# POLYSACCHARIDE SULFATES. I. CELLULOSE SULFATE WITH A HIGH DEGREE OF SUBSTITUTION[1]

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(Received May 20th, 1971; accepted in revised form June 28th, 1971)

ABSTRACT

Previous methods for the sulfation of cellulose have a number of disadvantages, among which excessive degradation and incomplete substitution are the most common. These disadvantages are overcome if a complex of sulfur trioxide with a neutral, highly polar compound, such as *N*,*N*-dimethylformamide, is used as the sulfating agent. For the sulfation of cellulose with this complex, any grade or type of cellulose is suitable. The resulting products usually have degrees of substitution greater than 2. The viscosities of their aqueous solutions are relatively high, indicating that degradation is minor. Two of the most interesting properties of this relatively undegraded cellulose sulfate are its reactivity with proteins and the gelation of its aqueous solutions to form thermoreversible gels in the presence of potassium, rubidium, or cesium ions. The properties are surprisingly similar to those of carrageenan, a polysaccharide sulfate occurring naturally in a number of red marine algae.

During the past few decades, a number of methods have been suggested for the sulfation of cellulose; common reagents include sulfuric acid[2,3], sulfur trioxide[4,5], chlorosulfonic acid in pyridine[6] or quinoline[7], and sulfur trioxide diluted with an inert solvent such as sulfur dioxide[8]. Other agents found useful are complexes of sulfur trioxide with tertiary amines, such as pyridine[5] or triethylamine[9]. The method that has come closest to practical utilization is sulfation with sulfuric acid in the presence of an aliphatic alcohol[10].

However, all of these methods suffer from one or more disadvantages, among which excessive degradation and incomplete substitution are the most common. Often, the substitution is nonhomogeneous, or only the surface of the fiber is substituted. If the reaction is conducted in the presence of a tertiary amine, the resulting cellulose sulfate is obtained in the form of its trialkylammonium salt, necessitating additional effort to obtain the alkali or other metal salt, which, especially for commercial applications, is the more desirable product.

It is now reported that complexes of certain neutral, highly polar compounds, in conjunction with sulfur trioxide, are useful sulfating agents for cellulose. These agents produce high degrees of substitution, and cause little degradation of the cellulose molecule, as indicated by viscosity measurements. The type of neutral

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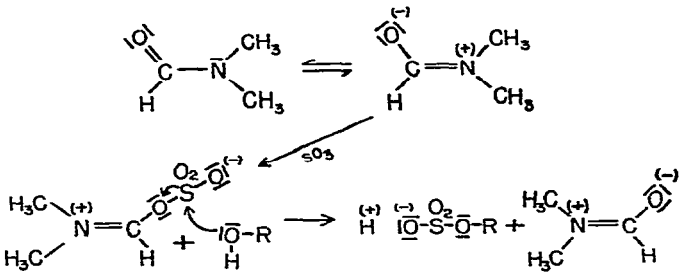
compounds most suitable for this purpose was found to be *N,N*-dialkylacylamides. *N,N*-Dimethylformamide (DMF) was found most suitable, since it is readily available and because its complex with sulfur trioxide, as well as DMF itself, are quite stable. Also, DMF is an excellent solvent for a great number of polymers, polysaccharides, and polysaccharide derivatives. If both the starting material and the reaction product, or at least the latter, are soluble or readily swollen in the reaction medium, a more homogeneous and complete reaction may be possible.

The complex has been used previously in dehydration and condensation reactions, and the like[11], and for the sulfation of chitosan in connection with work on synthetic heparin[12]. Its structure as suggested by Wolfrom and Shen Han is as follows (Scheme 1). The sulfur trioxide, with its electron-deficient sulfur atom adds onto the negatively charged oxygen atom of the polar mesomer of DMF. The sulfation presumably proceeds as shown in the lower sequence—replacement of the DMF by the alcohol in a similar manner— with formation of the sulfuric ester and reformation of DMF.



