Application of Poly(butadiene-*co*-acrylic acid)–Sucrose as Gel in the Separation of Different Substances

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SYNOPSIS

The synthesis of a new hydrophobic gel by reacting cooligomer of butadiene and acrylic acid (M_w 4500) with sucrose crosslinking in best conditions is described. Application of this new gel swelled in different organic solvents is studied. Separation of organic substances in benzene was achieved with higher retention of more polar substances. By this way, cholesterol was separated from lecithin, acrylic acid from polybutadiene with terminal carboxylic groups, and metals such as copper from organic solvents.

INTRODUCTION

The synthesis of gels swellable in water or in organic solvents is an important subject depending on the different properties and applications they can offer, e.g., in gel permeation chromatography,[1] as a material able to separate different organic substances,[2,3] in the retention of metallic ions,[4–7] as an immobilized catalyst,[8,9] etc.

Gel filtration has become a widely and commonly applied method for the separation of water-soluble substances. This technique has been extended to the fractionation of substances soluble in organic solvents, such as lipids and other compounds with similar solubility properties.

Reports have appeared describing Sephadex G 25,[1] Sephadex derivatives,[10] and polystyrene crosslinked with DVB.[11] Mixtures of carbohydrates were separated in an aqueous phase in the first example, and substances such as lipids, sterols, etc, were well separated in the last two examples. Separation is apparently due to different factors, such as molecular weights, polarity, adsorption, etc.

In a previous work,[12] we reported the synthesis of soluble products by reaction of poly(butadiene-*co*-acrylic acid) (BUAA) and sucrose with some degrees of crosslinking.

This work describes the synthesis and chromatographic applications of a new hydrophobic gel obtained by reaction of BUAA and sucrose in the best conditions. This gel was swellable in organic solvents.

EXPERIMENTAL

Preparation of BUAA–Sucrose Gel

This product was synthesized from BUAA-purified fractioned oligomer in a crosslinking reaction with sucrose. The cooligomer I (BUAA) (M_w 4,500, determined by VPO) was synthesized by bulk polymerization using 1,3-butadiene and acrylic acid as monomers and benzoyl peroxide as a catalyst.[13] This was purified by fractional precipitation using benzene as solvent and methanol as nonsolvent. Fractions F_1, F_2, and F_3 were collected.

The modified polymer (BUAA–sucrose gel) was synthesized from F_2 with an average carboxyl content of 0.35 equiv/100 g. The introduction of sucrose was possible through the carboxyl group of the obtained prepolymer I, which was reacted with thionyl chloride in a ratio of 1 : 1.5, respectively, in an ice bath by dropping the solution of prepolymer I at 60% P/V in dry benzene as solvent onto the solution of thionyl chloride at 40% P/V in the same solvent over 2 h. The overall reaction product was kept at room temperature for an additional 15 min and afterward the temperature was raised to 45°C for 1 h.

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From the reaction product, solvent and volatile products were eliminated. Then the acid chloride derivative obtained was reacted in an ice bath with a solution of sucrose in a ratio of 1 : 1, respectively, in dry DMF (11% P/V) containing 0.1% dry pyridine.

An insoluble swellable gel was formed as soon as the acid chloride was dropped into the solution. The gel was purified by several washes in a column with benzene:DMF (1 : 1) until no more soluble products were eluted from the column.

The purified gel swelled well in benzene and DMF. Swelling indices and percentages were measured by the modified technique of the ASTM Norm D 3616-77 in the following way: A weighed sample was inmersed into the selected solvent for 1 h at room temperature; the swelled sample was slurried on glass fibers and weighed after this operation. This procedure was repeated at regular time intervals until constant weight was achieved; the formulas applied were:

$$\% \text{ of swelling} = \frac{Wt \text{ of the swelled } S - Wt \text{ of the dry } S}{Wt \text{ of the dry } S} \times 100$$

$$= \text{Swelling index} = \frac{Wt \text{ of the swelled } S}{Wt \text{ of the dry } S},$$

where Wt = weight and S = sample.

The gel characterization was carried out by IR spectroscopy and differential scanning calorimetry (DSC) determinations on a Nicolet 5-SXC spectrophotometer, Fourier transform infrared (FTIR) spectrometer, and a Du Pont 990 equipment, respectively.

