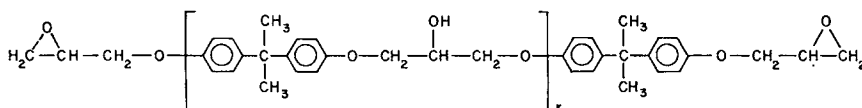


Recycle Gel Permeation Chromatography. II. Analysis of Epoxy Resins

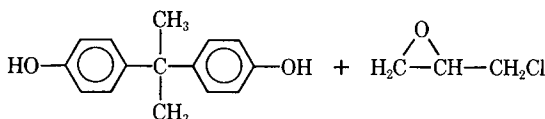
Recycle in gel permeation chromatography (GPC) has been used as long ago as 1962.¹ The purpose of this communication is to describe the application of a new recycle device² for GPC to the analysis of epoxy resins.

If the repeating unit R in a linear-chain polymer $[R]_x$ is small in size, as is often the case with addition-type polymers, its GPC spectrum will usually be a continuous curve with a single maximum. This signifies that molecules with different values of x cannot be resolved during fractionation. When R is large, however, as with condensation-type polymers, it is possible to obtain GPC spectra showing individual peaks for each low molecular weight oligomer ($x = 1, 2, \text{etc.}$). For this reason we have chosen epoxy resins with which to demonstrate recycle.

We shall use the formula $E[BE]_xBE$, in which BE is the repeating unit R, to represent the epoxy polymer molecule



Two processes are commonly employed to manufacture epoxy resins. One is the so-called "conventional" process, which utilizes a bisphenol-A and epichlorohydrin as start-



ing materials, and therefore gives a polymer product which contains molecules having all possible values of x . The other is the so-called "fusion" process, in which the diglycidyl ether of bisphenol-A (EBE) and bisphenol-A are the starting materials and which therefore is not capable of yielding polymer molecules with odd-numbered values for x .

If separation in GPC is purely mechanical, as is usually presumed, then a universal calibration curve must exist, in principle, for a given GPC system. That is, all solute molecules having equal values of an appropriate size parameter S should exit from the GPC at precisely the same retention volume, or "count." The calibration curve usually takes the form of a straight line when $\log S$ is plotted against retention volume and should be independent of solute type if S correctly characterizes the size of the solute molecules in solution. The key to successful application of universal calibration to the determination of molecular weight, or x , lies in the proper choice of S . Popular examples of S are Hendrickson and Moore's effective chain length³

$$S = M/Q \quad (1)$$

and Benoit's hydrodynamic volume⁴

$$S = [\eta]M = KM^{a+1} \quad (2)$$

where Q is the so-called Q -factor,⁵ or molecular weight per angstrom unit; $[\eta]$ is intrinsic viscosity; and K and a are Mark-Houwink constants.

In this work we have used the so-called "effective carbon number" for S , which is based upon Hendrickson and Moore's work and has previously been applied to epoxy resins by Larsen.⁶ Our GPC calibration curve is shown in Figure 1. Single-pass spectra for four competitive epoxy resins are shown in Figure 2, and recycle spectra for the same four materials, in Figure 3. These materials are Shell Epon 1004, Ciba 6084, Dow 664, and Union Carbide Corporation 2013. The recycle spectra, owing to their manifestly

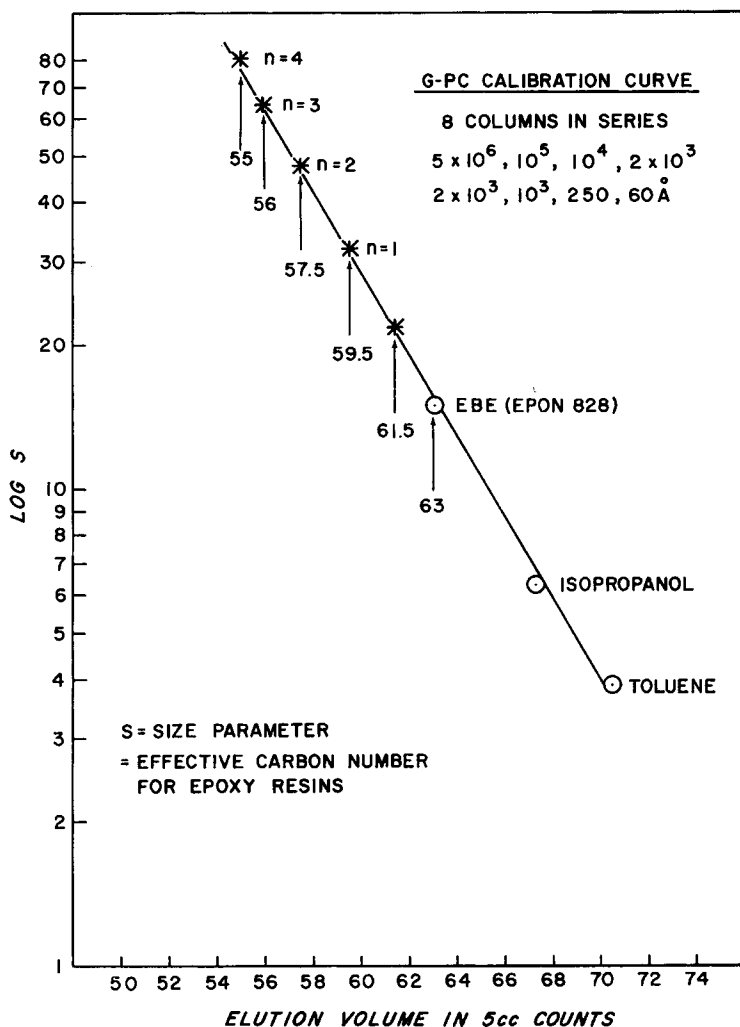


Fig. 1. GPC calibration curves for fractionation of epoxy resins with eight columns packed with polystyrene beads.

