COMMENTARY

Reflections on "A Universal Calibration for Gel Permeation Chromatography," by Z. Grubisic, P. Rempp, and H. Benoit, *J. Polym. Sci.*, 5, 753 (1967)

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In 1964 the *Journal of Polymer Science* published a paper, written by J. C. Moore[1] which was entitled Gel Permeation Chromatography; it was a kind of revolution in the experimental methods to study polymer solutions, since it did allow the measurement of polydispersity much faster than by the classical batch or column fractionation, which were the only possibilities at the time. Since our lab was specialized in the field of polymer solutions, this technique was highly desirable and I decided to acquire the machine manufactured by the Waters company. This was not easy and with the help of industry, we were able, at the end of 1965, to install this equipment in the Centre de Recherche sur les Macromolecules and to hire a student, Zlatka Grubisic, to run the machine and prepare her doctoral thesis on the applications of this technique.

The first step, when you use a set of G.P.C. columns, is to establish a calibration curve relating the elution volume to the molecular weight (MW) of various samples of narrow polydispersity (usually polystyrene). This procedure is perfect when you study polystyrene but there is a problem when you want to study another polymer, since there is no reason for the curve established for polystyrene to be valid for other polymers. Since it is practically impossible to make a new calibration curve each time a new polymer is studied, one has to find a way to use the polystyrene calibration curve for all polymers. The first method is to assume that, regardless of the nature of the polymer, the calibration curve

obtained for polystyrene is valid. This is still used in some cases but the authors are cautious and call this "the equivalent polystyrene MW," which means that this MW is really the MW of a polystyrene having the same elution time.

This is not satisfactory since the relation with the equivalent polystyrene molecular weight and the real MW is unknown and, due to the importance of this problem for users of G.P.C., the scientific community was looking for a better solution. One has to bear in mind that, at that time, nobody had clear ideas about the mechanism of the separation. Some believed that it was a hydrodynamic effect, some others that it was a size exclusion effect.

The first approach that was suggested was to take the contour length of the polymer for amorphous polymers (or the length of the crystal in the direction of the chain) and to say that two polymers having the same length had the same elution volume. Evidently there was no reason for this to be the case and, due to the difference between amorphous and crystalline polymers, it could just have been qualitative. This was not satisfying and other different methods were suggested. Our feeling was that it was the dimensions in solution which were important and my first idea was to use the radius of gyration as determined by light scattering. Unfortunately, this quantity can only be measured for rather large molecular weights and one could never have enough points for a precise determination. I therefore decided, after discussions with Paul Rempp, to use (for commodity reasons) the intrinsic viscosity as a measure of size, or, more precisely, the product $[\eta]M$ since, following Einstein, it is what one usually calls

the hydrodynamic volume of the coil, a measure of the dimensions of the coil in solution. We had at our disposal a large number of samples prepared via anionic polymerization by the group of P. Rempp and doctoral student Z. Grubisic. They checked whether, when plotting $[\eta]M$ as a function of the elution volume for different polymers, one obtained a unique curve. The result was astonishingly good and published first in a French journal.[2] Since it did not attract any attention I felt obliged to publish a short note as a *Polymer* letter, which is the only paper referred to in the literature.

In fact, the first paper was more complete and showed that for the few samples for which we had determined the radii of gyration by light scattering, viscosity was a much better parameter. More surprising was that, for branched polymers, the $[\eta]M$ plot was far better. This led me to conclude that separation was due to the flow process and to the perturbation of the flow by the macromolecules. We had to wait until E. Casassa published a very important paper[3] showing that one can interpret the universal calibration by considering just equilibrium between free molecules and molecules confined in the pores. Since the Casassa paper, nothing new has been added to our understanding of this phenomenon and, if advances have been made on this technique, they are essentially of technical nature, making available better columns and better detectors.

It is interesting to understand why this method of calibration is called Universal Calibration, which at first might seem presumptuous. I am not the father of this expression; it had been used before by a scientist who was proposing an inaccurate method. My feeling was that the universal calibration was just temporary and that, with the use of multidetectors like measuring viscosimetry and light scattering, no calibration would be needed since the result of a chromatography would give a complete characterization of the fractions. In fact this is not the case: the sensitivity of the actual detectors is such that there is only a small range of sizes where the results of both techniques are precise enough to be used simultaneously and Universal Calibration is still in use in many laboratories. This shows that a simple idea with only little theoretical support can survive for a long time, a fact that I would never have suspected.

REFERENCES AND NOTES

1. J. C. Moore, *J. Polym. Sci.,* **A-2,** 835 (1964).
2. H. Benoit, Z. Grubisic, P. Rempp, D. Decker and J. G. Zilliox, *J. Chim. Phys.,* **63,** 1507 (1966).
3. E. F. Casassa, *J. Polym. Sci.,* **B-5,** 773, (1967).