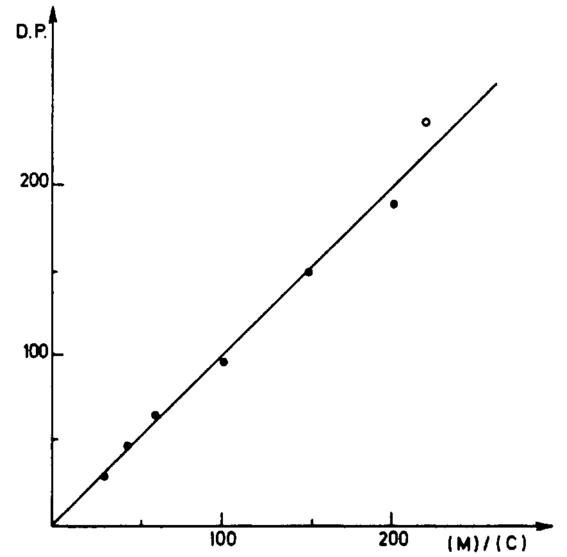

Figure 1. Dependence of DP on monomer/catalyst molar ratio in the polymerization of caprolactone: (●) vapor pressure depression method; (○) membrane osmometry.

average molecular weight is exactly doubled (21,500-44,300), while the polydispersity remains unchanged. The molecular weight distribution ($\bar{M}_w/\bar{M}_n$, calculated from GPC data) is usually in the range of 1.3-1.5, indicating that the initiation rate is not definitely much faster than the propagation.

The structure of the main products obtained with [M]/[C] ratio of 1 and 2 has been determined by various measurements (Table I); it fits with an insertion of the monomer molecules into an Al-OR bond of the catalyst through acyl-oxygen cleavage of the lactone ring. After hydrolysis of the metal-oxygen bond, hydroxyesters of the type $H[-O(CH_2)_5CO-]_xOC_4H_9$ are obtained.

These results indicate also the presence of only one growing chain for every AlOZnOAl unit, despite the presence of four potential precursor OR groups.

This relationship most probably depends on the previously reported[4] coordination association of the catalytic units. Cryoscopic determinations have indeed indicated that in the present case there is no important dissociation of the catalytic aggregates by the monomer. This hypothesis is substantiated by experiments performed in the presence of 1-butanol, which is known to dissociate completely these oxoalkoxide aggregates. Under these conditions, the mean DP of the polyester obtained corresponds to (M)/4(Zn); in other words, every OR group is now able to start a polymer chain. Experiments are now being performed with other oxoalkoxides having different degrees of association to confirm this relationship between the association and the number of chains produced.

Further studies on the mechanistic and preparative implications of this new living polymerization system are also in progress.

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Conformation of Guanosine Cytidine 3',5'-Monophosphate (GpC)

We report here the results of a calculation to determine the conformation of a dinucleoside phosphate, guanosine cytidine 3',5'-monophosphate (GpC), for which X-ray diffraction data were available in this laboratory. This calculation was made by computing the conformational energy of the molecule and then searching for minima with respect to the eight flexible dihedral angles (see Figure 1), which were permitted to vary simultaneously. Previous calculations of the energy of mono- and polynucleotides have been made,[1,2] but there was no attempt to minimize the energy simultaneously with respect to all the parameters.

The energy calculation was modeled after that of Scott and Scheraga[3] on polypeptides. The total energy was taken as the sum of the contributions by nonbonded, electrostatic, and torsional potentials

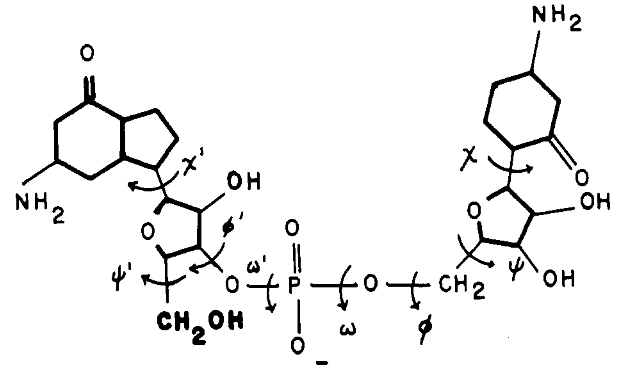

Figure 1. Definition of conformational angles of guanosine cytidine 3',5'-monophosphate (GpC) following the convention of Sussman.[7]

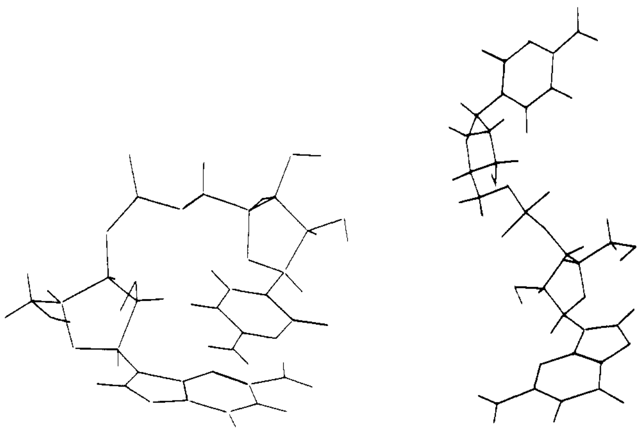

Figure 2. (a, left) Lowest energy conformation of GpC; (b, right) next lowest energy conformation of GpC.