superior resolution, show peaks which are not visible on their single-pass counterparts, including those corresponding to molecules with values of x up to 3 and 4. Retention counts in the recycle spectra have values approximately twice as large as corresponding peaks in their single-pass spectra. However, to facilitate comparison, they are identified in terms of their single-pass retention counts (in parentheses) in Figure 3.

Our assignment of x -values to peaks was found to correlate well with the effective carbon number method as shown by the calibration curve, Figure 1. However, the components eluting at 60.5 and 61.5 counts are believed not to be oligomers, since their effective carbon numbers are below the value expected for $x = 1$. Moreover, it is clear that odd-numbered peaks are absent in the Ciba 6084, Dow 664, and UCC 2013 materials but are present in Epon 1004, from which we may conclude that the latter is certainly not manufactured by the fusion process.

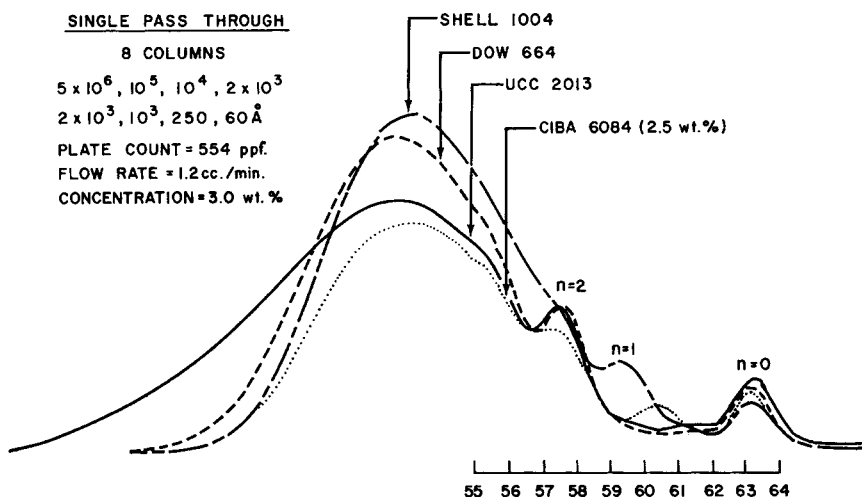


Fig. 2. Epoxy resin GPC spectra resulting from one pass through eight columns.

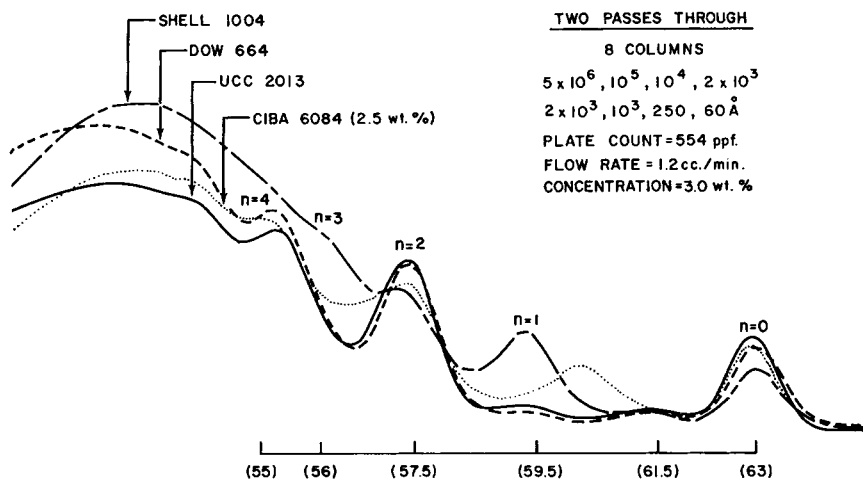


Fig. 3. Epoxy resin GPC spectra resulting from two passes through eight columns.

In conclusion, we have attempted to demonstrate the potential of recycle in the GPC analysis of polymers without resorting either to columns with extraordinarily high plate counts or to columns having a preponderance of resolving power specific to the molecular size region of interest: in this case, low molecular weight oligomers. Our overall plate count was 544 plates per foot of column, and only two of the eight columns contained low-porosity packing. Thus, we have shown that a recycle device, which is simple to install, may be used with a general purpose column set having a broad range of porosities to improve resolution in a specific region. This resolution may be amplified manifold beyond that demonstrated in this work by repeated recycling of only that portion of the polymer sample which lies in the region of interest.

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