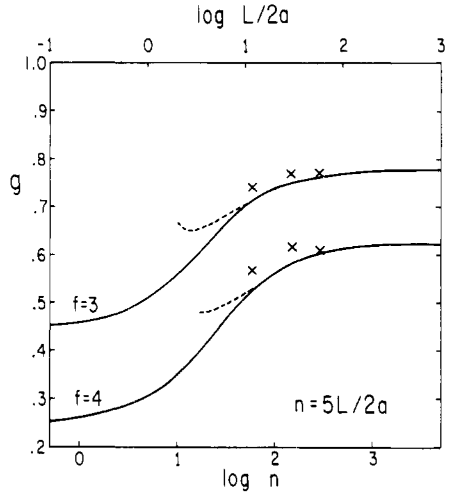

Figure 2. Mean-square radius ratios g as a function of chain length for regular paraffinic stars of three and four rays: crosses from Tonelli;[7] dashed curves from Mattice and Carpenter;[10] solid curves, wormlike stars, eq 12 with $L/2a = n/5$.

Further, it has been pointed out to us by Mattice[15] that certain RIS models, including several of those treated by him and Carpenter,[10] cannot possibly be imitated by a wormlike treatment. For example, as can be seen in Figure 1, our g values always increase with increasing L, but this is not true of some of the RIS stars, notably those with physically unusual statistical weights (e.g., excessive tolerance of g^+g^- sequences). For such chains the directional correlation functions are necessarily quite unlike the exponential form of eq 1. We expect that our results may be useful when the corresponding linear polymer can be usefully represented as a wormlike chain and when the branches are sufficiently long. But it is important to remember that excluded-volume effects near the branch point are not taken into account.

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Added Note. We have just become aware of some RIS calculations on star polypeptides by Oka and Nakajima.[16] Their results in general are very similar to those of Mattice and Carpenter.

Appendix

Here we show that $F = -f/2$ is the minimum possible F and that this occurs when the initial directions of all rays cancel. Represent by $\mathbf{u}_i$ the unit vector tangent to the ith ray at the junction point of the star. Let $\mathbf{q}_i = \sum_{j\neq i}\boldsymbol{u}_i$ and let $\mathbf{s} = \sum_j \boldsymbol{u}_j = \mathbf{q}_i + \mathbf{u}_i$ be the sum of all $\mathbf{u}_i$. We wish to show that when $\mathbf{s} = 0$, $F = -f/2$ and is minimal. Expressing $\mathbf{u}_i$ in spherical-polar coordinates provides the following:

$$F = \sum_{i<j} \sin\theta_i \sin\theta_j \cos(\phi_i - \phi_j) + \sum_{i<j} \cos\theta_i \cos\theta_j \tag{17}$$

F is extremal whenever its derivatives with respect to θ_i and ϕ_i are zero for all i. Differentiation with respect to θ_i and ϕ_i yields expressions that may be written as follows:

$$(\partial \boldsymbol{u}_i/\partial\theta_i)\cdot\mathbf{q}_i = 0 \tag{18}$$

$$(\mathbf{u}_i \times \mathbf{q}_i)_z = 0 \tag{19}$$

The result must be independent of coordinate system, and we may thus write eq 19 as

$$\mathbf{u}_i \times \mathbf{q}_i = 0 \tag{20}$$

The derivative $\partial\boldsymbol{u}_i/\partial\theta_i$ is normal to $\mathbf{u}_i$. This means that eq 18 is true whenever eq 20 is, so that eq 20 is the only condition necessary for F to be extremal. Therefore, F is extremal whenever $\mathbf{u}_i$ and $\mathbf{q}_i$ are collinear. Then $\mathbf{q}_i = \alpha_i\boldsymbol{u}_i$ for α_i some scalar. Then $\mathbf{s} = \mathbf{u}_i + \mathbf{q}_i = (1 + \alpha_i)\mathbf{u}_i$ and $\mathbf{s}$ is collinear with each $\mathbf{u}_i$. Therefore there are two cases in which F is extremal: either (1) $\mathbf{s} = 0$, or (2) the $\mathbf{u}_i$ are all collinear, with f_1 in one direction, f_2 in the opposite direction, $f_1 + f_2 = f$, and $f_1 \neq f_2$ (obviously $f_1 = f_2$ would fall under the first case). In these two cases we may evaluate F:

Case 1:

$$F = \tfrac{1}{2}\sum_i\sum_{j\neq i}\mathbf{u}_i\cdot\mathbf{u}_j = \tfrac{1}{2}\sum_i\mathbf{u}_i\cdot\mathbf{q}_i = -\tfrac{1}{2}\sum_i\mathbf{u}_i^2 = -f/2$$

Case 2:

$$F = \tfrac{1}{2}[f_1(f_1 - 1) + f_2(f_2 - 1) - 2f_1f_2]$$

The latter exceeds the former by the amount $(f_1 - f_2)^2/2$, which establishes the proof.

