NOTES

Properties of Films from Bacterial Polysaccharide B-1459*

Unsupported films of good quality can be made from an aqueous solution of the exocellular polysaccharide produced from glucose by *Xanthomonas campestris* NRRL B-1459.¹ Films of even better quality are obtained merely by heating the aqueous solution of the native polysaccharide to 80°C. before casting the film (from a cooled solution) or by using deacetylated polysaccharide.¹ Characteristics of the films demonstrate properties of this native polysaccharide, and of its modified forms, upon which practical applications can be based.

The native polysaccharide, made up of p-mannose, p-glucose, and p-glucuronic acid (as the potassium salt) and with an acetyl content of about 5%,² lends itself to large-scale production.³ This polysaccharide first aroused interest because of its high viscosity in water: a 2% solution has a viscosity of about 10,000 centipoises (measured with a Brookfield LVF viscometer at 30 rpm and 25° C.). This viscosity falls between that of the natural gums tragacanth and guar.

Films normally were cast from 1% solutions of the polysaccharide in water¹ because the high viscosity of solutions of higher concentration made even distribution of the solutions difficult. When dried, the solutions gave unsupported films of good quality, especially if care was taken to eliminate bubbles before the actual film casting. Films were cast on a smooth surface, such as metal, glass, or Plexiglas. If metal or glass was used, the dry film seemed to strip better from a plate which had been pretreated with a very dilute solution of silicone DC200 in carbon tetrachloride, but with Plexiglas no pretreatment was necessary. The solutions were allowed to dry spontaneously at 50%R.H. and 25°C. for 2 or 3 days. The dried films, which were about 1 mil (0.025 mm.) thick, were stripped from the casting surface and allowed to equilibrate under the same conditions for at least 2 more days before physical testing.

Physical tests determined tensile strength, elongation, and double-fold values. Tensile strength and elongation were both determined with a Scott IP2 incline plane serigraph having, at zero load, a 40-mm. distance between jaws. Double-folds were measured by use of a Schopper doublefold machine in which the test strip is given 120 doublefolds/min. while under a constant tension of 1 kg.

Values for physical properties reported in Table I are the average of at least 10 test strips. Values for corn amylose films⁴ are included for comparison. Improvement in tensile strength and in double-fold values is evident for the films made from heated or deacetylated polysaccharide.

* Presented before the Carbohydrate Division, 137th meeting American Chemical Society, Cleveland, Ohio, April 1960. Also shown is the greater effect glycerol had as a plasticizer in decreasing the tensile strength and fold values of amylose films as compared to its effect on the B-1459 films.

Properties of water-soluble films from polysaccharide B-1459 compare favorably with those of water-insoluble corn amylose films. Plasticization to reduce brittleness allows retention of considerable strength. In general, it seems that polysaccharide B-1459 may have value as a sizing or finishing agent. Further improvements in film proper-

TABLE I Average Test Values of Films

Polysaccharide	Glycerol, %	Tensile strength, kg./mm. ²	Elonga- tion, %	Double folds, actual number
Native B-1459	0	5.8	3	6
	15	4.0	4	40
	30	3.6	6	1500
Heated B-1459	0	8.0	5	70
	15	5.5	6	380
	30	4.0	11	2000
Deacetylated				
B-1459	0	7.0*	4	45
	15			
	30	5.0	8	3600
Corn amylose	0	7.2	13	900
	15	5.4	20	280
	30	2.0	46	Ъ

* 7 kg./mm.² = 10,000 lbs./in.².

^b Too much stretch for testing.

ties can be expected from study of methods of preparation and attainment of better reproducibility. Some indication of the possibilities is given by the fact that single specimens of B-1459 films gave test values as high as 10.5 (heated, no glycerol) for tensile strength and 30,000 (deacetylated, 30%glycerol) double-folds. Certainly an advantageous property of B-1459 films, which may be cast from cold aqueous solutions, is that they do not retrograde and may be redissolved and recast.

Mention of specific equipment or commercial products does not necessarily constitute an endorsement by the U. S. Department of Agriculture.

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Received July 21, 1961

Graphical Presentation of Copolymer Composition

The relationship between copolymer composition and monomer composition is often shown in graphic form by a plot of F_1 versus f_1 , where F_1 is the mole fraction of monomer 1 in the copolymer being formed at the instant when f_1 is the mole fraction of monomer 1 in the unconverted monomer. In terms of relative reactivities,

$$\frac{F_1}{F_2} = \left(1 + \frac{r_1 f_1}{f_2}\right) / \left(1 + \frac{r_2 f_2}{f_1}\right) \text{ or } Y = r_1 X \frac{(1 + r_1 X)}{(r_1 r_2 + r_1 X)}$$

where $Y = F_1/(1 - F_1)$, $X = f_1/(1 - f_1)$, and r_1 and r_2 = relative reactivities.¹

Usually the compositions are plotted as F_1 against f_1 on arithmetic coordinates similar to x,y diagrams for vaporliquid equilibria. However, a diagram of log Y versus log X





 $(r_1r_2 = 1)$ plot as straight lines with a slope of 1. Even systems with $r_1r_2 \neq 1$ show much less curvature and there-

fore require fewer calculated points to estimate completely.

Moreover, since r_i and X appear together, a plot of log Y

versus log X (when $r_1 = 1$) is changed (from that when $r_1 \neq 1$) merely by adding log r_1 to the abscissa.

In the second place, the log X, log Y diagram can be used as a graphic solution for F_1 as a function of f_1 , r_1 , and r_2 . In Figure 1, the abscissa and ordinate are labeled f_1 and F_1 although log X and log Y are actually plotted. The shifting of the f_1 axis is done graphically by a logarithmic scale of r_1 . Example: Copolymer composition (F_1) desired when $f_1 =$ 0.4 for vinyl acetate (monomer 1) and vinyl chloride (monomer 2); $r_1 = 0.23$, $r_1r_2 = 0.39$. (a) Follow f_1 (at bottom of figure) to intersection with $r_1 = 0.23$. (b) Move vertically to line for $r_1r_2 = 0.39$, read $F_1 = 0.24$.

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Received February 27, 1961

A Convenient Preparation of a Hydroquinone Redox Polymer

Many types of polymers have been described in the literature known as either redox polymers, electron-exchange polymers, or nondiffusible reducing agents. Examples of these are polyvinyl hydroquinone,^{1,2} copolymers of vinyl hydroquinone,³ polyvinyl gentisal,³ polyacrylylascorbic acid,³ and poly-3-(2,5-dihydroxyphenyl)propylene oxide.⁴

Recently we have had occasion to prepare polymers containing the monosubstituted hydroquinone structure, linked by a chemical bond stable to concentrated alkali. Most of the polymers listed above are tedious to prepare, and we now wish to report a convenient synthesis of polymeric hydroquinones. The method involves the reaction of a polymeric primary or secondary amine with 2,5-dihydroxyhydrocinnamic acid lactone. An optimum polyamine is polyethyleneimine because the amine equivalent weight is low, resulting in a high hydroquinone content on a weight basis, and also because the resulting tertiary amide structure is quite stable to alkali.



Experimental

The 2,5-dihydroxyhydrocinnamic acid lactone was prepared by conventional methods from 2,5-dimethoxybenzaldehyde and malonic acid followed by reduction and simul-