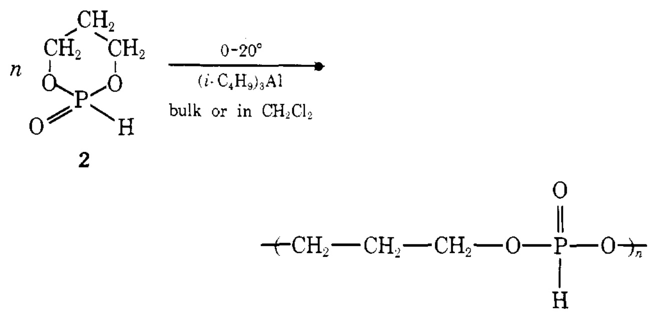
($(C_2H_5O_4P)_n$, mol wt 124.04): C, 19.36; H, 4.07; P, 24.97. Found: C, 19.55; H, 4.61; P, 23.46. Calcd for 90% poly-**1B** + 10% poly-**1**: C, 20.03; H, 4.47; P, 24.71.

An intention of preparing a polymer similar to our poly-**1B** has been mentioned in ref 7, where a reference is given to an unpublished work.

Poly(hydroxy-1,3-propylene phosphate) (Poly-2). Poly-**2** has been prepared by polymerizing the corresponding monomer (synthesized according to ref 12 from dimethyl phosphite) either thermally or at 0–20° with $(i\text{-}C_4H_9)_3Al$ (0.5–3.0 % mol) in CH_2Cl_2 solution.



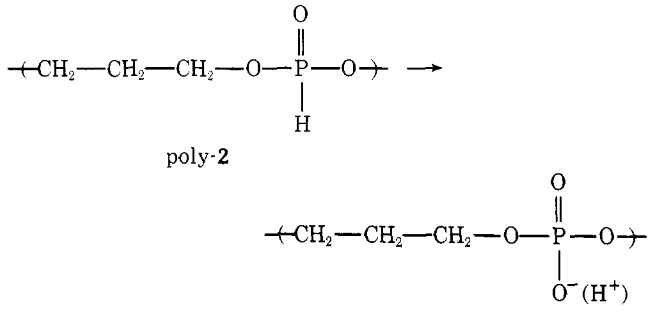
2

poly-**2**

The poly-**2**, obtained by both methods, are highly elastic colorless solid materials, very much hydrophilic and soluble, e.g., in methanol, dimethyl sulfoxide, and in water. Poly-**2** is unstable in water at room temperature and apparently hydrolyses readily. $\bar{M}_n$ measured by a high-speed membrane osmometry (in $CHCl_3$ solution) gave values up to 9.10^4

The polymer structure has been established according to the ^1H NMR spectra. The characteristic absorption of H coupled to P in the P–H bond (δ 0.95 and 13.6 ppm, $^2J_{PH}$ = 760 Hz) confirms the linear structure and the virtual absence of rearrangement during polymerization. Anal. Calcd for poly-**2** ($C_3H_7O_3$, mol wt 122.07): C, 29.52; H, 5.79; P, 25.37. Found: C, 29.10; H, 5.66; P, 24.35.

Poly-**2** was converted into the corresponding polyacid by using N_2O_4 as an oxidizing agent in CH_2Cl_2 solution at 0°:



$$-\!\left(CH_2-CH_2-CH_2-O-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{P}}-O\right)\!- \longrightarrow -\!\left(CH_2-CH_2-CH_2-O-\underset{\underset{O^-(H^+)}{|}}{\overset{\overset{O}{\|}}{P}}-O\right)\!-$$

poly-**2**

poly-**2A**

In the ^1H NMR spectrum of poly-**2A** no absorption due to the P–H bonded hydrogen atoms could be detected. The quantitative transformation of poly-**2** into the polyacid (poly-**2A**) was confirmed by titration data. Anal. Calcd for poly-**2A** ($C_3H_7O_4P$, mol wt 138.07): C, 26.10; H, 5.11; P, 22.43. Found: C, 25.57; H, 5.06; P, 21.31.

Thus, poly-**1B** and poly-**2A** are the first high molecular weight representatives of a new class of polyacids, directly related to the naturally occurring polymers. Indeed, the backbone of poly-**2A** is similar to the backbone of the nucleic acids. Thus, the polymerization technique has proved to be a valuable method for preparation of polymers of this structure.

