n$  directly by sedimentation.

<sup>c</sup> Mixtures of two fractions.

<sup>d</sup> Isotactic.

### III. RESULTS

Figure 1 shows the  $\delta$  vs.  $T$  curves above  $T_g$  for all the materials except the mixtures. Only enough points to identify the curves are shown. Figure 2 shows a plot of the minimum value of the logarithmic decrement  $\delta_m$  against  $\bar{M}_n$  for materials 1, 2, and 3; this defines the equation

$$\bar{M}_n = \delta_m^{-1.9} \times 10^5 \quad (1)$$

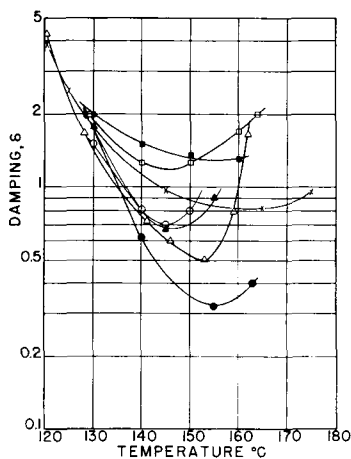


Fig. 1. Dynamic mechanical dissipation factor vs. temperature for various materials: (●) material 1; (▲) material 2; (■) material 3; (○) material 4; (△) material 5; (□) material 6; (×) material 10.

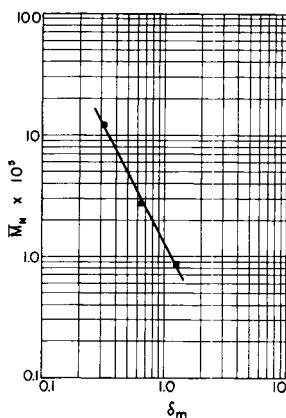


Fig. 2. Number-average molecular weight vs. dynamic mechanical dissipation factor; symbols as for Fig. 1.

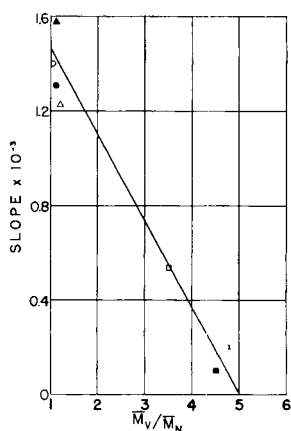


Fig. 3. Slope of  $\delta$  vs.  $(\Delta T)^2$  lines plotted against  $\bar{M}_v/\bar{M}_n$ ; symbols as for Fig. 1.

The  $\bar{M}_n$  calculated by means of eq. (1) are given in Table I. When  $\delta$  is plotted against  $(\Delta T)^2$ , where  $\Delta T$  is defined as the difference in temperature between  $\delta$  and  $\delta_m$ , with the  $\delta$  chosen to lie between  $T_g$  and the temperature of  $\delta_m$ , a straight line results. Figure 3 is a plot of the slope of such lines versus the  $\bar{M}_v/\bar{M}_n$  ratio. The equation of this line is

$$\bar{M}_v/\bar{M}_n = 5.0 - 6.9 \log (\delta_{m-20}/\delta_m) \quad (2)$$

where  $\delta_{m-20}$  is the  $\delta$  at temperature 20°C. lower than that of  $\delta_m$ .

Calculations from eq. (2) are listed in Table I.

## IV. DISCUSSION

The accuracy of the predictions from eq. (1) is fairly good for sharp fractions and for polydisperse materials having continuous distribution curves of molecular weight. It is better than the results of the measurements of a single sample among different laboratories ( $\pm 25\%$ ).<sup>5</sup> It cannot be better than the accuracy of the osmotic measurements upon which the correlation is based (ca.  $\pm 10\%$ ). For materials 7, 8, and 9, which have two-peaked distributions, the predictions of eq. (1) are not as accurate. Presumably the viscoelastic response to dynamic stress as a function of temperature is not simply related to the  $\bar{M}_n$  of the mixture. Nimomiya<sup>6</sup> has shown the complexity of the molecular weight dependence of the dynamic mechanical properties of such mixtures.

The error of the predictions from eq. (2) is larger than  $\pm 10\%$ , which reflects the uncertainties in measuring both molecular weights. Equation (2) will permit a conclusion as to whether the test polystyrene is "sharp" or "broad," and probably more than this should be not claimed for it yet.

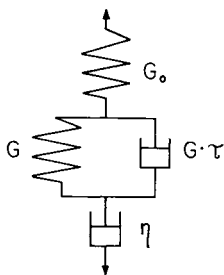


Fig. 4. Four-parameter model, see text.

The predictions of both equations become poorer as the  $\bar{M}_v$  approaches 200,000. The flow of the sample above  $T_g$  becomes too great for precise measurement of  $\delta$ .

