

## Solution Viscosity-Molecular Weight Relationship for Polystyrene

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### Synopsis

The 10% solution viscosity has been used extensively as a measure of molecular weight for the commercial production of polystyrene. Recently, poor correlations have been observed between 10% solution viscosity and molecular weight as measured by gel permeation chromatography. Lowering the concentration improves the correlation. At 0.2%, the log-log plot of viscosity versus molecular weight becomes linear.

### INTRODUCTION

Recent work in these laboratories and elsewhere<sup>1</sup> has shown that the 10% solution viscosity of polystyrene does not correlate as well as might be expected to molecular weight determined by gel permeation chromatography (GPC), particularly in the molecular weight range of most commercial products. Since solution viscosity is frequently used as a measure of molecular weight in industrial processes, it seems pertinent to determine viscosity as a function of solution concentration and attempt to correlate with the average molecular weight as measured by GPC.

### EXPERIMENTAL

Solution viscosities were determined in toluene at 25°C for a range of commercial, crystal polystyrenes using suitably selected Cannon-Fenske viscometers.

A Waters Associates Model 200 gel permeation chromatograph was used to determine the molecular weight of the samples. The instrument was fitted with four columns of nominal permeability limits  $10^2$ ,  $10^3$ ,  $3 \times 10^4$ , and  $10^5$  Å, and the eluting solvent was trichlorobenzene at 130°C. The average weight of sample injected, as a 0.25% w/w solution, was 0.25 mg. The instrument was calibrated with the commonly used anionic polystyrenes of known molecular weight. The experimental chromatograms were converted to molecular weight distributions but were not corrected for instrument spreading.

The classification of the samples as determined by GPC is listed in Table I, and their 10% solution viscosities are plotted as a function of average molecular weight in Figure 1. The experimental points are indi-

TABLE I  
Molecular Weight as Determined by GPC

Sample	$\bar{M}_w \times 10^{-3}$	$\bar{M}_w / \bar{M}_n$
1	160	2.6
2	130	2.4
3	240	3.0
4	200	2.5
5	290	2.3
6	300	2.7
7	280	4.8
8	360	3.0
9	110	2.7
10	230	2.6
11	350	2.9
12	210	2.8
13	200	2.7
14	260	2.4
15	180	3.1
16	210	2.4

cated by the sample number for ease of identification. Keskkula and Taylor<sup>1</sup> found that the plot was composed of two distinct straight line portions intersecting at a molecular weight of 260,000. Both these lines and a straight line representing the best fit to the present results are drawn in Figure 1. In both cases considerable scatter is observed.

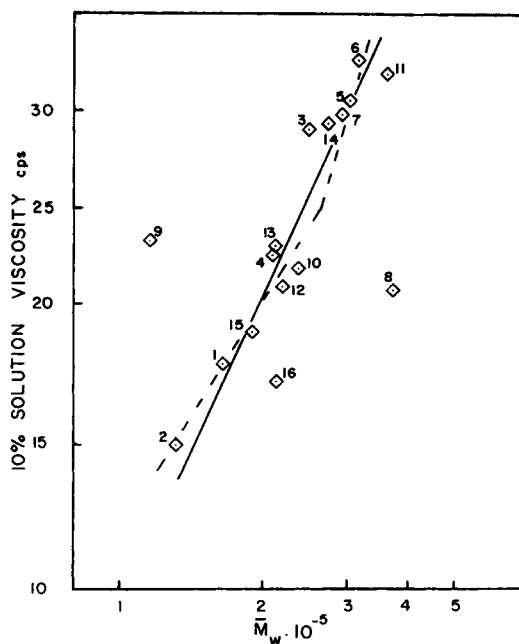


Fig. 1. Plot of viscosity versus molecular weight for 10% polystyrene solutions of the 16 samples listed in Table I.

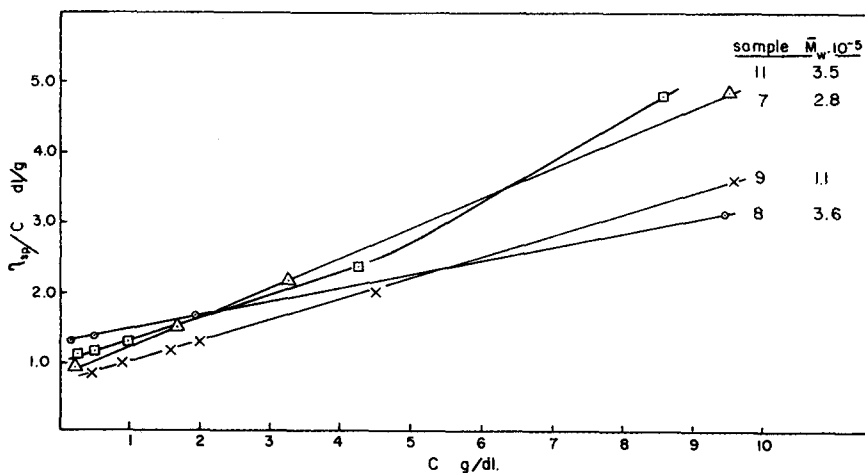


Fig. 2. Plot of viscosity number,  $\eta_{sp}/C$ , versus concentration of samples 7, 8, 9, and 11 listed in Table I.

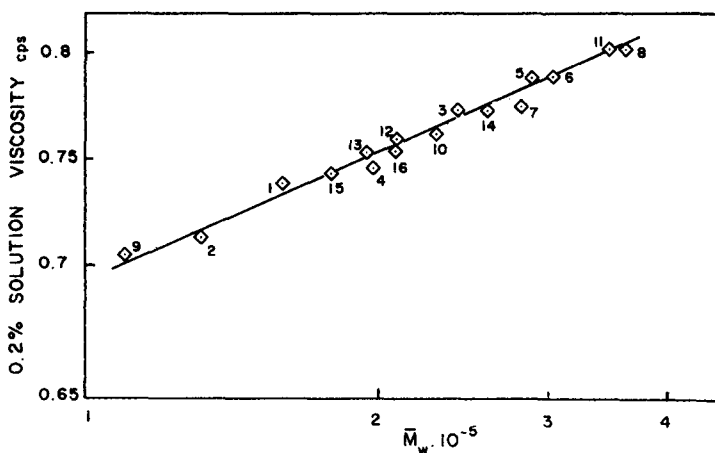


Fig. 3. Plot of viscosity versus molecular weight for 0.2% polystyrene solutions of the 16 samples listed in Table I.

When the viscosity number,  $\eta_{sp}/C$ , which expresses the average contribution of the solute molecules at concentration  $C$  to the viscosity,<sup>2</sup> is plotted as a function of  $C$ , crossover is evident as the molecular weight of the sample changes (Fig. 2). Keskkula and Taylor<sup>1</sup> suggested that chain entanglements were occurring in 10% solutions; but, whatever the nature of the interactions, it is evident from Figure 2 that they might occur at concentrations as low as 1%. As the solution concentration is further reduced, the plots of viscosity number versus concentration appear to align themselves in the expected order. In the present set of experiments,

a good correlation between solution viscosity and  $\bar{M}_w$  was found when the concentration was reduced to 0.2% w/w (Fig. 3).

In summary, it is evident that structural effects occur in concentrated polystyrene solutions that influence viscosity measurements. In order to use solution viscosity as an analytical measure of molecular weight, it is recommended that a lower concentration than has been customary in the past be used. The present results show that 0.2% w/w solutions would be suitable.

### References

1. H. Keskkula and W. C. Taylor, *J. Polym. Sci.*, in press.
2. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, Interscience, New York, 1965, Section IV-I.

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