When sulfating with this complex[13], it is most important to treat the cellulose with DMF prior to the reaction. This treatment apparently activates the cellulose to some extent, possibly by association of the highly polar DMF with the polar hydroxyl groups. If omitted, an incomplete reaction results, and, additionally, a highly degraded product is obtained. Although the presence of some excess DMF is necessary as a diluent, a large excess is disadvantageous because the rate of reaction is considerably decreased. A highly increased time of reaction favors degradation. The yields of sodium cellulose sulfate (**1**) after neutralization with sodium hydroxide are quantitative with respect to the cellulose. The sulfating agent has to be used in excess for satisfactory results. Any type or grade of cellulose is suitable and leads to a high degree of substitution (d.s.) of greater than 2. The only apparent variation is in the viscosities of the reaction products, probably resulting from differences in the d.p. values of the celluloses used. Thus, the viscosity of 1% aqueous solutions of products from cellulose that has been treated chemically varies between 5 and 50 centipoises, that of products from wood pulp between 50 and 150 centipoises, whereas cotton linters give produts having the highest viscosities, between 150 and 500 centipoises. The highest d.s. (about 2.6–2.7) is obtained from highly chemically treated

cellulose. Under the same conditions the other two types of cellulose lead to a slightly lower d.s., usually about 2.2–2.6.

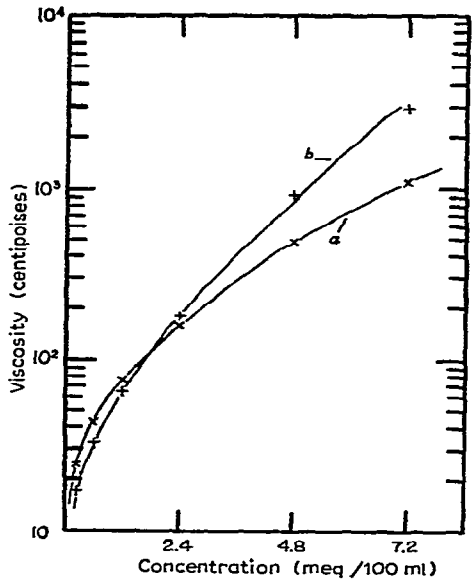



Fig. 1. Viscosity *vs* concentration of (*a*) sodium cellulose sulfate (**1**) and (*b*) *O*-(carboxymethyl)-cellulose (**2**) solutions in water at 25°.

Fig. 1 shows a plot of the viscosity *vs.* concentration of a medium viscosity **1** in comparison with that of a high viscosity *O*-(carboxymethyl)cellulose (**2**). The concentrations are given on an equivalent basis rather than by weight, in order to adjust for the difference in the molecular-unit weight. The viscosities of **1** as an indication of the molecular weight compare favorably with those of **2**, although such comparison is, at best, qualitative. However, the viscosity curve of **2** is considerably steeper than that of **1** at concentrations above 0.2–0.3%. The presence of salt in the products, of course, would affect the curves in this fashion, since **1** is significantly more sensitive to ions—1% sodium chloride for example decreases its viscosity to one third—than **2**, and this effect would become more pronounced at the higher concentrations. Both samples, however, had been dialyzed so that contamination with impurities may be considered negligible. Therefore, he principal reason most probably is not the presence of extraneous matter, but rather in the nature of the macromolecules, such as in their ability to associate with one another by (for example) intermolecular, viscosity-contributing, hydrogen-bond formation. Thus, the infrared spectrum of **2** shows absorption at about 3380 $cm^{-1}$ and that of pure cellulose[14] at about 3330 $cm^{-1}$ both values definitely originating from bonded hydroxyl groups. Since unmodified cellulose exhibits intensive, intermolecular hydrogen-bonding (this is the reason for its insolubility in water) it may well be expected that in **2**, a derivative that is substituted just enough to become water soluble, intermolecular hydrogen-bonding is still

sufficient to increase the viscosity noticeably. Such hydrogen-bond formation is expected to become more intensive with increasing concentration, and consequently, a relatively steep viscosity-curve, as shown in Fig. 1, would be produced. The i.r.-spectrum of **1** shows the hydroxyl peak at 3500 $cm^{-1}$ or at slightly higher wavenumber; definitely in the area characteristic of non-bonded hydroxyl groups. This excludes any contribution by hydrogen bonding to the viscosity of **1**.