$$E = \sum_{i<j}\sum (a_{ij}r_{ij}^{-6} + b_{ij}r_{ij}^{-12}) + \sum_{i<j}\sum 332q_iq_jr_{ij}^{-1}\epsilon^{-1} + \sum_{k=1}^{8} \frac{V_{0,k}}{2}(1 + \cos 3\theta_k)$$

In this equation, the double sums extend pairwise over all atoms i and j, where r_{ij} is the distance between the two

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Table I
Selected Minimum Energy Conformations of GpC

Starting Conformation Dihedral Angles (deg)								Sugar Pucker	Final Conformation Dihedral Angles (deg)								Energy, E (kcal/mol)	Final Order
χ'	ψ'	ϕ'	ω'	ω	ϕ	ψ	χ		χ'	ψ'	ϕ'	ω'	ω	ϕ	ψ	χ		
								$C_{3'}$endo										
15	50	225	180	290	180	60	15		2	62	205	296	279	183	56	25	−39.0	1
15	50	225	290	290	180	60	15											
15	50	225	60	60	180	60	15		5	61	181	183	79	194	60	44	−38.1	2
15	50	225	290	60	180	60	15		−7	62	240	315	106	205	76	39	−37.3	3
15	50	225	60	290	180	270	15		−3	61	190	129	238	100	350	39	−31.1	5
15	50	225	180	60	180	60	15		−2	62	187	214	59	169	53	33	−23.3	12
15	50	225	180	290	180	270	15		2	62	189	192	295	171	303	38	−18.7	17
								$C_{2'}$endo										
55	50	225	290	60	180	180	55		−15	294	299	332	282	178	171	153	−16.7	1

Table II
Dihedral Angles Proposed for Helical RNAs

RNA	ϕ'	ω'	ω	ϕ	ψ	χ	Ref
10-fold	203	285	257	188	88		5
		291.1	259.1	189.1	80.1	10.1	6
11-fold	216	273	282	165	74		5
	203.7	292.8	288.7	186.2	58.5	13.4	6
12-fold	193.8	298.0	282.9	175.6	63.3	18.5	6

atoms, q_i is the charge on atom i, a_{ij} and b_{ij} are the parameters in the 6–12 potential, and ϵ is the dielectric constant. The single summation extends over all eight flexible dihedral angles (Figure 1), where θ_k is the kth dihedral angle, and $V_{0,k}$ is the rotational barrier height for that rotation. Values computed in ref 1 were used for the parameters a_{ij} and b_{ij}, as well as for q_i, V_0, and ϵ. Units of energy are in kilocalories per mole.

The energy was minimized by a modified version of the algorithm of Powell,[4] the dihedral angles being the variable parameters. As starting conformations various combinations of the eight dihedral angles, representative of the allowed conformations of known di- and polynucleotides,[5,6] were chosen. In particular, the initial conformations used were $\chi' = 15°$ (anti), $\psi' = 50°$, $\phi' = 225°$, $\omega' = 60$, 180, and 290°, $\omega = 60$ and 290°, $\phi = 180°$, $\psi = 60$, 180, and 270°, and $\chi = 15°$ (anti). The sugar conformations were fixed at $C_{3'}$ endo for one series of trials and at $C_{2'}$ endo for another. Table I gives the results obtained for the three lowest energies, and for a selection of other conformations.

From the set of 18 starting conformations for $C_{3'}$-endo sugars, 17 different local minima were obtained. The lowest energy conformation, resulting from two different sets of initial conditions, has dihedral angles in the range of observed helical RNAs[5-7] (see Table II). Next in energy is an extended conformation comparable to one deduced from nmr data by Barry *et al.*[8] Figure 2a,b shows the lowest and next lowest energy form, respectively. For $C_{2'}$-endo sugars, the lowest energy conformation found here was extended, and was of much higher energy than the best $C_{3'}$-endo value (see Table I).

The above computations were extended to include the effects of intermolecular hydrogen bonding, as well as additional parameters to minimize the energy with respect to position and orientation of the GpC molecule in the unit cell. Further details of these calculations, which relied heavily on use of a PDP-10/LDS-1 interactive computer graphics system, will be supplied in the future. The results indicate that the helical RNA conformation found by energy minimization, with additional refinement, satisfies our X-ray diffraction data and is in agreement with the general nature of an independent structure determination of GpC using standard crystallographic methods by Seeman *et al.*[9] The extended conformation which was near in energy to this helical form could not be packed into our crystal cell. Thus, the conformation of GpC both in the crystal and in solution, appears to be predictable by elementary energetic considerations.

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Asymmetric Pentadiene Polymerization

By using a catalyst system consisting of titanium (−)-(menthoxide)$_4$ and Al(C_2H_5)$_3$, Natta and coworkers succeeded in obtaining optically active 1,3-pentadiene polymers having a prevailingly cis-1,4 isotactic structure.[1] The sign of rotation of the polymers was (−).

Thinking of the true catalyst complexes as containing a reactive titanium–carbon bond and at least one (−)-menthoxide substituent, as suggested by the above authors, we tried to polymerize *trans*-1,3-pentadiene in the presence of catalyst systems prepared by reacting (−)-menthol with

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