



AMERICAN NATIONAL
STANDARD

ANSI/ASTM D 3592 - 77

Standard Recommended Practice for DETERMINING MOLECULAR WEIGHT BY VAPOR PRESSURE OSMOMETRY¹

This Standard is issued under the fixed designation D 3592; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

1. Scope

1.1 This recommended practice covers the determination of the number average molecular weight, $\bar{M}_n$, by means of vapor pressure osmometry (VPO). It is applicable to all polymers that dissolve completely without reaction or degradation.

1.2 The practical molecular weight range for vapor pressure osmometry is generally considered to be between 10 000 and a lower limit that is determined by the requirement that the solute have negligible vapor pressure. The upper molecular weight limit can be extended by the use of special techniques.

1.2.1 The use of low molecular weight standards to determine the calibration constant is only an approximate procedure (1,2);² this approximation becomes less accurate as the molecular weight difference between the calibration material and the unknown solute is increased. Therefore, for samples having number average molecular weights larger than 10 000, a revised calibration procedure must be employed.

1.2.2 The precision with which $\bar{M}_n$ of high molecular weight solutes can be determined is critically dependent on the non-ideality of the solute-solvent system. For non-ideal polymer systems, in which the solvent is a relatively good solvent for the solute, the differential thermistor resistance, ΔR , of the system is represented as follows:

$$\Delta R = A_1 C + A_2 C^2 + A_3 C^3 + \dots \quad (1)$$

A_1 is proportional to the reciprocal of $\bar{M}_n$, C is the weight concentration, and A_2 and A_3 are the second and third virial coefficients respectively. The higher order terms become more

significant (3) as the molecular weight is increased, necessitating a polynomial fit of the data to determine the coefficient A_1 , from which $\bar{M}_n$ is obtained. The precision of the measurements is improved for high polymers as the apparatus sensitivity is increased (4) so that lower concentrations can be used; this use of low concentrations decreases the importance of the nonlinear terms. Another limiting factor in determining $\bar{M}_n$ of high molecular weight polymers is the potential presence of small amounts of low molecular weight impurities.

2. Significance

2.1 The number average molecular weight, $\bar{M}_n$, is a molecular weight value that is quite sensitive to the low molecular weight homologs present in a polydisperse polymeric material. $\bar{M}_n$ may be defined simply as follows:

$$\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i} \quad (2)$$

where n_i is the number of moles of molecular weight M_i .

2.2 The number average molecular weight is an important parameter of polymers that can be related both to the reaction kinetics of polymerization and physical properties of the bulk material such as tensile strength, melting

¹ This recommended practice is under the jurisdiction of ASTM Committee D-20 on Plastics, and is the direct responsibility of Subcommittee D 20.70 on Analytical Methods.

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² The boldface numbers in parenthesis refer to the list of references at the end of this recommended practice.