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Influence of Dibenzo-18-crown-6 Ether on the Kinetics of Anionic Polymerization of β-Propiolactone

Model systems free of complicating side reactions, that are suitable for study of anionic propagation, are small in number and have been limited to propagations with carbanions,[1,2] alkoxyanions,[3,4] and thioalkoxyanions.[3,5] A further limitation is imposed by the limited number of monomers in these large groups that give polymers truly "living" in the sense proposed by Szwarc.

Since it is known that carboxylate anions are stable, we have been looking for conditions for polymerizing lactones to the high molecular weight polymers by anionic initiators. Polymerization of lactones without termination or transfer by use of organometallic initiators has been previously described[6,7] and there were also some indications that at least some of the lactones can polymerize anionically in the same way.[8,9] However, the rates of anionic polymerization of these monomers, that we calculated from the experimental data of various authors, are usually low at the moderate temperatures (e.g., 70 °C; k_p(obsd) ≈ $6 \times 10^{-5}\ M^{-1}\ s^{-1}$ for β-propiolactone)[10] and the further increasing of the temperature leads to the side reactions. In the polymerization initiated by carboxylate anions proton transfer from monomer is well known.[7]

We report in this communication on a new living system, namely polymerization of β-propiolactone (**1**) initiated with carboxylate anions in the presence of a crown ether, a cation complexing agent. Indeed, as it will be shown in this communication, the apparent (measured) bimolecular rate constant of propagation of **1** initiated with sodium acetate (**2**) increases not less than 10^2 times when the complexing crown ether (dibenzo-18-crown-6 ether (**3**)) at the [**3**]/[**2**] ratio higher than 3 is present; polymerization at these conditions has a living character. The substantial increase of the rate of polymerization allowed us to lower the polymerization temperature and this, apparently, slowed down the mentioned above transfer reactions.

Monomer. β-Propiolactone (**1**) (Fluka AG) was distilled; the fraction boiling at 61.0–61.3 °C (20 mm) was collected. After drying over CaH_2 at room temperature for 1 week it was distilled again on a hyvac line, directly into the ampoule with breakseals used as receivers. Ampoules were sealed off and stored in the dark below 0 °C.

Initiator. Sodium acetate (**2**), anhydrous (POCh, Po-

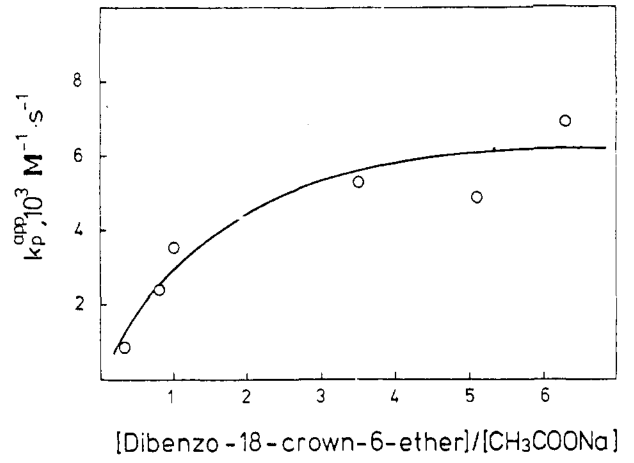


Figure 1. Dependence of the apparent rate constant of propagation (k_p^{app}) on the [3]/[2] ratio for the polymerization of 1 in CH_2Cl_2 at 35 °C: $[1]_0 = 3$ M, $[2]_0 = 38 \times 10^{-3}$ M.

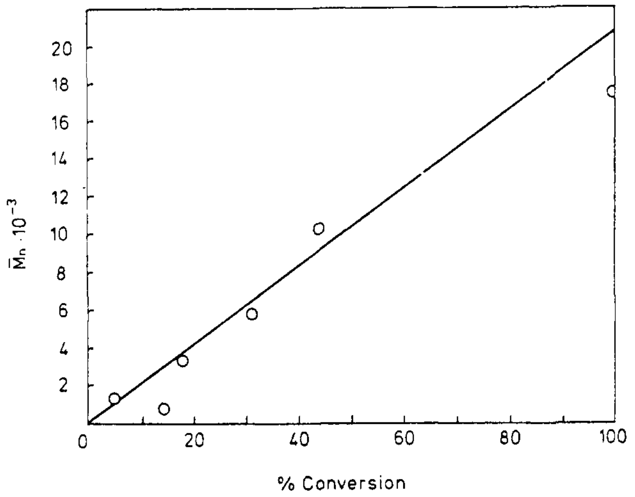


Figure 2. Dependence of the $\bar{M}_n$ of poly-*1* on conversion in the polymerization of 1 in CH_2Cl_2 at 35 °C: $[1]_0 = 2.32$ M, $[2]_0 = 7.79 \times 10^{-3}$ M, $[3] = 1.48 \times 10^{-2}$ M.

land), was heated at 100 °C under high vacuum during 24 hr and distributed under vacuum into subsequently sealed off phials.

