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APPENDIX I

MOLECULAR-WEIGHT DETERMINATION

by

Dilute Solution Viscosity

Molecular size is an important property that influences processing characteristics and determines finished product qualities. Consideration of the size of polymer molecules can be complex and highly mathematical, but the basic principles are simple.

Number average molecular weight, $\overline{M}n$, and weight average molecular weight, $\overline{M}w$, are two general expressions of molecular size. The most common way to measure number average molecular weight of high polymers is osmometry. This measures the osmotic pressure of polymer solution and pure solvent between semipermeable membranes. To determine the weight average molecular weight, light scattering techniques are used.

The most widely used method to characterize the average molecular weight of PVC is dilute-solution viscometry(25). This is by far the easiest of the various methods and requires simple apparatus. It is based on the fact that the viscosity of a solution of high-molecular-weight polymer is considerably greater than the viscosity of the solvent. The suggestion was made by Staudinger in 1930 that the relative magnitude of this difference could be correlated with molecular weight(25). This started numerous investigations that have led to the present-day concepts of dilute solution viscosity.

Classically, viscosity measurements are made so that $[\eta]$, intrinsic viscosity, can be determined. This term is defined as

$$[\eta] = \lim_{C \to 0} \frac{\ln \eta_{rel}}{C}$$

where

$$\eta_{rel} = \text{relative viscosity}$$

$$= \frac{\text{viscosity of solution}}{\text{viscosity of solvent}}$$

and

$$C = \text{concentration, g polymer/100 ml solution}$$

The term $\ln \eta_{rel}/C$ is defined as the inherent viscosity, or logarithmic viscosity number.

To determine $[\eta]$ of a polymer, the inherent viscosities of solutions of various concentrations of polymers are determined and plotted against the respective concentration. The intercept of the line at zero concentration is $[\eta]$.

The measurement of $[\eta]$ alone gives only a relative comparison of molecular weight between various samples of PVC. However, the intrinsic viscosity can be related to the molecular weight M as follows :

$$[\eta] = K\bar{M}_v^a$$

The constants, K and a, are determined for a given polymer/solvent system. For PVC/tetrahydrofuran system at 25°C; $k = 1.50 \times 10^{-4}$, $a = 0.77$(34). Consequently, the molecular weight of PVC samples can be determined.

VITA

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