The d.s. of the products is usually greater than 2, even if an insufficiency of complex is used for the reaction. In the latter case, a lower yield of a high-d.s. product, together with unreacted cellulose fibers, is obtained, the amount of unreacted fibers increasing with decreasing amount of sulfating agent. Apparently, the reaction occurs at the surface of the cellulose fiber. As soon as the outer layer is sufficiently substituted to become soluble in the reaction medium, it peels off, and substitution of the fiber can proceed further in the same manner, while the soluble, partially substituted macromolecules become sulfated to their maximum d.s. This so-called peeling process probably applies mainly to the highly crystalline regions. The amorphous portion presumably is penetrated quite rapidly by the reaction medium, and becomes substituted without difficulty. Consequently, if the extent of the amorphous regions could be increased, the preparation of a cellulose sulfate of lower d.s. may be possible simply by decreasing the amount of sulfating agent. Products having values below 2 were indeed obtained in this way, after the cellulose had been ball-milled or beaten in a Waring Blendor as an aqueous suspension and the water subsequently replaced by DMF. In contrast, the sulfation of Avicel, a highly crystalline cellulose (FMC Corporation, American Viscose Division, Marcus Hook, Pennsylvania.), proceeded only slowly and with difficulty, even when a large excess of sulfating agent was employed.

Cellulose sulfate exhibits a remarkable stability to alkali. For example, a product having a d.s. of 2.5, presumably containing di- and tri-substituted residues, could not be desulfated to any appreciable extent by heating in M or 2M sodium hydroxide. A cellulose sulfate having a d.s. of 1.8, presumably containing mono- and di-substituted residues, lost only slightly more than 20 percent of its sulfate groups under the same conditions. Theoretical considerations by Percival[15] suggest that a sulfate group is easily removed only in the presence of an adjacent, *trans* hydroxyl group, or with the hydroxyl group at C-3 and a sulfate group at the C-6. Accordingly, the mono-substituted residue would be alkali labile, regardless of the substituent's location, whereas the tri-substituted residue would be expected to be stable. Among the di-substituted residues, only those having the substituents at C-2 and C-3 would be resistant, whereas the two isomers having one sulfate group at C-6 would be labile. The experimental results indicate possibly enough desulfation to account for the mono-substituted residues, but relatively little (d.s. 1.8) or hardly any (d.s. 2.5) to indicate saponification of di-substituted residues. However, the formation of an appreciable proportion of 2,3-disulfate is most unlikely because of the relatively high reactivity of the primary C-6 hydroxyl group, and also because of steric hindrance[9,16]. This stability is most probably caused by the high negative charge on the group, which

presumably repels hydroxide ions, and, therefore, Percival's rules are not applicable in the case of polysaccharide sulfates having d.s. values substantially greater than 1.

Like carrageenan, a commercially available polysaccharide sulfate extracted from red marine algae[17,18], cellulose sulfate shows a strong reactivity with proteins. The reaction appears to be one of cross-linking, presumably by formation of a salt between the negative sulfate groups of **1** and the basic sites of the protein. Thus, increases in viscosity or flocculation behavior is expected when solutions of **1** and a protein are mixed. This effect, however, is considerably stronger with **1** than with carrageenan, probably because of the higher degree of sulfation in **1**.

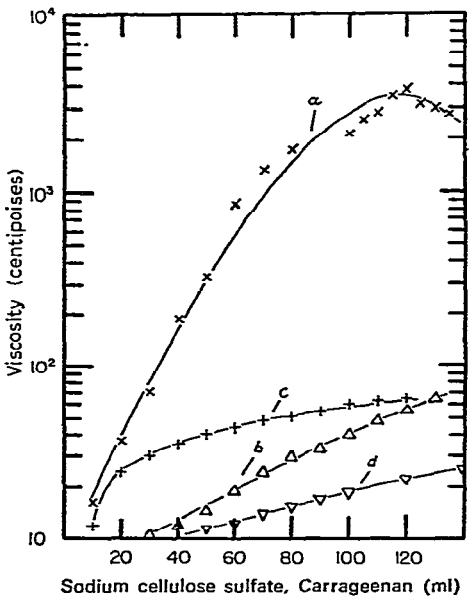



Fig. 2. Viscosities obtained after the addition of portions of (*a*) a 1% aqueous solution of sodium cellulose sulfate (**1**) to 200 ml of a 5% aqueous solution of sodium caseinate, (*b*) a 1% aqueous solution of λ-carrageenan to 200 ml of a 5% aqueous solution of sodium caseinate, (*c*) a 1% aqueous solution of sodium cellulose sulfate (**1**) to 200 ml of water and (*d*) a 1% solution of λ-carrageenan to 200 ml of water.

