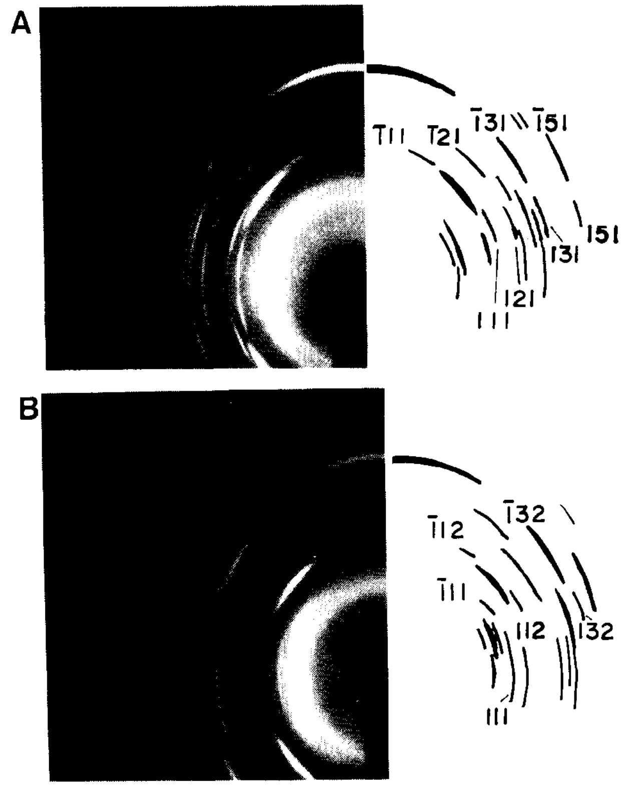

Figure 1. X-ray diffraction patterns and their schematic representations for the tilt samples of (A) form II and (B) form III.

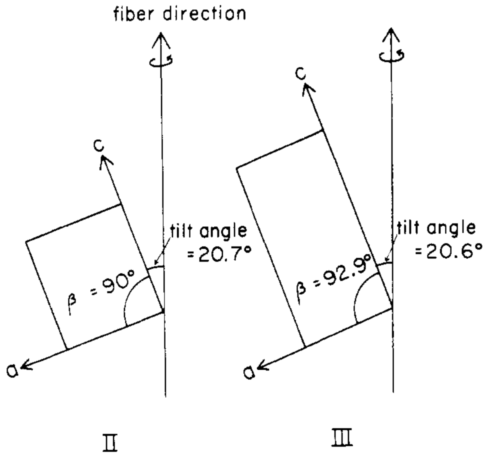

Figure 2. Orientation of the crystallites in the tilt samples of forms II and III.

Table I
Intensities of *hkl* and $\bar{h}kl$ Pairs of Reflections by the Tilt Sample of Form II

index	rel intens[a]	$\|F_c\|$
111	m	22.2
$\bar{1}11$	w	11.3
121	vw	10.6
$\bar{1}21$	w	18.1
131	vw	7.9
$\bar{1}31$	w	23.4
141	vw	10.6
$\bar{1}41$	w	29.1

[a] m = medium, w = weak, vw = very weak, vvw = very very weak.

Table II
Intensities of *hkl* and $\bar{h}kl$ Pairs of Reflections by the Tilt Sample of Form III

index	rel intens[a]	$\|F_c\|$
111	w	42.0
$\bar{1}11$	vvw	15.6
112	vw	29.2
$\bar{1}12$	vvw	16.8
131	vw	32.4
$\bar{1}31$	vvw	22.9
132	vw	24.7
$\bar{1}32$	m	68.5
151	vw	27.6
$\bar{1}51$	vw	34.2

[a] See footnote of Table I.

Å, $\alpha = \beta = \gamma = 90°$)[1] and the reflections in Figure 1B can be indexed by the unit cell of form III (a = 4.96 Å, b = 9.58 Å, c (fiber period) = 9.23 Å, β = 92.9°, $\alpha = \gamma = 90°$). In both samples, the c axes of the crystallites tilt about 20° around the b axes from the fiber axis of the sample and the crystallites are equally distributed over all angles around the fiber axis (Figure 2). In the case of the form II, it was found that the tilt angle depends on the heat treatment temperature, and the sample with the angle about 45° is obtained by annealing at 175 °C.

