Detecting Low Molecular Weight Homologs in Poly(ethylene Glycols) by Gel Permeation Chromatography

The technique of gel permeation chromatography (GPC) has proved to be a versatile tool for the fractionation of a homologous series of macromolecules according to molecular size.[1-4] The separation is based on the extent or rate each molecular species penetrates the gel; the largest molecules show the least penetration and are eluted first, especially if they are nonionic.

During a study of the penetration of polymeric materials into wood substance, it became necessary to determine whether the poly(ethylene glycols) (PEG) used contained an appreciable quantity of low molecular weight components. GPC appeared to be a practical method for determining the relative concentration of such components.

The gels used in this study were the commercially available, crosslinked dextrans (Sephadex), supplied by A. B. Pharmacia, Uppsala, Sweden, designated G-50 and G-100. The G-100 gel has a smaller crosslink content than the G-50 gel; hence, G-100 allows greater penetration with greater retardation of higher polymeric species. The PEG samples used for this study were supplied by the Dow Chemical Company, Midland, Mich. The number-average molecular weights $\bar{M}_n$ of these materials as measured by endgroup analysis[5] are shown in Table I.

TABLE I
Molecular Weights of PEG's by Endgroup Analysis

PEG	$\bar{M}_n$
1000	1,000
2000	2,700
4000	4,900
6000	7,400
9000	9,900

The G-50 column was 1.5 × 100 cm., and the G-100 column was 3 × 122 cm. The eluant was distilled water at a flow rate of 0.3 ml./min. for the G-50 column, and 0.2 ml./min. for the G-100 column. The PEG samples were added to the column as 3% solutions at room temperature. Eluate samples of 3 ml. were collected and analyzed for polymer content with a differential refractometer (Zeiss Laboratory Interferometer).

GPC studies on Sephadex G-50 and G-100 showed that the PEG-4000, 6000, and 9000 samples did not contain any detectable amount of those species present in the PEG-1000 and 2000 materials. The elution curve of a mixture of equal amounts of PEG-2000, 4000, and 9000 on Sephadex G-100 is shown in Figure 1. From the chromatogram for blue dextran (MW = 2,000,000) shown in Figure 1, the void volume of the column can be determined. When PEG-6000 was added to the mixture, the peak for the PEG-9000 increased and these two PEG samples could not be separated by GPC on Sephadex G-100.

Since there was some overlap in the PEG-4000 and 9000 elution curves, an attempt was made to estimate the quantity of PEG-4000 that could be present in PEG-9000. The elution curves in Figure 2 show the results obtained on a Sephadex G-100 gel from PEG-9000 and blends of PEG-9000 containing 2.5% and 5.0% PEG-4000. The results in Figure 2 clearly show that as little as 2.5% PEG-4000 can be detected in a PEG-9000 sample.

The tail on the PEG-9000 curve in Figure 2 suggested that the material initially contained some of the molecular-weight species present in PEG-4000. The elution curves

of PEG-9000 samples fractionated by the method of Almin[6] or by GPC techniques, however, showed a similar tail. It was concluded that this tail was a column artifact and did not indicate the presence of any PEG-4000 in PEG-9000.

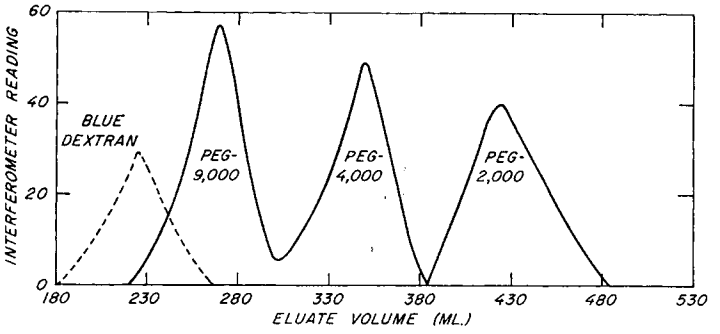

Fig. 1. Elution curve of a mixture of PEG-2000, 4000, and 9000 on Sephadex G-100.

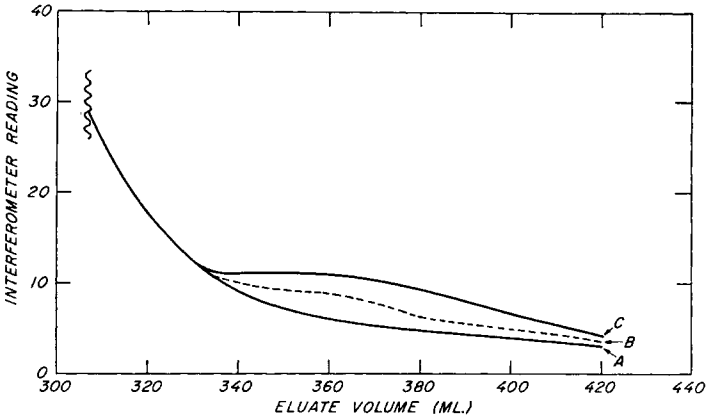

Fig. 2. Elution curves of (*A*) PEG-9000, (*B*) PEG-9000 containing 2.5% PEG-4000, and (*C*) PEG-9000 containing 5.0% PEG-4000; all were on Sephadex G-100.

In conclusion, it has been shown that with relatively simple equipment and the GPC technique, the presence of as little as 2.5% PEG-4000 can be detected in a sample of PEG-9000. It has also been shown by GPC that the PEG-4000 and 9000 samples do not contain any detectable amount of material present in PEG-1000 or 2000.

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