Plots of the viscosity of 5% aqueous solutions of sodium caseinate *vs* added portions of (*a*) a 1% solution of **1**, and (*b*) a 1% solution of λ-carrageenan, are shown in Fig. 2. Large viscosity increases over the blank (Fig. 2, *c*) are obtained with **1**, whereas increases with λ-carrageenan are only slight. With **1** there seems to exist a stoichiometric relationship, since a viscosity maximum is obtained without the formation of a precipitate or of haze. The maximum is reached at a similar **1**: caseinate ratio if, instead of **1** having a medium molecular weight (indicated by 168 centipoises at 1% concentration), a **1** having a lower molecular weight (55 centipoises at 1%) but having the same d.s. is used. Viscosity changes obtained with **1** in fresh milk (skim or whole) are shown in Fig. 3. A maximum is reached at relatively low concentrations

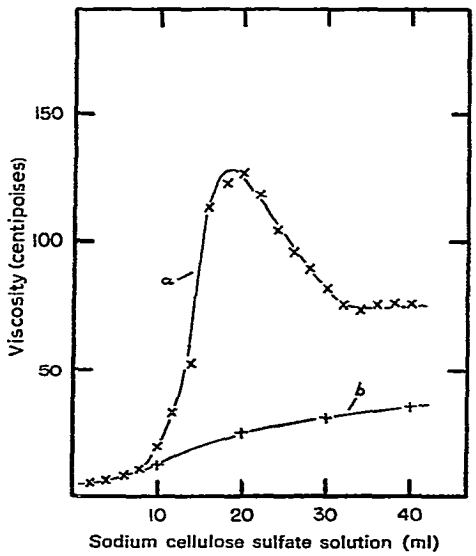



Fig. 3. Viscosity measured after the addition of portions of a 1% solution of sodium cellulose sulfate (**1**) to 200 ml of (*a*) whole or skim milk, and (*b*), water.

of **1**. At this point, flocculation occurs, and is accompanied by a sharp drop of the viscosity. On further addition of **1**, the solution becomes smooth again, and the viscosity levels off at a lower value. Increases in viscosity from the casein, especially at a concentration of about 2.5% as in milk, would be expected to occur at a comparatively high concentration of **1**. As a result, the sharp peak at about 20 ml must be due to the interaction of **1** with another protein that apparently is present at a relatively low concentration.

Other indications of the reaction of **1** with protein are the facts that gelatin gels have higher strengths and higher melting points when **1** is added (Table II, p. 227), and that gelatin films, especially after subsequent treatment with a weak acid, exhibit more water resistance when **1** is added. There is also evidence that, in the presence of **1**, certain enzymes are inhibited or, at least, their rate of action is highly decreased. However, more data will be needed for sufficient experimental support.

Aqueous solutions of **1** gelatinize when potassium, rubidium, or cesium ions are added, and **1** is the only synthetic polysaccharide sulfate exhibiting such properties. Of the naturally occurring polysaccharide sulfates, only κ-carrageenan reacts with these ions in a similar way. The gels are thermoreversible. The gel strength increases in the order: K<Cs<Rb (Table III, p. 228). To obtain these gels, the molecular weight of the **1** has to exceed a certain minimum indicated by a viscosity of about 10 centipoises at a 1% concentration. If the viscosity is lower, gel formation is not possible, and, at best, a precipitate or haze will be obtained*.

*During the long delay in submitting this publication, another method of sulfating cellulose was reported by R. L. Whistler, U. S. Patent 3,507,855 (1970), employing a dimethyl sulfoxide–sulfur trioxide complex. This method appears to produce sulfated products usually having a d.s. of about 1.5 irrespective of reaction conditions.

## EXPERIMENTAL

*Preparation of DMF–$SO_3$ complex.* — *N,N*-Dimethylformamide (DMF, 1500 ml) was cooled by stirring in a 3000-ml, 3-necked round-bottom flask immersed in an ice bath. The flask was equipped with a mechanical stirrer, a $CaCl_2$ tube, and a dropping funnel. Sulfur trioxide (900 g) was then added dropwise during 2–3 h. The reaction was highly exothermic, and care had to be taken to maintain the temperature below about 40°. The DMF–$SO_3$ complex was obtained as a yellowish, crystalline mass wet with excess DMF. This mixture of complex and DMF was stored under refrigeration and used in the following sulfations without filtration or further purification. The amounts of complex given below are referring to this mixture and not to the actual amount of complex.