On the diffraction pattern of form III, it is observed that the arc of the 132 reflection is located outside the arc of $\bar{1}32$. This suggests that the β unit cell parameter deviates from 90° (β = 92.9°). Lovinger also observed this deviation by electron diffraction.[6] In both cases of forms II and III, *hkl* and $\bar{h}kl$ reflections have different intensities. This clearly shows that the crystal structures of forms II and III should belong not to the orthorhombic system but to the monoclinic system. Tables I and II give observed intensities and calculated structure factors for some pairs of *hkl* and $\bar{h}kl$ reflections of forms II and III, respectively. Here, the structure factors were calculated on the basis of the reported crystal structures.[1,2] The tables showed good agreement between observed and calculated values. This suggests that our monoclinic structures are correct. In form II, a slight discrepancy between observed and calculated intensities can be found.[1] This should be interpreted by a kind of disorder contained in the crystallite of form II. A study of structure and disorder of form II is now in progress and the results will be published soon.

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Iodide-Specific Formation of κ-Carrageenan Single Helices. ^{127}I NMR Spectroscopic Evidence for Selective Site Binding of Iodide Anions in the Ordered Conformation

The carrageenans are sulfated D-galactans extracted from certain marine red algae and characterized by al-

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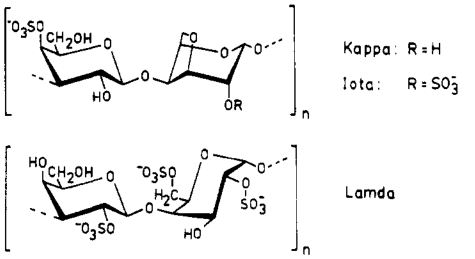
Chart I



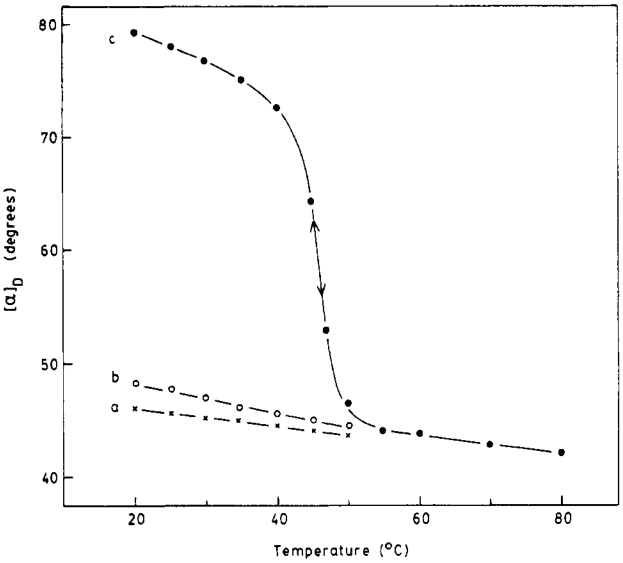


Figure 1. Specific optical rotation of 1% (w/v) aqueous tetramethylammonium κ-carrageenate ($\bar{M}_n$ = 150 000) at different temperatures in the absence of salt (a), the presence of 0.15 M $N(CH_3)_4Cl$ (b), and the presence of 0.15 M $N(CH_3)_4I$ and 10^{-3} M $Na_2S_2O_3$ (c).

ternating α(1→3), β(1→4)-linked structures. The 4-linked units are sometimes in the 3,6-anhydro form. Differences in degree of sulfation and 3,6-anhydrogalactose content probably exist both among and regionally within molecules in most extracts. Those from *Eucheuma cottonii*, *Eucheuma spinosum*, and *Gigartina acicularis*, however, appear to approach the idealized structures depicted in Chart I with the names κ-, ι-, and λ-carrageenan, respectively.[1-5] Their physical properties, particularly the gel-forming ability, are very different.

Ions play an essential role in the molecular processes associated with conformational transitions and gelation of carrageenans.[1,2,5-7] Previous studies have mostly dealt with cation-specific helix–coil transitions and aggregations of helices. The reported independence of the nature of the anions[8] suggests that they do not take part in these processes.

However, the iodide anion seems to be an exception. Even in the presence of the strong gel-promoting potassium ions the iodide anions may prevent aggregation and gelation, as seen in Table I.

