

Variation of Refractive Index of Polystyrene with Molecular Weight: Effect on the Determination of Molecular Weight Distributions

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Synopsis

Sensitive refractive index measurements on solutions have indicated that the narrow molecular weight polystyrene samples prepared by the Mellon Institute method exhibit a small systematic molecular weight-refractive index dependence up to 300,000 and higher. This upper limit is higher than had previously been suggested. Sensible consistency is generally assumed above a few thousand molecular weight. The effect on this molecular weight-refractive index dependence on gel permeation chromatography and light-scattering molecular weight measurements on polystyrene standards is illustrated.

The relationship between molecular weight and refractive index of a polymer is generally assumed to be a constant, independent of molecular weight for molecular weights above a few thousand. While this assumption is true in a general sense when refractive index is measured by Abbé, Pulfricht, and dipping refractometers, it is possible that a small systematic change may continue into the middle molecular weight range. Changes in the constant below molecular weight 4000 have been reported by several workers for poly(ethylene oxide)¹⁻³ and *p*-oligophenylenes.⁴ However, small changes in the refractive index-molecular weight constant in the middle molecular weight range would affect molecular weights calculated from light-scattering measurements. Errors would be induced in molecular weight distributions calculated from gel permeation chromatographic (GPC) data by a change in the constant with molecular weight since the weight of polymer eluting at any time is customarily determined by automatic, highly sensitive differential refractometry.

Therefore, measurement of the differential refractive index of ten narrow molecular weight samples of polystyrene in two solvents, methyl ethyl ketone and toluene, have been carried out. The styrene samples were chosen because of their general importance in the calibration of molecular weight measuring methods.

EXPERIMENTAL

Instrumentation

The differential refractive indexes of the polymer solutions were measured at 25°C. with a Phoenix Precision Instrument Company B-S differential refractometer. The instrument was thermostated to $\pm 0.1^\circ\text{C}$. using a circulating water thermostat. Samples were equilibrated in the refractometer cell for 15 min. prior to measurement. Six sets of measurement were made on each sample. The instrument constant was determined with 12 data points daily. Measurements of each sample were made at 4360 and 5460 Å. with the use of interference filters to obtain pure spectral lines from a mercury vapor lamp.

Samples

The polystyrene samples were obtained from Pressure Chemical Company, Pittsburgh, Pennsylvania. The manufacturer stated that these samples were made by using the techniques developed at the Mellon Institute and reported by Altares⁵ and Wyman.⁶ These are narrow molecular weight distribution samples as can be seen in Table I.

TABLE I
Polystyrene Molecular Weight Standards

Weight-average molecular weight	Weight-average/ number-average molecular weight
2,030	1.10
4,800	1.10
10,300	1.06
19,800	1.06
51,000	1.06
97,200	1.06
498,000	1.20
600,000	1.20
860,000	1.15
1,800,000	1.20

Exactly 1.00000 ± 0.00005 g. of polymer sample was weighed into a 50-ml. new volumetric flask. The sample was dissolved at 50°C. in 20 ml. of Baker Chemical Company reagent-grade toluene or methyl ethyl ketone (MEK) under a nitrogen blanket.

Upon complete dissolution of the sample, the solution was diluted with solvent at 25°C. to 50 ml. The solvent had previously been deaerated by passing a stream of nitrogen gas through the solvent storage flask for 15 min. The diluted sample was measured in the differential refractometer versus a portion of the pure solvent within 24 hr. of final dilution. The foregoing treatment was regarded as necessary to avoid atmospheric oxidation of the unstabilized polymer.

Results and Discussion

The refractive index-molecular weight relationships for polystyrene in toluene and MEK are shown in Figures 1 and 2. The toluene curve shows a relatively sharp dependence between refractive index and molecular weight up to 20,000 molecular weight. The value does not become sensibly constant until 300,000. In MEK, the refractive index-molecular weight relationship is not constant at 1,800,000 molecular weight.