*Sulfation of cellulose.* — Cellulose (100 g), dried for 3 h at 110°, was mixed with 300–700 ml of DMF and kept for several h at ~25°. The mixture was then cooled in a refrigerator, placed in a jacketed Day Mixer, and 450–500 g of the DMF–$SO_3$ complex, cooled to 5°, was added to 3 equal portions. The mixer was cooled by circulating ice–water through the jacket. The temperature was maintained below 15° throughout the reaction. The total reaction time was about 3 h. The reaction mixture was dissolved in ice–water, neutralized with dilute sodium hydroxide, and filtered through a Büchner funnel. The product was precipitated by pouring the solution slowly into one volume of methanol, and was pressed out, and dried. For further purification, the product was redissolved in water and reprecipitated with methanol. The method was performed successfully with cotton linters (cotton linter pulp, Type IER-4000, from The Buckeye Cellulose Corp., Memphis, Tenn.; cotton linter pulp, Type NO-2000, from Southern Chemical Cotton Co., Inc., Chattanooga, Tennessee), bleached sulfite wood-cellulose (Bleached sulfite wood cellulose, Raybond-P-HV, from Rayonier, Inc., New York, N. Y.), unbleached kraft pulp (Weyerhaeuser Co., Tacoma, Washington), and highly purified cellulose Whatman cellulose powder, CF II, and Genuine Whatman No. 41 filter paper. All of the reaction products had a d.s. greater than 2, and differed only in the viscosities of their aqueous solutions.

For preparing a product having d.s. of below 2, cotton linters or wood pulp was beaten for 1 or 2 h, as an aqueous suspension, in either a Niagara 1.5 lb. beater or a Waring Blendor. The solids were squeezed out to remove excess water, suspended in DMF, filtered off, and pressed out about 5 times. DMF was then added to give a cellulose: DMF ratio of about 1:8 to 1:10. The reaction was carried out as already described, by using various amounts of between 250–400 g of complex per 100 g of cellulose. Because filtration through a Büchner funnel in most cases was difficult, a centrifuge was used. All products had values of below 2. A d.s. of below 1.5 was more difficult to achieve, and was obtained only in a few cases when the amount of complex was about 300 g per 100 g of cellulose and wood-pulp cellulose was used. However, the results, were inconsistent. Ball milling the dry cellulose or beating a suspension of cellulose in DMF instead of in water were less successful in producing a product of low d.s.

The i.r. spectra were obtained from films by using a Perkin–Elmer spectrophotometer, Model 337. Films of **1** (d.s. 2.5; 168 centipoises at 1%) and *O*-(carboxymethyl)cellulose (**2**) (Cellulose Gum 7HSXP, was purchased from Hercules Powder Co., Inc., Wilmington, Delaware) were prepared from aqueous solutions by casting them on a glass plate, drying the plates for 1 h at 80°, and peeling off the films with a razor blade.

All viscosities were determined with a Brookfield Viscometer, LVF Model, at 60 r.p.m. and 25°. Data in Fig. 1 were obtained with dialyzed samples of **1** (d.s. 2.5; 168 centipoises at 1%) and of a high-viscosity **2**. The viscosities of the solutions of **1** were determined at 3.0, 2.0, 1.0, 0.5, 0.25, and 0.1% concentrations, those for **2** at the same equivalent concentrations with respect to molecular-unit weights of 417 and 234, respectively.

*Determination of the d.s.* — Part of **1** was dissolved and dialyzed against distilled water for 48 h. The dialyzate was concentrated to low volume and the product was precipitated by methanol and dried *in vacuo* at 80°. An aliquot was dissolved in 10% hydrochloric acid and the solution was refluxed overnight. After filtration, the sulfuric acid was precipitated with barium chloride and weighed as barium sulfate, whose weight indicated the d.s. Amounts of barium sulfate indicating d.s. values of 1, 2, and 3 were calculated, and the values were plotted on a curve *vs.* the d.s. The d.s. values of the products were taken from this curve.

*Treatment with alkali.* — Portions (10 g) of a medium- and high-d.s. cellulose sulfate were dissolved separately in 200 ml of water (blank), 200 ml of M, 200 ml of 2M, and 200 ml of 4M sodium hydroxide. All solutions were kept for 2 h at 100°, adjusted to a pH of 8 with acetic acid, dialyzed against soft water for 48 h, and the dialyzates concentrated to low volume. The products were precipitated and washed with a mixture of methanol and acetone, and dried. Yields, viscosities of 1% aqueous solutions, and d.s. values were determined, and the results are given in Table I.