When the specific optical rotation, α_D, of tetramethylammonium κ-carrageenate in an aqueous solution of $N(CH_3)_4$ salt was measured as a function of temperature, a striking anion dependence appeared. The results in Figure 1 show that a conformational transition occurred by lowering the temperature in I^- salt as opposed to solutions in Cl^- salt. The transition temperature, 46 °C, defined by the inflection point, was independent of the polymer concentration within the range investigated, 0.1–3% (w/v), and there was no hysteresis. No turbidity or signs of aggregation were visually observed as the temperature was lowered.

Table I

Modulus of Rigidity, G_R, of 1% (w/v) Carrageenan[a] Gels Induced by Different Potassium Salts (0.1 N)

	anion						
	F^-	Cl^-	Br^-	I^-	NO_3^-	IO_3^-	SO_4^{2-}
G_R, $N\cdot cm^{-2}$	0.43	0.54	0.42	0	0.40	0.36	0.43

[a] Extract from *Chondrus crispus*.

Table II

Number-Average Molecular Weights, $\bar{M}_n$,[a] Second Virial Coefficients, B,[b] and Intrinsic Viscosities, $[\eta]$,[c] for Tetramethylammonium κ-Carrageenate Samples[d] in 0.15 M $N(CH_3)_4Cl$ and 0.15 M $N(CH_3)_4I$ at 25 °C

sample	coion	$\bar{M}_n$	$B \times 10^3$	$[\eta]$
1	Cl^-	32 000	3.0	80
	I^-	35 000	1.4	130
2	Cl^-	150 000	2.0	420
	I^-	150 000	1.2	730

[a] Determined in a Knauer membrane osmometer. [b] B in $(mL\cdot mol)/g^2$. [c] $[\eta]$ in mL/g; determined in a Cannon Ubbelohde capillary viscometer. [d] Sample 2 was prepared from *Eucheuma cottonii* by CECA SA, France. Sample 1 was the same sample hydrolyzed for 2 days at pH 5 at room temperature.

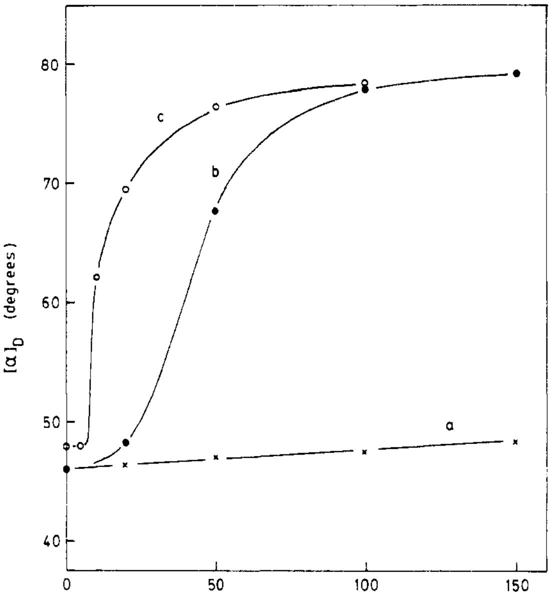


Figure 2. Specific optical rotation of 1% (w/v) aqueous tetramethylammonium κ-carrageenate ($\bar{M}_n$ = 150 000) at 25 °C and different concentrations of added salts: (a) $N(CH_3)_4Cl$; (b) $N(CH_3)_4I$ in the presence of 10^{-3} M $Na_2S_2O_3$; (c) $N(CH_3)_4I$ in the presence of 0.1 M $N(CH_3)_4Cl$ and 10^{-3} M $Na_2S_2O_3$.

The conformational transition was markedly dependent upon the ionic strength as seen in Figure 2. A critical ionic strength for the transition in $N(CH_3)_4I$ salt, ≈20 mM, is demonstrated by the sigmoid-shaped curve b (Figure 2). While the I^- anion is essential for the transition to occur, the concentration requirement is reduced when the ionic strength is increased by addition of Cl^- salt as indicated in curve c (Figure 2).

