

High-Resolution and High-Speed GPC on Oligomers and Plasticizers

Gel permeation chromatography (GPC) has been used primarily for high polymeric substances, while some applications to oligomers¹⁻³ or polymer additives⁴⁻⁶ have also been reported. In the measurements of these low molecular weight compounds, separation of constituent components of a sample as discrete species was often desired. However, it was difficult to attain satisfactory separation in a short time when ordinary equipment and column sets were used. Therefore, the separation was achieved with very long columns,⁷ recycle systems,^{7,8} or soft gels of low degree of crosslinking.¹ However, the analysis time was long in all these cases. Recently, it was shown that high resolution is attainable by using columns packed with very small gel particles.⁹ High-resolution columns of this sort are expected to be effective particularly to the separation of low molecular weight compounds. Here, applications of high-resolution GPC to oligomers and plasticizers are reported.

Measurements were made at 45°C on a gel permeation chromatograph HLC-801A (Toyo Soda Manufacturing Co., Ltd.) equipped with differential refractometer as a detector. TSK-GEL columns, Type-H, packed with polystyrene gel particles about 5 μm in diameter were used. Each column is 0.305 in. in inner diameter and 1 or 2 ft in length. The nominal porosity of the gel is 10^3 \AA , and the exclusion limit for polystyrene in tetrahydrofuran (THF) is approximately 8×10^3 in molecular weight. The number of theoretical plates measured with 0.05-ml injections of 2% acetone solution at a flow rate of 2 ml/min is about 12,000 plates/ft. THF was used as the solvent. The injection volume of the solution was 0.05 ml. Commercial standard polystyrene having a molecular weight of 600 (SPS 600, Pressure Chemical Co.) and polyethylene glycol of molecular weight 600 (PEG 600) were measured on 8-ft columns. Each measurement was completed within 2 hr. Elution curves of these samples are shown in Figure 1.

Sample SPS 600 has been chromatographed by many workers. Among them, Heitz et al.¹ have achieved the most effective separations by using soft polystyrene gels (2% divinylbenzene). The separation shown in Figure 1 is comparable to that reported in

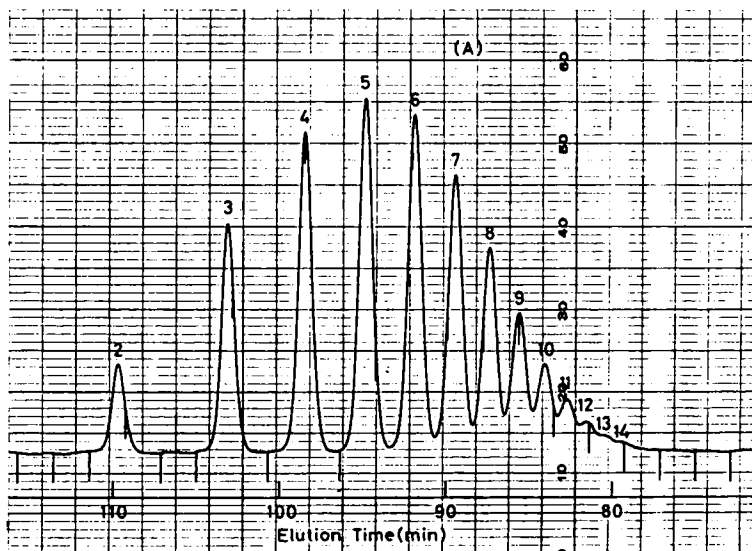


Fig. 1 (continued)

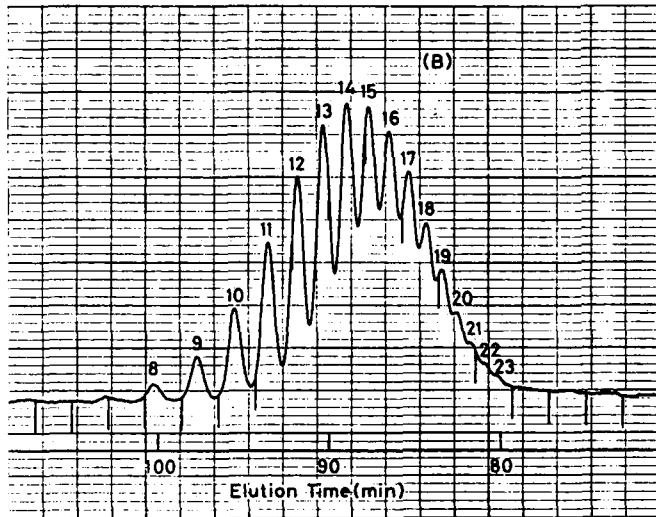


Fig. 1. GPC elution curves of (A) SPS 600 and (B) PEG 600 on 8-ft columns. Numbers in figures are degree of polymerization of each component. Flow rate, 0.6 ml/min; pressure drop, 110 kg/cm²; solution concentration, 40 mg/ml.

