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Determination of Polymer Branching with Gel Permeation Chromatography. Abstract of a Review*

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The effect of long- and short-chain branching in polymer molecules on GPC separation is reviewed (*1–4*). The calculation of branched GPC curves is developed from the universal calibration techniques, which is based on the concept of hydrodynamic volume ($M[\eta]$) and previously established relationships for the effect of branching on molecular dimensions. Typical calibration curves are shown for different branching models and degrees of branching. As the branching level increases, the curves are shown to approach a limiting value. Methods of characterizing branching levels and molecular-weight distributions of fractions and whole polymers from GPC and intrinsic viscosity data are presented. An iterative computer program is described which was written to calculate the degree of branching in whole polymers. Long-chain branching in several low-density polyethylene samples was determined, using both the fraction and the whole polymer methods. Effects of various experimental errors and branching models were investigated. For polyethylene, the data show that the effect of branching in intrinsic viscosity is best described by the relationship $\langle g_3 \rangle_w^{1/2} = [\eta]_{br}/[\eta]$ where $\langle g_3 \rangle$ is the Zimm-Stockmeyer expression for trifunctional branch points in a polydisperse sample.

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