Table III
Specific Retention Volumes for Poly(dimethylsiloxane)-Hydrocarbon Systems at 40°

	$V_g°$ (cm³/mole)							
	Column							
	1	2	3	4	5	Av	Summers	Dev (%)
n-Pentane	48.20	48.60	47.10	47.30	46.79	47.60	43.65	9.0
n-Hexane	124.2	126.8	123.0	124.5	122.5	124.2	114.8	8.2
Benzene	201.3	203.3	196.2	199.0	198.9	199.7	181.2	10.2
Toluene	520.3	525.1	504.8	517.0	515.8	516.6	463.7	11.40

Table IV
Specific Retention Volumes for Poly(dimethylsiloxane)-Hydrocarbon Systems at 55°

	$V_g°$ (cm³/g)		
	Column 5	Summers	Dev (%)
n-Pentane	29.80	27.43	8.6
n-Hexane	70.50	66.45	6.1
Benzene	112.5	105.4	6.7
Toluene	269.2	251.4	7.1

technique for measuring polymer-solvent interaction is still open to question.

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Communications to the Editor

A New Catalyst for the Living Polymerization of Lactones to Polyesters

The mechanism of ring-opening coordination polymerization of heterocyclic monomers such as oxiranes and lactones to high polymers has been thoroughly investigated in the presence of several types of catalysts; however, clear experimental evidence on the reaction mechanism are usually difficult to obtain, owing often to the poor knowledge of the structure of the actual catalytic species.

Table I
Characterization of the Main Products from the First and Second Steps of CL Polymerization

	Mol Wt[a]		Calcd (%)			Found (%)			
Esters	Calcd	Found	C	H	O	C	H	O	Spectroscopic Analysis
From [CL]/[Zn] = 1[b]	188	200	63.79	10.71		64.38	10.77	25.46	Ir and nmr spectra are identical (as well as glc)
$HO(CH_2)_5COO$-*n*-C_4H_9[c]	188	198			25.50				
From [CL]/[Zn] = 2[d]	344	340	62.76	9.36	27.87	63.29	9.71	27.00[e]	Nmr spectrum corresponds to $CH_3CO[-O(CH_2)_5CO-]_2O$-*n*-C_4H_9

[a] Obtained in toluene solution by vapor pressure depression method. [b] Isolated by distillation after hydrolysis. [c] Synthetized by refluxing CL in an excess of *n*-C_4H_9OH in the presence of *p*-toluenesulfonic acid. [d] Isolated by molecular distillation after hydrolysis and acetylation. [e] Calculated by difference.

A recent publication[1] prompts us to report here a new and rather clear-cut example of ring-opening polymerization of lactones to the corresponding polyesters. The catalyst used is a well-characterized aluminum-zinc oxoalkoxide, $(n\text{-}C_4H_9O)_2AlOZnOAl(n\text{-}C_4H_9O)_2$, obtained by an improvement[2] of the condensation method described earlier.[3]

This catalyst is a highly active one for some oxirane and lactone polymerizations. ε-Caprolactone (CL) is a particularly interesting monomer. Under mild conditions (10°, [CL] = 1.0 *M*, [Zn] = 1.83×10^{-2} *M*, in toluene solution) the half-polymerization time is only 23 min, and at 30° the reaction is already extremely rapid and difficult to control.

The characteristic feature of this polymerization reaction is the lack of chain termination or transfer, as indicated by the accurate correspondence between the mean degree of polymerization (DP, obtained from $\bar{M}_n$ determinations) and the monomer over catalyst molar ratio ([M]/[C] = [CL]/[Zn], at total conversion (Figure 1).

The "living" character of the propagation is also demonstrated by polymerization resumption experiments, involving the addition of a new and equal amount of monomer to a completely polymerized system. The viscosity-

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(1) J. G. Noltes, F. Verbeek, and H. G. J. Overmars, *J. Organometal. Chem.*, **24**, 257 (1970).

(2) T. Ouhadi, A. J. Hubert, and Ph. Teyssié, in preparation.

(3) M. Osgan and Ph. Teyssié, *J. Polym. Sci., Part B*, **5**, 789 (1967).

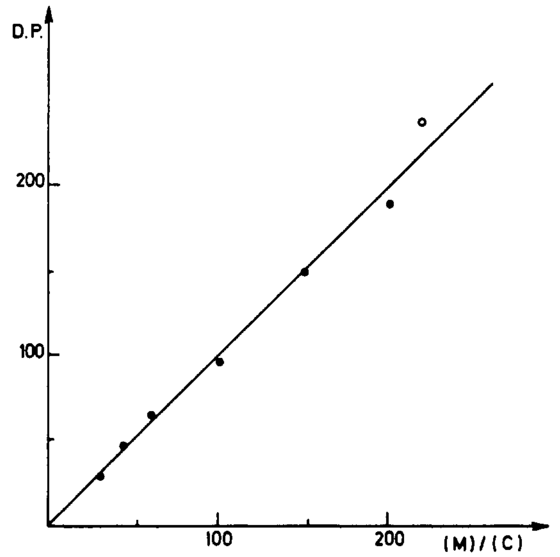

Figure 1. Dependence of DP on monomer/catalyst molar ratio in the polymerization of caprolactone: (●) vapor pressure depression method; (○) membrane osmometry.

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

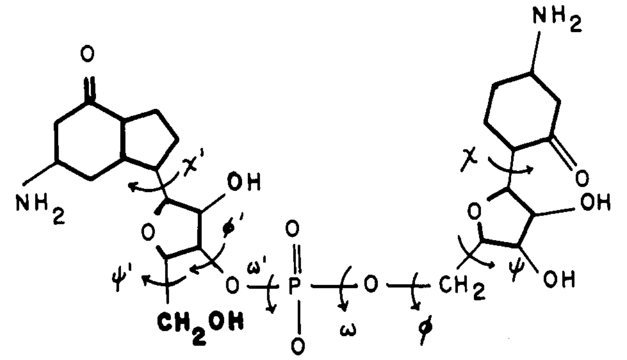

Figure 1. Definition of conformational angles of guanosine cytidine 3′,5′-monophosphate (GpC) following the convention of Sussman.[7]

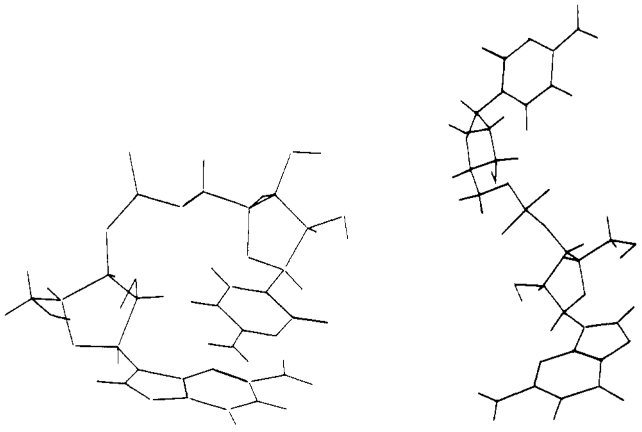

Figure 2. (a, left) Lowest energy conformation of GpC; (b, right) next lowest energy conformation of GpC.

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

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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