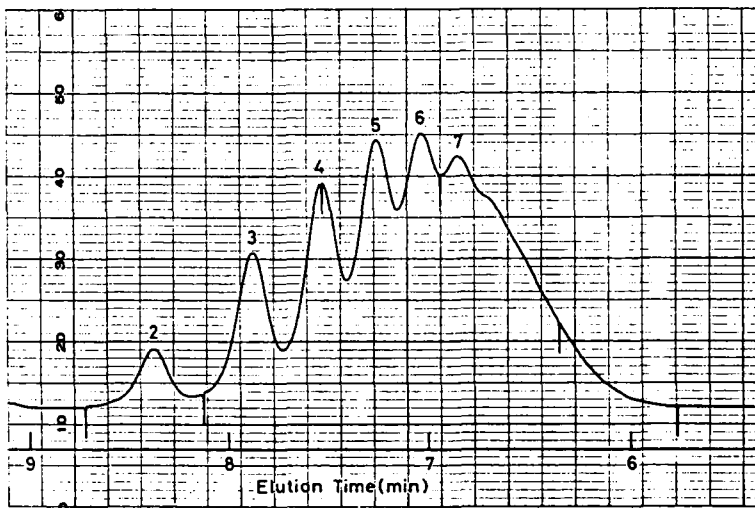


Fig. 2. GPC elution curve of SPS 600 on 2-ft columns. Flow rate, 2 ml/min; pressure drop, 90 kg/cm²; solution concentration, 20 mg/ml.

reference 1. However, soft gels must be used at low flow rates as they swell appreciably, and, therefore, a long analysis time is needed. Heitz and co-workers used a 2-m column, and the analysis time was about 13 hr. Therefore, from the point of view of analysis time, it can be said that a semirigid gel with particles of small diameter is preferable to a soft gel in attaining high resolution. The separation of PEG 600 is also comparable to that reported by Heitz and co-workers.¹

The elution curve of SPS 600 measured on 2-ft columns is shown in Figure 2. Analysis time was shorter than 10 min in this case. Peaks corresponding to dimer through the heptamer are recognizable in the elution curve. Peaks for dimer through the hexamer appeared in the elution curve of the same sample obtained on 20-ft columns of con-

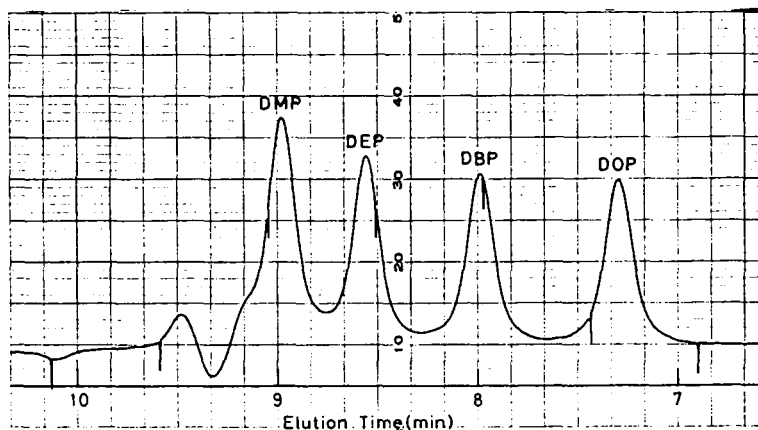


Fig. 3. GPC elution curve of a mixture of DOP, DBP, DEP, and DMP.

ventional type.¹⁰ In measurements of oligomers, if the components of different degree of polymerization are separated, a calibration curve can be obtained. Average molecular weights can be calculated using this calibration curve if the molecular weight dependence of refractive index is negligible.¹¹

The separation of a mixture of dioctyl terephthalate (DOT), dibutyl terephthalate (DBT), diethyl terephthalate (DET), and dimethyl terephthalate (DMT) is shown in Figure 3. Experimental conditions are the same as in Figure 2. These compounds are often used as plasticizers. The four components are separated almost completely within 10 min.

From the above results, high-resolution GPC appears attractive for measuring the average molecular weights of oligomers or for rapid quantitative analysis of polymer additives.

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