Preparation of the Column

The dried gel was mixed with the solvent to be used. After 2 h of equilibrium, the slurry was packed into a 58×0.8 cm chromatographic column, the lower end of which was plugged with glass wool. The gel in the column was allowed to settle by gravity with benzene as solvent flow. It was washed with about 1 L benzene before the first use. The samples (from trace amounts up to 50–60 mg) were applied to the top of the column in 0.5 mL solvent, and elution was carried out with the same solvent. Fractions of 1 mL were taken.

Analysis of Eluents

All samples were eluted and plots of weight (mg) vs. volume of solvent eluted (mL) were obtained. IR spectra of each fraction were run to identify each product.

Separation of mixtures of cholesterol (M_w, 386) from lecithin (M_w, 733), retinol palmitate (M_w, 524.46) from retinol acetate (M_w, 328.46), and commercial butarez (a polybutadiene carboxy terminal resin) (M_w, 5,000–5,500) from acrylic acid (M_w, 72) were determined.

RESULTS AND DISCUSSION

Synthesis and Characterization

Determinations of the swelling indices and percentages of the gel are summarized in Table I, where it can be observed that the purified gel obtained could swell well in the selected solvents, requiring prolonged times of contact with benzene to reach its maximum value.

The IR spectra of the purified gel showed new signals compared with the prepolymer I. Absorption at 3090–3600 cm^{-1} was attributed to sucrose hydroxyl groups incorporated into the structure and bands at 1050 and 1700–1720 cm^{-1} were assigned to ester groups and carbonyl groups of ester, respectively.

The DSC determinations for the gel showed that it was stable until 180°C with an exothermic maximum peak at this point. This value differed from that of prepolymer I, which had an exothermic maximum peak at 160°C, probably due to some crosslinking and internal rearrangements of the macromolecules.

Chromatographic Separation of Different Compounds

The applicability of the hydrophobic and swellable gel as a bed in a chromatographic column is demonstrated in Figure 1, where we can observe separation of a mixture of lecithin from cholesterol.

Separation of the two components and recovery of 100% of each one was carried out through a column with 3 g gel, swelled in benzene, using benzene as eluent. Flow rate was 0.6 mL/min. Fraction size was 1 mL.

Table I Percent and Index of Swelling of the Gel

Solvent	Swelling %	Swelling Index	Required Time (h)
Benzene	490	5, 9	36
DMF	510	6, 0	5

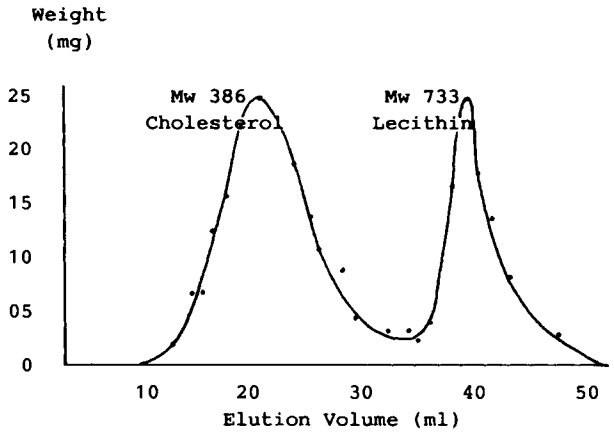

Figure 1 Separation of cholesterol from lecithin by using a BUAA–sucrose gel.

With a mixture of the acetate and palmitate of retinol, separation was only partially achieved under the conditions used, but with mixtures of butarez and acrylic acid we recovered 100% of butarez, with retention of the acrylic acid in the column. Likewise, some metals such as copper were retained from organic solvent solutions even in trace amounts. In this way, it was found that the new synthesized gel was valuable for the separation of soluble compounds in organic solvents. It was evident that the separation obtained with this material was not principally due to gel filtration. The polarity of the gel is apparently large enough to lengthen retention times for polar materials.

Differences in polarity between gel and elution solvent and the results obtained from separating different organic substances lead us to think more in terms of a partition chromatography system, where substances are eluted according to their polarity, probably due to interaction with hydrogens present in the crosslinked structure.

Drawing some molecular models for the crosslinked structures of BUAA–sucrose and comparing sizes of polybutadiene segments with those of sucrose, differences on the order of 100 are observed, thus making understandable the swellability in organic solvents such as benzene. When the polymer is swollen in benzene, the hydrophilic sucrose segments are sheltered by the solvent-swollen polybutadiene segments. Retention of polar substances by interaction with the hydrogens of the sucrose could take place in this described network structure.

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