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Polymerization of 1-Oxa-3-thiacyclopentane. Structure of the Polymer

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Introduction

The cationic polymerization of 1,3-dioxolane has been widely investigated in the past.[1-6] However, no definitive conclusion can be obtained about the polymerization mechanism of this cyclic acetal due, among other reasons, to the obscure initiation reaction and to the well-known fact that there are a few active species which carry the propagation reaction in the cationic polymerization of cyclic ethers.[7-9] A monomer similar to 1,3-dioxolane is 1-oxa-3-thiacyclopentane. The former polymer can be schematically converted to the latter by substituting a sulfur atom for one of the oxygen atoms in the 1,3-dioxolane ring. Very few studies have been reported dealing with the polymerization of 1-oxa-3-thiacyclopentane.[10,11] A very recent study[11] on the cationic polymerization of this monomer indicates that, although the polymerization seems to be initiated by quantitative formation of ethylsulfonium, the propagation is not the simple repeating formation of sulfonium ions, which are the propagating

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Table I
Elemental Analysis and Chemical Shifts (^{1}H NMR) for the Monomer and for the Polymers

	elem anal.		^{1}H NMR (CDCl$_3$)	
	% C	% H	δ	$\overline{M}_n$
monomer	39.43	6.71	3.0 (t, 2 H), 4.0 (t, 2 H), 4.9 (s, 2 H)	
polymer A	39.60	6.69	2.85 (t, 4 H), 3.77 (t, 6 H), 4.68 (s, 2 H)	2000
polymer B	38.84	6.67	2.85 (t, 4 H), 3.76 (t, 6 H), 4.70 (s, 2 H)	5000
theoretical	39.97	6.67		

species in the polymerization of thiiranes and thietanes.[12]

The purpose of this work was to determine the structure of the polymer obtained by cationic polymerization of 1-oxa-3-thiacyclopentane. Attention was also given to the analysis of the structure of the polymer obtained by the condensation reaction of 2-mercaptoethanol and paraformaldehyde during the synthesis of the monomer.

Experimental Section

Materials. 2-Mercaptoethanol, paraformaldehyde, and benzene (all purities exceeding 99%) were used as received.

Synthesis of the Monomer. 1-Oxa-3-thiacyclopentane was obtained by condensation of paraformaldehyde (1 mol) and 2-mercaptoethanol (0.5 mol) under refluxing benzene, using *p*-toluenesulfonic acid as catalyst (≅2%). Water was separated as the azeotrope in a Dean–Stark distillation trap, and the reaction mixture was a viscous mass composed of polymer and monomer (1-oxa-3-thiacyclopentane). The solvent and the monomer were removed from the reaction products by distillation on a high-vacuum line. The residual mass was washed several times with distilled water to eliminate the catalyst and it was then dissolved in chloroform and precipitated with methanol. Finally, it was freeze-dried from benzene (polymer A). The yield of polymer was 60% and that of monomer 20%.

1-Oxa-3-thiacyclopentane was purified by successive fractional distillations [bp 122 °C (710 mmHg)]. It was further refluxed with sodium for 2 days and distilled in vacuo into a sodium mirror.

Cationic Polymerization of 1-Oxa-3-thiacyclopentane. The cationic polymerization of the purified monomer was carried out at 70 °C for 2 h, in vacuo, using BF$_3$·Et$_2$O as catalyst. The yield of the polymer, purified as in the above case, was about 25%.

Characterization. The monomer and both polymers obtained by condensation (polymer A) and by cationic polymerization (polymer B) were characterized by elemental analysis and by ^{1}H NMR spectroscopy (Varian XL-100). The molecular weight of the polymers was measured with a Knauer vapor pressure osmometer. The principal characteristics of the monomer and of the polymer are indicated in Table I.