In order to indicate that a relationship between  $\delta_m$  and molecular weight has a basis in linear viscoelastic theory, the response to sinusoidal stress of the model pictured in Figure 4 was calculated as a function of temperature. For this model, which has been thoroughly analyzed in the literature,<sup>7</sup> the dynamic compliances are

$$\begin{aligned} J'(\omega) &= (1/G_0) + (1/G)(1/1 + \omega^2\tau^2) \\ J''(\omega) &= (1/\omega\eta) + (1/G)(\omega\tau/1 + \omega^2\tau^2) \end{aligned} \quad (3)$$

$J'$  and  $J''$  were evaluated at  $\omega = 1$  for different molecular weights  $M$  over a range of temperatures. The modulus  $G_0$  was taken to be  $10^{13}$  dynes/cm.<sup>2</sup>, independent of temperature and  $M$ . The Voigt element modulus  $G$  was assumed to have the constant value of  $10^7$  dynes/cm.<sup>2</sup>. The retardation time  $\tau$  of the Voigt element dashpot was arbitrarily assumed to be 10 sec. at  $100^\circ\text{C}$ ., and the viscosity of the Voigt element dashpot was assumed

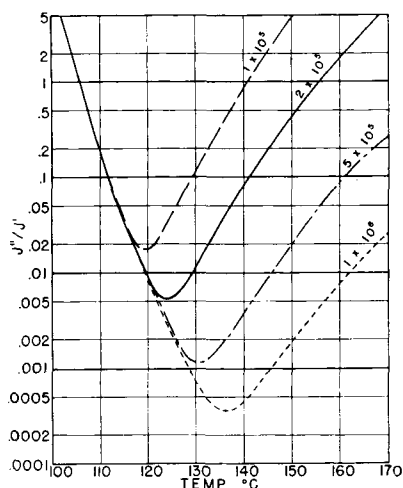


Fig. 5. Calculated dissipation factor vs. temperature curves as a function of molecular weight.

to vary with temperature in accordance with the Williams-Landel-Ferry equation.<sup>8</sup> The viscosity  $\eta$  of the independent dashpot was assumed to have a 3.4 power dependence upon  $M$ , as reported for polystyrene by Fox and Flory<sup>9</sup> and the temperature variation of  $\eta$  was calculated again from the Williams-Landel-Ferry equation.

The results of the calculation are shown in Figure 5, where the logarithm of  $J''/J'$  is plotted against temperature for four molecular weights. ( $J''/J'$  is proportional to the  $\delta$ .) The molecular weights are related to the  $J''/J'$  values at the minimum by an expression of the form of eq. (1) but, of course, with different numerical constants.

Further calculations for a broader spectrum of retardation times and more experimental dynamic mechanical data on carefully purified and characterized polystyrenes would be required before the full potential of this method could be unambiguously assessed.

## References

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### Synopsis

A procedure is described for the measurement of number-average molecular weight  $\bar{M}_n$  on a specimen in bulk form, utilizing a dynamic torsion pendulum. For both atactic and isotactic polystyrenes it has been found that the minimum value of the damping logarithmic decrement,  $\delta_m$ , (above the glass temperature) is related to  $\bar{M}_n$  measured osmotically in dilute solution by  $\bar{M}_n = \delta_m^{-1.9} \times 10^5$ . The  $\bar{M}_v/\bar{M}_n$  ratio can also be estimated directly from the  $\delta$  vs. temperature curve. A four-element spring-and-dashpot model yields similar  $\delta$  vs.  $T$  curves when the Williams-Landel-Ferry temperature dependence is assigned to the viscosity of the dashpots.

### Résumé

La procédé décrit ici se rapporte à la détermination du poids moléculaire moyen en nombre,  $\bar{M}_n$ , d'un échantillon préparé en bloc; il utilise un pendule dynamique de torsion. On a montré que dans le cas du polystyrène atactique aussi bien que le polystyrène isotactique la valeur minimum du décrement logarithmique  $\delta_m$  (au-dessus de la température de transition vitreuse) est reliée au  $\bar{M}_n$ , mesuré osmométriquement en solution diluée par  $\bar{M}_n = (\delta_m)^{-1.9} \times 10^5$ . Le rapport  $\bar{M}_v/\bar{M}_n$  peut être estimé directement à partir des courbes  $\delta$  vs. température. Un modèle comprenant un ressort à quatre éléments et un amortisseur donne des courbes  $\delta$  vs.  $T$  similaires lorsque la dépendance de température Williams-Landel-Ferry est attribuée à la viscosité des amortisseurs.

### Zusammenfassung

Das hier beschriebene Verfahren dient zur Messung des Zahlenmittels des Molekulargewichts,  $\bar{M}_n$ , an einer Probe in fester Substanz mittels eines dynamischen Torsionspendels. Für ataktische sowohl als auch isotaktische Polystyrole wurde gefunden, dass der Wert des Minimums für das logarithmische Dekrement der Dämpfung,  $\delta_m$ , (oberhalb der Glastemperatur) mit dem osmotisch in verdünnter Lösung gemessenem  $\bar{M}_n$  durch die Beziehung  $\bar{M}_n = (\delta_m)^{-1.9} \times 10^5$  verknüpft ist. Das Verhältnis  $\bar{M}_v/\bar{M}_n$  kann ebenfalls direkt aus der Kurve  $\delta$  gegen Temperatur bestimmt werden. Ein Feder-Reibungsmodell aus vier Elementen ergibt ähnliche  $\delta$  gegen  $T$ -Kurven, wenn man der Viskosität der Reibungselemente eine Williams-Landel-Ferry-Temperaturabhängigkeit zuschreibt.

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