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Lignin Gels as a Medium in Gel Permeation Chromatography

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Synopsis

The preparation of spherical lignin gel beads, based on the crosslinking reaction between epichlorohydrin and kraft lignin (Indulin AT), is described. The lignin gels prepared were found to be an efficient resin in gel permeation chromatography. The separation of polystyrenes in dimethylformamide is described. The resin was found to separate polystyrenes with molecular weights up to 110,000. An inverse linear relationship between log M and elution volume or the partitioning coefficient was established.

INTRODUCTION

Our knowledge of lignin has evolved over a period of more than one hundred years, and their importance is widely recognized. It is now known that lignins exist as a polymeric wall constituent in almost all dry land plants and, among the natural polymers, lignins are second only to carbohydrates in natural abundance.

Black liquors from the conventional kraft (sulfate) pulping process contain lignin (kraft lignin), hemicelluloses, acids derived from carbohydrates, and small amounts of extractives. Of these, only lignin is precipitated on acidification, and it can thus be easily separated. Lignin is recognized as a polyphenolic resin. The chemical and polymeric properties of lignin have been described in textbooks on the subject.[1]

This paper describes a technique to prepare spherical crosslinked lignin beads suitable for gel permeation chromatography (GPC). The use of these gels to separate polystyrenes in dimethylformamide (DMF) is also demonstrated.

EXPERIMENTAL

Preparation of Gel Beads

A commercially available kraft lignin (Indulin AT, manufactured by Westvaco Co., Charleston, U.S.A.) was used in this investigation. Some characteristic data of the lignin can be found in Sarkanen and Ludwig.[1] All chemicals used were of analytical grade.

Lignin, 200 g, was dissolved in 600 g 2M sodium hydroxide. The solution was stirred for 4 h in order to ensure complete dissolution. This solution was then

thoroughly filtered on glass frits and finally on a glass fiber filter (Whatman GF/A) in order to remove small amounts of residual cellulosic fibers and colloidal material.

The lignin solution was added to a three-necked 5-l. reaction vessel equipped with a high-intensity stirrer. Freshly distilled 1,2-dichloroethane (bp 88–90°C), 3 l., was then added and the two-phase system was stirred for 15 min. During the stirring, some (<10%) of the lignin was dissolved in the dichloroethane phase. After this period of stirring, 15 g emulsifier (Cremophor EL, BASF) was added and the mixture stirred for another 2 h.

At this point, the crosslinking agent (60 g epichlorohydrin) was added to the reaction vessel. The crosslinking reaction was run in two steps, first for 48 h at the same temperature as before (21°C) and then for 24 h at an elevated temperature (40°C), with continuous stirring. After cooling to room temperature, the reaction product was picked up on a screen with 0.18 mm in open diameter and washed thoroughly, first with 2*M* sodium hydroxide and then with tap water. Finally, a small quantity of coarse beads was removed on a 0.35-mm screen. The gel beads were stored in tap water under slightly alkaline conditions in a refrigerator. The total yield in the preparation of the gel beads was approximately 85%.

Prior to column packing, the lignin gel beads were washed with 0.5*M* sulfuric acid in order to convert the acidic groups to the hydrogen form. The gels were then washed with distilled water to neutral pH and finally with DMF. The gel beads in DMF were spherical and of fairly uniform size (Fig. 1). The mean diameter was found to be 220 μm.

Gel Permeation Chromatography

The gel beads were deaerated and packed in a glass column (height 65 cm, diameter 1 cm) equipped with two Teflon seals. The column was connected between a peristaltic pump and a differential refractometer (Waters Associates, Milford, Massachusetts, U.S.A.) and a drop counter (LKB-Produckter AB,

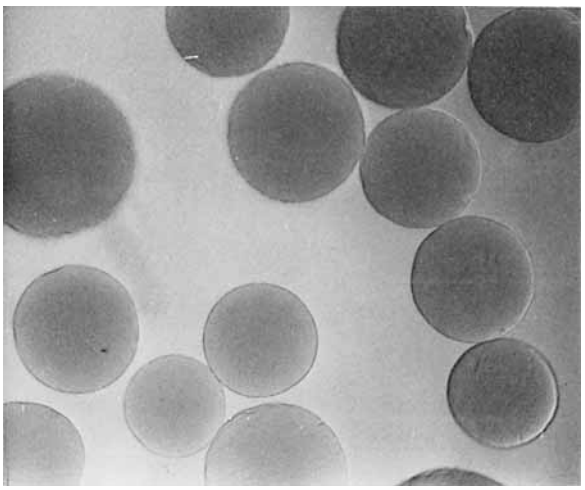

Fig. 1. Gel beads photographed in DMF.