*Reaction with protein.* — Sodium caseinate (10 g) was dissolved in 200 ml of distilled water, and 5-ml portions of a 1% aqueous **1** were added with stirring. The solution of **1** had a viscosity of 168 centipoises. After each addition, the viscosity of

TABLE I

COMPOSITIONAL DATA

| | *Blank* | M *NaOH* | 2M *NaOH* | 4M *NaOH* |
|---|---|---|---|---|
| D.s. | 1.80 | 1.45 | 1.35 | 1.25 |
| Viscosity (centipoises) | 126 | 24.5 | 15.8 | 7.5 |
| Yield (g) | 8.50 | 5.95 | 6.30 | 5.05 |
| D.s. | 2.45 | 2.55 | 2.40 | 2.15 |
| Viscosity (centipoises) | 164 | 142 | 84.2 | 11.7 |
| Yield (g) | 8.57 | 9.12 | 8.92 | 9.56 |

*For the analyses, aliquots were dried *in vacuo* for 2 h at 80°.

the mixture was measured and plotted on the curve *vs.* the amount (ml) of solution of **1** added (Fig. 2, *a*). In another experiment, instead of **1**, 5-ml portions of a 1% aqueous solution of λ-carrageenan (184 centipoises) (λ-Carrageenan, under the trade name "Seakem 402", from Marine Colloids, Inc., Springfield, N. J.) were added. Viscosity measurements were taken as before, and the results were plotted on a curve (Fig. 2, *b*). In the blanks, portions of the solutions of **1** or λ-carrageenan were added to 200 ml of distilled water instead of to the 5% solution of sodium caseinate. The results are shown in Fig. 2, *c* and Fig. 2, *d*, respectively. Additionally, portions of a 1% aqueous solution of **1** were added to 200 ml of whole milk and, as a blank, to 200 ml of distilled water. The viscosity data are given in Fig. 3, *a* and 3, *b*, respectively.

For determining the effect of **1** on gelatin gels at neutral pH, gelatin (Knox unflavored gelatin, type A, acid processed) and mixtures of gelatin and **1** (168 centipoises at 1%) at various ratios were dissolved in 500 ml of water each by heating for 5 min to about 95° and stirring. One 100-ml portion of each was poured into a 150-ml specimen bottle (height 86 mm, inside diameter of neck, 41 mm) and allowed to set at room temperature and, a duplicate series, under refrigeration. The gel strength was measured after 2.5 and 24 h. No gels were obtained after 2.5 h at room temperature. Measurements were taken with a Bloom Gelometer, by using a Lucite plunger of 1-inch diameter. The approximate melting point of two of the gels was determined. The composition of the gels and the results are given in Table II.

TABLE II

COMPOSITION OF GELS

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *Composition:* | | | | | | | | | | | |
| Gelatin (g) | 7.6 | 8.1 | 8.6 | 9.1 | 9.6 | 10.6 | 7.6 | 7.6 | 7.6 | 7.6 | 7.6 |
| **1** (g) | 0 | 0 | 0 | 0 | 0 | 0 | 0.10 | 0.25 | 0.50 | 0.75 | 1.00 |
| *Gel strength* | | | | | | | | | | | |
| 24 h, 25° | 13 | 14 | 18 | 21 | 27 | 32 | 19 | 47 | 48 | 72 | 91 |
| 24 h, 4° | 64 | 88 | 93 | 109 | 131 | 149 | 70 | 82 | 83 | 158 | 168 |
| 2.5 h, 4° | 42 | 47 | 55 | 58 | 74 | 103 | 49 | 56 | 67 | 109 | 113 |
| *M.p.* (°C) | | | | | | ~30 | | | | | ~40 |

*Gelation with $K^+$, $Rb^+$, and $Cs^+$.* — Compound **1** (1.5 g) and 1.1 g of KCl were dissolved separately in distilled water, the solutions heated to about 80°, mixed, and the volume adjusted to 100 ml with distilled water. This procedure was repeated but, instead of KCl, 1.78 g of RbCl, and, in a third experiment, 2.48 g of CsCl were used. The solutions were cooled and kept for 3 h at room temperature. All three samples formed gels during this time. The gel strength was measured as already described, with a Bloom Gelometer equipped with a plunger of 0.5-inch diameter. The readings are given in Table III.

TABLE III

GEL STRENGTHS

| *Ion* | $K^+$ | $Rb^+$ | $Cs^+$ |
|---|---|---|---|
| *Gel strength* (g) | 26 | 534 | 232 |

All gels liquefied when heated in a hot-water bath, and re-set on cooling.

ACKNOWLEDGMENT

The author thanks Mr. Thomas R. Andrew for experimental assistance.

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