

NOTE

The Refractive Index Increment for Poly- α -Methylstyrene at 633 nm in Tetrahydrofuran

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Poly- α -methylstyrene (P- α MS), while not as extensively studied as polystyrene, has been the subject of numerous investigations. Different methods of polymerization have been examined, for example, anionic^{1,2} and free radical³ polymerization, and the system has been a model for study of polymerization thermodynamics because of its relatively low ceiling temperature. The physical properties of P- α MS have also been the subject of considerable study; for example, intrinsic viscosities,¹ sedimentation coefficients,⁴ and second virial parameters⁵ have all been evaluated.

A number of previous studies have included determinations of the refractive index increment (dn/dc) for P- α MS in a variety of solvents. Most of the determinations have been made as a necessary adjunct to the assessments of molecular weight averages using light scattering techniques. Values obtained previously are presented in Table I. It is apparent that there is a variation in the value of dn/dc , depending on the solvent used and the wavelength of measurement (it should also be noted that some of the previous studies indicate a variation in dn/dc values with temperature⁵).

At the onset of our study of copolymerization reactions involving α MS, it was noted that the dn/dc value was not available in tetrahydrofuran (THF) for P- α MS at 633 nm. For molecular weight average measurements, our laboratories utilize room temperature (25°C) gel permeation chromatography (GPC) that uses

Table I Refractive Index Increments for Poly α -Methylstyrene

| Solvent | Wavelength (nm) | dn/dc (ml/g) | Reference |
|----------------------|-----------------|----------------|-----------|
| Toluene | 546 | 0.129 | 1 |
| Toluene | ? | 0.131 | 2 |
| Benzene | 436 | 0.134 | 4 |
| Cyclohexane | 436 | 0.200 | 4 |
| Cyclohexane | 436 | 0.206 | 5 |
| Benzene | 546 | 0.138 | 6 |
| Benzene | 436 | 0.124 | 7 |
| Cyclohexane | 436 | 0.197 | 7 |
| Toluene | 436 | 0.131 | 7 |
| Ethylene dichloride | 436 | 0.176 | 7 |
| Cyclohexane | 546 | 0.192 | 8 |
| Cyclohexane | 436 | 0.204 | 8 |
| Cyclohexane | 366 | 0.219 | 8 |
| Toluene | 546 | 0.126 | 8 |
| Toluene | 436 | 0.130 | 8 |
| Toluene | 366 | 0.135 | 8 |
| Carbon tetrachloride | 546 | 0.168 | 8 |
| Carbon tetrachloride | 436 | 0.178 | 8 |
| Carbon tetrachloride | 366 | 0.193 | 8 |

THF as the solvent. The detectors within the GPC system are a Dawn multi-angle laser light scattering (MALLS) detector with a He-Ne laser operating at 633 nm in series with a Waters DRI detector. The Astra software package for molecular weight analysis (Wyatt Technology) uses dn/dc values as a key parameter to calculate molecular weights. The variation in dn/dc values for P- α MS with respect to solvent and wave-

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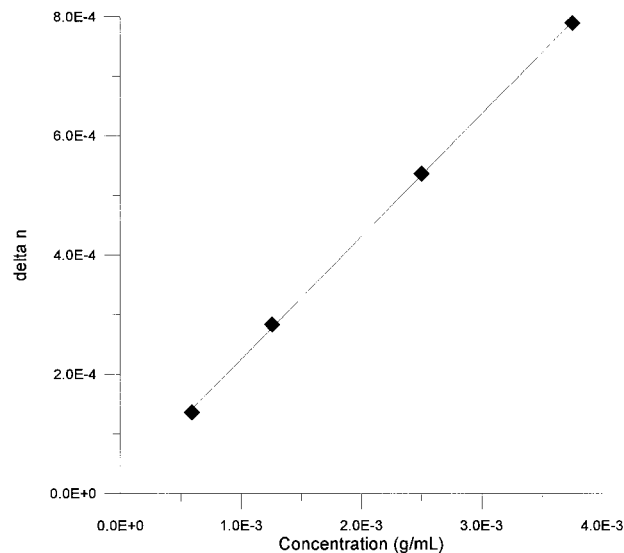


Figure 1 Change of refractive index with concentration for P- α MS (molecular weight = 19,000).

length of measurement meant that none of the previously reported values could be used with any degree of confidence for the measurement of molecular weight averages of α MS containing copolymers.

The dn/dc values of P- α MS standards (Polymer Source, Dorval, Quebec) were measured in THF at 25°C

using a Chromatix KMX-16 laser differential refractometer operating at 633 nm. Linear plots of refractive index changes versus concentration (Fig. 1 shows a typical one) gave values for dn/dc of 0.2044 mL/g (standard error = 0.002273) and 0.2056 mL/g (standard error = 0.001522) for standards with molecular weights of 19,700 and 72,000, respectively.

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