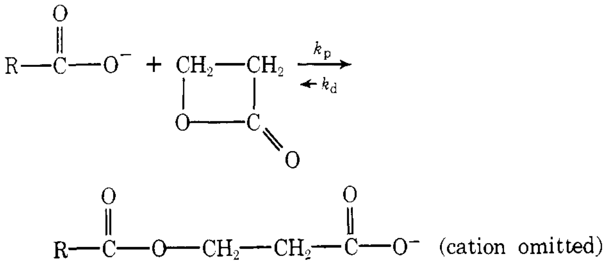
Crown ether (3) was prepared and purified according to literature[11] and distributed into phials in the same way as described for initiator.

Solvent. Methylene chloride was purified by our standard procedure of consecutive treatments with concentrated H_2SO_4, water, and a solution of Na_2CO_3, water, and $CaCl_2$. At this stage of purification it was distilled onto CaH_2, kept over CaH_2 for a few days, distilled again, and put under vacuum over fresh CaH_2. Sealed ampules, provided with breakseals, were stored below 0 °C in the dark.

Kinetic measurements were performed in the vacuum dilatometers, essentially in the same way as reported recently.[12]

Number average molecular weights ($\bar{M}_n$) were determined with a Hewlet Packard 302 B Vapor Pressure Osmometer.

Polymerization of 1 initiated by carboxylate anions proceeds with a regeneration in every propagation step of the carboxylate anion.[13]



$$R{-}C({=}O){-}O^- + CH_2{-}CH_2{-}C({=}O){-}O \underset{k_d}{\overset{k_p}{\rightleftharpoons}} R{-}C({=}O){-}O{-}CH_2{-}CH_2{-}C({=}O){-}O^- \quad \text{(cation omitted)} \qquad (1)$$

The ring strain of 1 is sufficiently large and, therefore, no appreciable amount of monomer can be left unreacted because the rate of depropagation reaction (k_d in eq 1) should be low.

Therefore, polymerization kinetics, provided that initiation is fast in comparison with propagation, can be described by a simple equation of a bimolecular growth:

$$-d[M]/dt = k_p^{app}[M]\Sigma[p_i^*] \qquad (2)$$

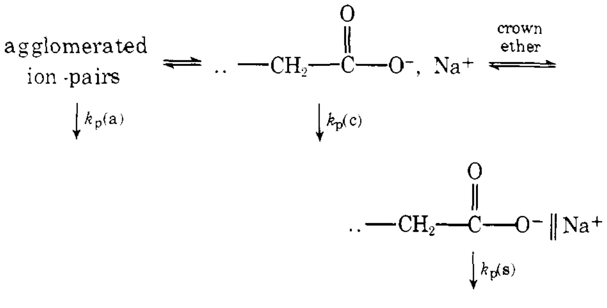
In eq 2 $\Sigma[P_i^*]$ denotes a sum of concentrations of the growing species of various kinds and is taken in our further treatment as equal to the starting concentration of initiator $[I]_0$.

Therefore, the variation of the "constant" k_p^{app} reflects the changes of the proportions of various more and less reactive species, described by $\Sigma[P_i^*]$.

Polymerization of 1 initiated with 2 in the presence of 3 in CH_2Cl_2 solvent proceeds as internally first order on monomer, according to eq 2.

In the absence of 3 no polymerization was observed up to 72 h at 35 °C; increasing the ratio [3]/[2] ([2] kept constant), the steady increase of k_p^{app} was observed until a plateau was reached. This is shown in Figure 1. Apparently addition of 3 converts some inactive species into active ones and it can tentatively be assumed that these are inactive contact ion-pairs or their agglomerates converted into crown ether separated ion pairs, as it was observed in other anionic systems, involving low and high molecular weight anions[14,15] (eq 3).