To ensure that the effect was not due to the formation of iodine complexes, which is well-known for amylose,[9] all iodide solutions were made 10^{-3} M in $Na_2S_2O_3$ to prevent oxidation. The results were independent of the small

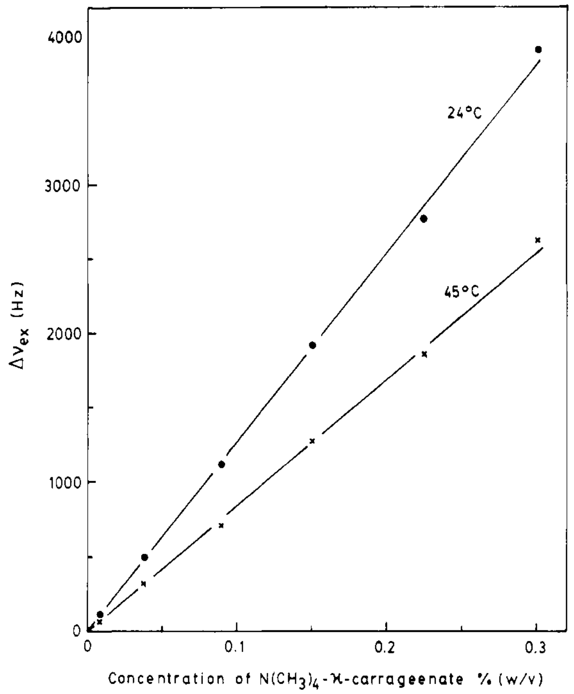


Figure 3. Variation of ^{127}I excess NMR line width, $\Delta\nu_{ex}$ (full width at half-maximum), with tetramethylammonium κ-carrageenate concentration, % (w/v), obtained at 19.9 MHz with a JEOL FX-100 NMR spectrometer equipped with a multinuclear observation system. In addition to the carrageenan, the solutions contained 0.15 M $N(CH_3)_4I$ and 10^{-3} M $Na_2S_2O_3$.

amount of sodium thiosulfate present.

Values of the number-average molecular weights of samples of tetramethylammonium κ-carrageenate in $N(CH_3)_4$ salts determined by osmometry at 25 °C (Table II) did not show any anion dependence. This result together with the concentration independence of the conformational transition in $N(CH_3)_4I$ salt indicates that the transition must be *intra*molecular. The lower second virial coefficients for the I^- solutions indicate a decrease in the solubility of the molecules compared to the Cl^- solutions.

The increase in intrinsic viscosity in the I^- solutions (Table II) indicates that the transition is associated with a marked stiffening of the chains, typical for the formation of some asymmetric intramolecular ordered conformations which might be single helices.

Since the halide ions may be conveniently studied by NMR,[10] we found it expedient to probe halogen–polysaccharide interactions through observation of the coions themselves. The halogen nuclei all have spin quantum number $I > {}^1/_2$ and possess a sizable quadrupole moment. Their relaxation is mainly due to interactions between their quadrupole moments and the fluctuating electric field gradients at the nucleus.[10] While the symmetric environment and rapid motion of aqueous halide ions make quadrupolar relaxation ineffective, the relaxation rate is greatly enhanced when these ions interact or bind to a macromolecule. This is due to the combined effect of a large field gradient created by ionic charges and dipole moments at the binding site on the macromolecule and a retarded molecular motion. Hence, if the anions are exchanging rapidly between the free state in solution and the bound state on the macromolecule, the interaction shows up as a line broadening of their NMR signal which is proportional to the fraction of bound ions.

This is just what we observed for the ^{127}I NMR resonance in the presence of κ-carrageenan below the transition temperature. As shown in Figure 3, the excess line width, $\Delta\nu_{ex} = \Delta\nu_{obsd} - \Delta\nu_0$, $\Delta\nu_{obsd}$ being the observed line width and $\Delta\nu_0$ that obtained in the absence of polysaccharide, increases linearly with κ-carrageenan concentration. The line width was not affected by the small amount of $Na_2S_2O_3$ present, and the line broadening is certainly not a result of chemical exchange of ^{127}I between I^- and I_3^-.[11] Hence, this observation points unambiguously to the binding of a fraction of iodide anions to the κ-carrageenan. Furthermore, it implies that the intrinsic relaxation rate of polysaccharide-bound iodide anions and the number of iodide binding sites per macromolecule stay constant independent of carrageenan concentration. It is worth noting that no effect on the ^{127} I NMR resonance was observed for either ι- or λ-carrageenan. In any event, it is perhaps not surprising that the more highly charged ι- and λ-carrageenans do not retain iodide binding sites. The ^{35}Cl NMR resonance was not affected by any of the carrageenans.