Results and Discussion

The results of the elemental analysis show that the chemical composition of both polymers (A and B) is identical with that of the monomer. In the same way, the NMR spectrum of the monomer presents two triplets and one singlet, the ratio and position of the peaks being in agreement with the structure of 1-oxa-3-thiacyclopentane. The NMR spectra of the two polymers are equivalent (Figure 1) and present two triplets and one singlet, but in this case, the signals of the peaks present an intensity ratio of 2:4:6, corresponding to the singlet (δ 4.68) and to the two triplets (δ 2.85 and 3.77), respectively. It is obvious that the structure of the polymers differs from that expected for poly(1-oxa-3-thiacyclopentane), since then the two triplets and the singlet should have the same intensity. According to the spectrum of Figure 1, the structure of the polymers corresponds to that of an ideally alternating copolymer of 1,3-dithiolane and 1,3-dioxolane, whose repeating unit is given in Figure 2. Actually, in the proposed structure there are four types of protons, indicated in the figure as a, b, c, and d. The singlet corresponding to the a protons (δ 4.68) is similar to that observed for the same kind of protons in poly(1,3-dioxolane)[13] (δ 4.78). The singlet for the b protons (δ 3.77) is the same as that detected for the methylenic protons with two adjacent sulfur atoms in poly(1,3-dithiacyclooctane)[14] (δ 3.67). Moreover, the singlet overlaps with the triplet of the two c protons (δ 3.77), which possess the same chemical shift as that in poly(1,3-dioxolane)[13] (δ 3.73), poly(thiodiethylene glycol)[15] (δ 3.70), and poly(1,3-dioxa-6-thiocane)[16] (δ 3.73). As a consequence, the triplet corresponding to the c protons has a higher intensity than expected because the signal is increased by resonance (singlet) with the b protons. Finally, the d protons (δ 2.85) have a resonance similar to that of equivalent protons in polymers of the poly(thiodiethylene glycol)[15] (δ 2.75) and poly(1,3-dioxa-6-thiocane)[14] (δ 2.73) type.

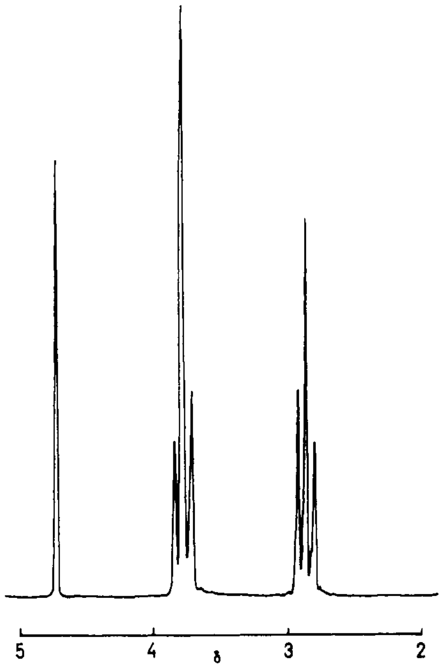


Figure 1. NMR spectrum of the polymers obtained by condensation (polymer A) and by cationic polymerization (polymer B).

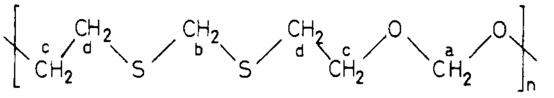
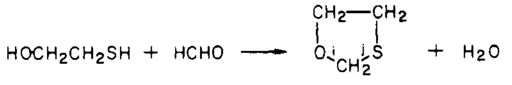


Figure 2. Structural unit for both A and B polymers.

The reason that condensation of 2-mercaptoethanol and formaldehyde gives an alternating copolymer of 1,3-dithiolane and 1,3-dioxolane, instead of poly(1-oxa-3-thiacyclopentane), is the high acidity of the thiol groups in comparison with that of the hydroxyl groups. As a result, the former groups react faster with formaldehyde than the latter, so that, during the first stages of the condensation, two competitive reactions may occur:

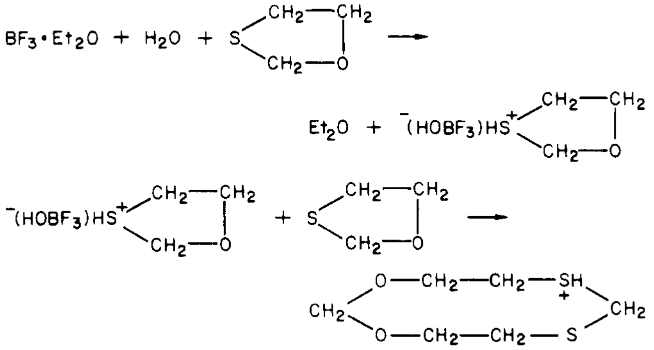
$$2OHCH_2CH_2SH + HCHO \longrightarrow HO(CH_2)_2SCH_2S(CH_2)_2OH + H_2O \quad (a)$$



(b)

The glycol obtained in the first reaction can further react with paraformaldehyde to give the polymer described above. It should be stressed that the reason for disregarding possible random reactions between different active groups is the necessity of making the condensation mechanism conform to experimental results, according to which the methylenic groups should not be between an oxygen atom and a sulfur atom.

The details of the mechanism of the cationic polymerization of 1-oxa-3-thiacyclopentane are at present obscure. A kinetic mechanism which might explain the structure obtained implies either that bond scission occurs in a rigorously alternate order at i bonds and at j bonds on the monomer or that the formation of a cyclic dimer takes place probably according to the following mechanism:[17]



In this case the polymerization should proceed by a process of ring expansion in a way similar to that proposed by Plesch and Westermann[13] for the polymerization of 1,3-dioxolane.

Very recently, Kawakami et al.[11] have discussed the reaction mechanism of the polymerization of 1-oxa-3-thiacyclopentane with oxonium salts. According to these authors, the foreseeable structure of the polymer, $CH_2CH_2OCH_2S$, might be modified by extensive chain transfer or back-biting in the polymerization system; hence the complexity of the NMR spectrum and the low molecular weight of the reaction product. In our case, however, the clear and simple NMR spectra as well as the relatively high molecular weight ($\bar{M}_n = 5000$) of the polymer suggest that chain-transfer reactions are not present, possibly as a consequence of a different mechanism of polymerization.

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Raman Spectral Evidence for Molecular Orientation in Native Cellulosic Fibers

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Studies of the Raman spectra of individual native fibers have revealed new information concerning ordering of molecular chains within the cell walls. Cellulose, the primary polysaccharide component of the walls, is the β-1,4-linked polymer of anhydroglucose. It is unique among cell wall polysaccharides in that all heavy-atom linkages to the pyranose rings are equatorial and that the methine CH bonds are all axial with respect to the individual anhydroglucose residues. Previous investigations, utilizing X-ray diffractometry and birefringence, detected the average angle of the molecular chains relative to the axes of the fibers.[1,2] The Raman spectra suggest that there is also a preferential orientation of the anhydroglucose units in tangential planes and a correlated preferential orientation of the methine CH bonds in the radial direction.

The evidence for preferential orientation is derived from the response of the intensities of characteristic bands in the spectra of single fibers to changes in the polarization of the incident exciting radiation relative to the axis of the fiber.

Three spectra are presented. The first two were recorded on a Spex 1401 double monochromator in the back-scattering mode. The unfolded schematic representation in Figure 1 shows the relative polarizations of the incident exciting radiation and the Raman scattered light in each recording mode; the depolarized spectra were identical for both orientations of the incident beam. The laser-illuminated portion of the fiber was imaged in the plane of the entrance slit such that the fiber axis was parallel to the slit. The signal received was thus an average, characteristic of the portion of the fiber image admitted through the entrance slit. Figure 2 is the spectrum of a Ramie fiber; Ramie is known to have molecular chains essentially parallel to the fiber axis.[3] Manifestations of this molecular orientation are noted in the changes in relative intensities of a number of the polarized bands when incident-beam polarization is altered. In particular, the 1098-cm^{-1} skeletal band[4] is very intense in the parallel mode and much reduced in the perpendicular mode. The reverse is true of the methine stretching bands at 2920 cm^{-1},[5] and this, of course, reflects the orientation of all the methine CH bonds essentially perpendicular to the direction of the cellulose chain.

Figure 3 shows analogous spectra of a cotton fiber recorded in the same modes. As was perhaps to be expected from a fiber with a variable fibril angle,[6] the intensity of the 1098-cm^{-1} skeletal was of the same order of magnitude in both modes. The unexpected feature in this spectrum was that the methine stretching band does not follow a

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