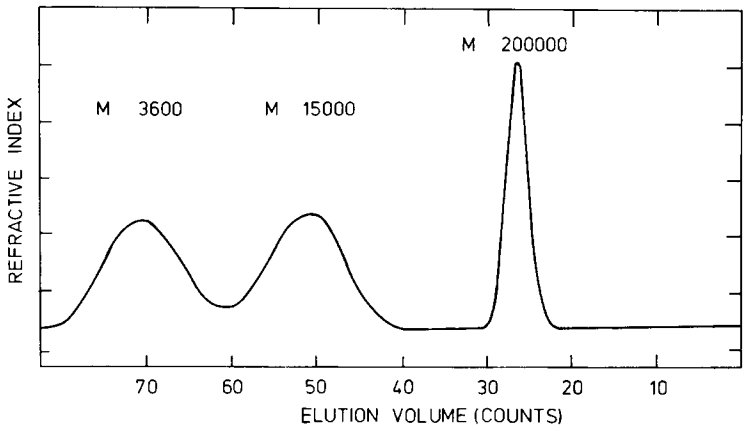

Fig. 2. Elution pattern for a polystyrene mixture (M 200,000, 15,000, and 3,600) (without correction for broadening).

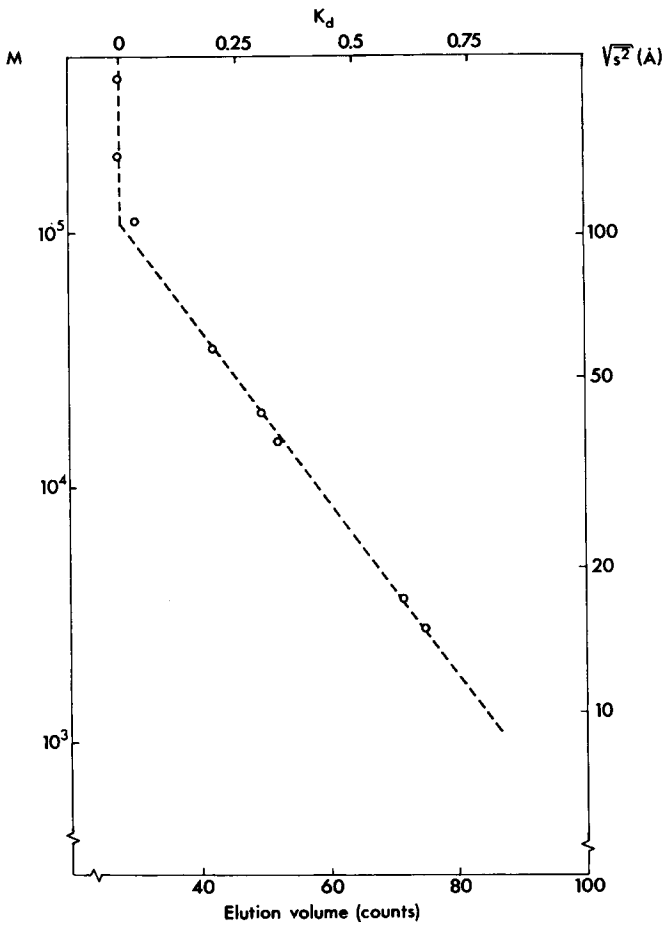

Fig. 3. Elution volume of polystyrenes of different molecular weights. The radius of gyration has been calculated by use of the Flory-Fox equation with a value of 2.1×10^{21} for the universal parameter.[2] The intrinsic viscosities of polystyrenes in DMF have been determined by Tsimpris et al.[3]

Bromma, Sweden) in series. A total of 3.0 m silicone tubings (diameter 1 mm) was used. The drop counter was adjusted to give a chart mark (= 1 count) for every 16 drops, which is equal to 0.484 ml. The column was thermostated to 25°C and protected from UV radiation with aluminum foil.

Narrow-molecular weight distribution polystyrene standards (Pressure Chemical Co., Pittsburgh, Pennsylvania, U.S.A.) of weight-average molecular weights (M) 2,900, 3,600, 15,000, 19,500, 35,000 110,000, 200,000, and 470,000 were used. The void volume was found to be 100 counts as determined from DMF labeled with C14 (The Radiochemical Center, Amersham, Buckinghamshire, England) and excluded volume 28.5 counts as determined with polystyrene 470000.

A change in sample concentration from 1 to 10 g/l. (sample load 1 count) did not affect the elution volume. At the highest concentration, no change in elution volume was detected at flow rates between 1.06 and 11.07 ml/h·cm^2. Normally, the flow rate was 3.75 ml/h·cm^2 and the sample concentration 5.0 g/l. The reproducibility was checked over a period of six months and was found to be M = 110,000: ±0.2 counts; and M = 2,900: ±0.5 counts.

A typical elution pattern for a polystyrene mixture (M 200,000, 15,000, and 3,600) is given in Figure 2.

DISCUSSION

Results from GPC measurements are commonly presented as log M versus elution volume or the partitioning coefficient, K_d, defined by

$$K_d = \frac{V - V_{\text{excl}}}{V_{\text{void}} - V_{\text{excl}}}$$

where V = elution volume; V_{excl} = exclusion volume; and V_{void} = void volume (elution volume of solvent). As shown in Figure 3, an inverse linear relationship is obtained within the separation region. From Figure 2 and 3, it can be concluded that the lignin beads are well suited for use in GPC. The separation ability can be expressed as plate counts.[4] For o-dichlorobenzene, a value of 360 (plates per foot) was found. This must, however, be too low since no correction for experimental broadening in tubings was made.

In this study, DMF has been used as an elution liquid since it is known to be a good solvent for lignin. It is, of course, possible to use other solvents and thereby change the behavior of the lignin gel as a GPC medium.

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