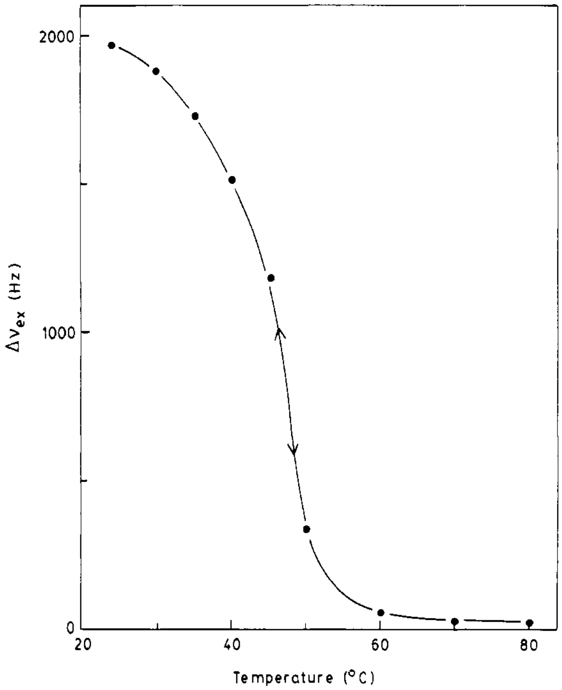


Figure 4. Temperature dependence of ^{127}I excess NMR line width, $\Delta\nu_{ex}$, for the sample defined in Figure 3 containing 0.15% (w/v) tetramethylammonium κ-carrageenate. The figure shows the effect of cooling and heating, allowing 10 min for equilibration at each temperature.

The ^{127}I excess NMR line width is shown in Figure 4 as a function of temperature for a sample containing 0.15% (w/v) tetramethylammonium κ-carrageenate in 0.15 M $N(CH_3)_4I$. Since this curve qualitatively closely resembles the behavior of the optical rotation (Figure 1), including no hysteresis, it demonstrates convincingly the interplay between the iodide binding phenomena and the conformational transition. κ-Carrageenan interacts with iodide anions only in its ordered conformation. This result clearly shows the feasibility of the NMR method to establish changes in ion binding occurring as a result of changes in secondary structure. It leads to the conclusion that iodide binding to κ-carrageenan gives rise to a structure stabilization of its ordered conformation below 46 °C provided the ionic strength is sufficiently high. The finding that the conformational transition temperature does not change with concentration, as also judged by the constant ratio between the ^{127}I excess NMR line width at 24 and 45 °C (Figure 3), strongly indicates an intramolecular ordered conformation, presumably a single helix, in accordance with the osmometry and viscosity data.

An important consequence of the present report is that specific site binding of inorganic anions to polyanions may occur and has to be taken into account in discussions of anion-dependent properties of acidic polysaccharides.

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Studies on Comblike Polymers. 6. Tacticity of Poly(octadecylethylene) by ^{13}C NMR and Differential Scanning Calorimetry

Comblike polymers have been intensively studied in recent years owing to their interesting structure and properties.[1] These polymers are known to crystallize through side-chain packing and, for most of them, the crystallization takes place independent of stereoregularity. Recent studies,[2,3] carried out in our laboratory have indicated that the stereoregularity of long-side-chain polyolefins and polyethers can be correlated with their thermal properties. Indeed, the crude products of the stereospecific polymerizations have been shown to be composed of two immiscible crystalline phases which can be separated by appropriate solvent fractionation.[4] In agreement with a previous suggestion made by Aubrey and Barnatt[5] for poly(hexadecylethylene), we supposed that the higher melting polymer was isotactic and that the lower melting one was atactic. We thought, therefore, that a simple calorimetric method could be used for a rough determination of the degree of tacticity of these polymers. To prove this, a direct measure of the stereoregularity of the polymers investigated was necessary. However, no such measure has been described so far for any of the comblike polymers studied, including the intensively investigated[5-9] long-side-chain polyolefins. We thought that useful information could be obtained by ^{13}C NMR. In this Communication we report the preliminary results of this study. A comparison of the ^{13}C NMR data with DSC data is also made.