The effect of molecular weight on the refractive index difference of poly(ethylene oxide) has received by far the greatest attention as compared to other polymers. Rempp² has reported results obtained both by Pulfricht refractometer and Zeiss Interferometer. The data show a 1% change in the refractive index difference from 1000 to 10,000 molecular weight. Heller and Pugh³ repeated the experiments in connection with another

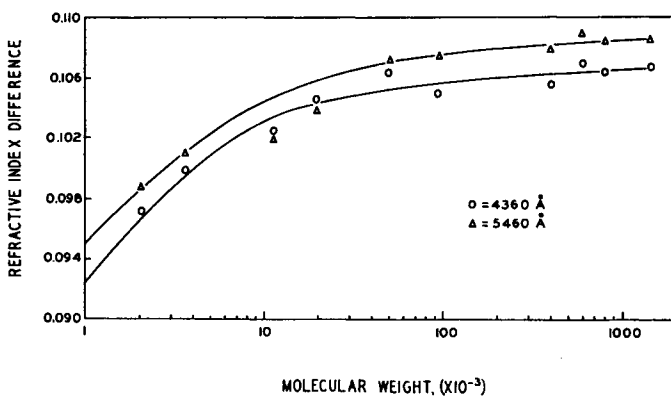


Fig. 1. Effect of molecular weight on toluene-polystyrene solution refractive index difference.

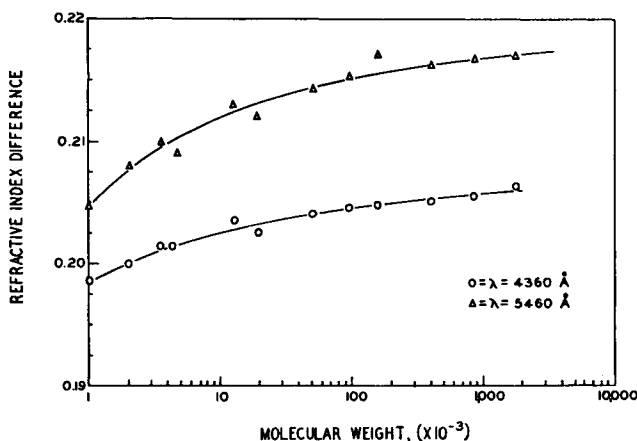


Fig. 2. Effect of molecular weight on MEK-polystyrene solution refractive index difference.

study, using a dipping refractometer. Although lacking in sensitivity, the two sets of results are roughly comparable. These workers concluded that significant molecular weight dependence vanished around 4000 molecular weight. Ingham and Lawson¹ using molten poly(ethylene oxide) found that the molecular weight refractive index relationship became essentially constant at 20,000 molecular weight.

Ziegler et al.⁴ have shown that the refractive index becomes constant by molecular weight 1000 for the poly (*p*-oligophenylene). This is to be expected since the phenyl ring connected in the *para* position is the only functional unit of the polymer. The phenyl at the chain end is only slightly different from a phenyl at midchain.

Therefore, it appears that the narrow molecular weight fractions of polystyrene prepared by the Mellon Institute method possess sufficient poly-functionality to cause the refractive index to depend on molecular weight at far heavier weights than heretofore experienced with other polymers. This proposed functionality is probably located not only at chain ends but also within the polymer. If chain end location of the dissimilar functionality were the case, styrene should behave more like poly(ethylene oxide) with respect to refractive index constant. The unusual molecular weight-refractive index dependence may be due to a nonstyrene moiety incorporated into the polymer during synthesis.

Whatever the origin of the dependence, its presence has been demonstrated in samples which are routinely used for molecular weight calibrations.

Effects on Molecular Weight and Molecular Weight Distribution

Table II shows the effect of using the actual refractive index difference versus a single high molecular weight difference on weight-average molecular weights measured by light scattering. The differences range from 1% at 500,000 to 12% at 5000.

TABLE II
Effect of Molecular Weight Dependence of Refractive
Index Increment Upon Weight-Average Molecular
Weight From Light Scattering

Uncorrected \bar{M}_w	Corrected \bar{M}_w
500,000	505,000
100,000	102,000
50,000	51,500
10,000	10,800
5,000	5,600

Table III illustrates the change on gel permeation chromatography results with the change in refractive index difference. The \bar{M}_n differ by about 12%, significantly changing the calculated inhomogeneity.

TABLE III
Effect of Molecular Weight Dependence of Refractive
Index Increment Upon Molecular Weight Distribution by GPC

	\bar{M}_n	\bar{M}_w	\bar{M}_z	$(\bar{M}_w/\bar{M}_n) - 1$
Uncorrected	6100	10,400	15,800	0.69
Corrected	5400	10,000	15,600	0.83

The calculations in Tables II and III assume that the refractive index increment is independent of concentration. In the usual equation to account for concentration dependence

$$\Delta n/C = A + BC$$

where Δn is the refractive index difference between a solution of concentration C (in grams/milliliter) and the solvent and A and B are constants, B is customarily assumed to be zero at concentrations below 0.03 g./ml.⁷ All measurements in this study were made at concentrations of 0.02 g./ml. This would indicate that the assumption of concentration independence is a valid one.

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