Poly(octadecylethylene) was prepared by stereospecific polymerization with α-$TiCl_3$–$Al(i\text{-}C_4H_9)_3$ (1/3.3 mole ratio) as already described.[2] The crude product of the polymerization (sample C, Table II) was extracted in a Kumagawa apparatus with boiling ether, giving a soluble fraction (sample E) and a residue (sample B). Sample A was obtained as described previously[4] by double crystallization from heptane solution. Sample D was a blend of samples A and E (32/68 w/w).

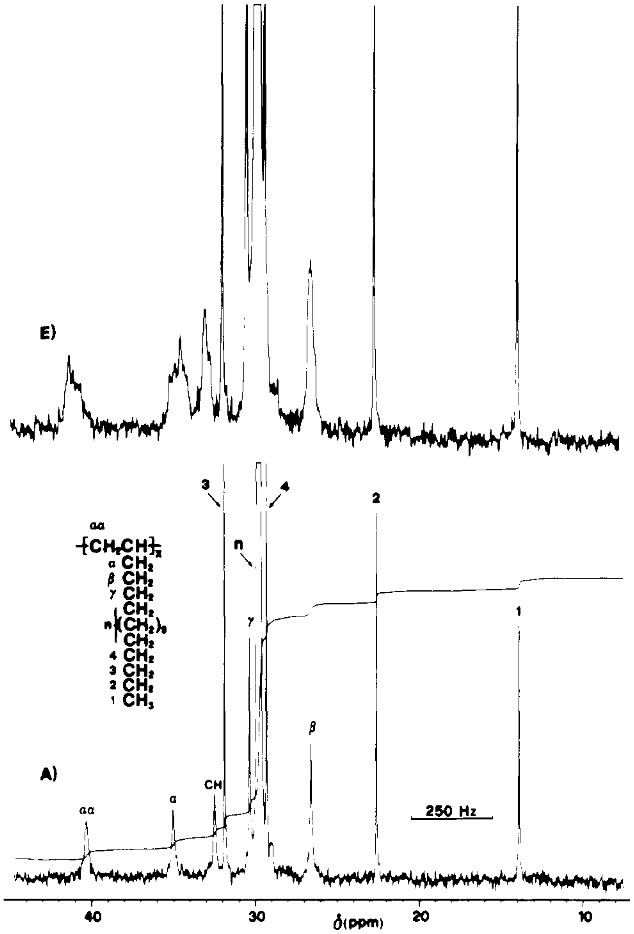

Figure 1. 50.28-MHz ^{13}C NMR spectra of poly(octadecylethylene) samples A and E in $CDCl_3$ (cf. Table II for sample identification).

^{13}C NMR spectra were run on a Bruker WP 200 apparatus operating at 50.28 MHz. The spectral conditions were as follows: pulse width 60°, relaxation delay 2 s, acquisition time 1 s. Since the T_1 values of the backbone carbons as well as those of the C_α and C_β carbons are less than 300 ms, the relevant resonances, which are sensitive to tacticity, were fully relaxed under these conditions. Different solvents and temperatures were tested: the best results were obtained with $CDCl_3$ solutions (5–10% w/v) at 323 K. Ppm, originally recorded from $CHCl_3$, were converted to the Me_4Si scale.

The DSC traces were obtained as described previously.[10]

The ^{13}C NMR spectra of samples A and E (cf. Table II for sample identification) are shown in Figure 1. The spectrum of sample A consists of well-defined, sharp signals and this fact has been considered as indicative of a regular enchainment of the monomer units, as expected for substituted vinyl polymers of high stereoregularity. The carbon assignments, in terms of a single repeating unit, have been made according to Lindeman and Adams.[11] The observed and calculated values of the chemical shifts are collected in Table I.

The spectrum of sample E (Figure 1) shows a more complex pattern. The resonances of the $C_{\alpha\alpha}$ and C_α methylene carbons appear as multiplets. Their fine structure may be reasonably attributed to tacticity effects and points to a low degree of stereoregularity of the sample. Sensitivity to stereosequences is also exhibited, to a lesser

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