Thus the tentative explanation of the rate enhancement can be illustrated by the following set of equilibria:



$$\text{agglomerated ion-pairs} \rightleftharpoons \,..{-}CH_2{-}C({=}O){-}O^-,\ Na^+ \overset{\text{crown ether}}{\rightleftharpoons} \,..{-}CH_2{-}C({=}O){-}O^- \| Na^+ \qquad (3)$$

If $k_p(s) \gg k_p(c)$, $k_p(a)$ then the value observed at the plateau (6×10^{-3} M^{-1} s^{-1} in CH_2Cl_2 at 35 °C) can be tentatively ascribed to $k_p(s)$. At the plateau level $[P^*] = [\ldots{-}CH_2{-}C({=}O){-}O^- \| Na^+] = [I]_0$ (where $\|$ denotes a molecule of a crown ether).

Polymerization at these conditions consists of the steady increase of the polymerization degree. This is shown in Figure 2. The line in Figure 2 shows the calculated change of $\bar{M}_n$ with conversion (based on the simple relation $\bar{M}_n = ([M]_0 - [M]/[I]_0)$; points are experimental. According to Figure 2, there is a fairly good agreement between the calculated and experimental values of $\bar{M}_n$ although the last point (calcd 21×10^3; found 17.3×10^3) indicates either some inherent transfer or the presence of some impurities in the system.

Thus, our preliminary results show that the anionic polymerization of 1 with complexed cations can provide a new system suitable for mechanistic studies as well as for preparation of block and graft copolymers.

Similar observations of the enhancement of the rate of anionic polymerization of lactones in the presence of cryptates and crown ether have recently been made by Boileau et al.[16]

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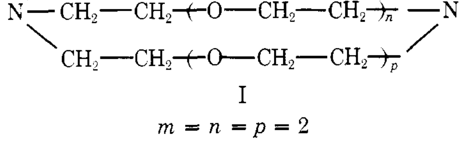
Use of Cryptates in Anionic Polymerization of Lactones

Macroheterobicyclic ligands such as I which form stable complexes with alkali metal cations[1] called "cryptates" have been recently used in anionic polymerization of vinyl, diene, and heterocyclic compounds.[2] They lead to the formation of complexed ionic species that are highly reactive.

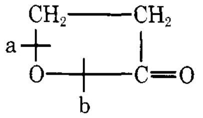


I

$m = n = p = 2$

designated [222]

Extensive studies have been made on anionic ring opening polymerization of β-propiolactone[3-9] and ε-caprolactone.[10] There are two modes of cleavage reaction of β-lactones; weak nucleophiles attack the CH_2 group with alkyl–oxygen fission (a), leading to carboxylate end groups, while attack of strong nucleophiles on the carbonyl group causes acyl–oxygen fission (b).



Cleavage of ε-caprolactone occurs only at the acyl–oxygen bond (b) and propagation thus proceeds through alkoxide groups. Many side reactions have been found to occur during the propagation when strong nucleophiles are used as catalysts.

We would like to report some preliminary results concerning the use of macrocyclic ligands for the polymerization of β-propiolactone and ε-caprolactone.

Monomers. β-Propiolactone (Koch-Light Lab.) was distilled under nitrogen at reduced pressure. The middle fraction was purified over several sodium mirrors in glass apparatus under high vacuum and then stored in the dark at −30 °C, in tubes fitted with break seals. ε-Caprolactone (Koch-Light Lab.) which has a high boiling point (bp 65 °C[10] (0.1 mm)) was distilled under nitrogen at reduced pressure and then purified under vacuum in toluene solution over sodium mirrors.

Solvents. Benzene, toluene, and tetrahydrofuran (THF) were purified over calcium hydride and over several potassium and sodium mirrors in glass apparatus sealed under high vacuum.

Initiators. Potassium *tert*-butoxide was prepared under vacuum by reaction of *tert*-butyl alcohol with a potassium mirror. Excess of alcohol was distilled off through a side tube. The potassium salt was then sublimed. Solutions of this salt in THF or toluene were filtered before use. A benzene solution of the dianion of 1,1,4,4-tetraphenylbutane was obtained by stirring a solution of 1,1-diphenylethylene and macrobicyclic ligand over a sodium mirror. This procedure produced rapidly the deeply red colored dianion with the complete disappearance of the sodium mirror. The absorption maximum of the solution is located at about 500 nm. This wavelength corresponds to that found for separated ion pairs and free ions of the sodium salt prepared in hexamethylphosphoramide.[11]

Ligands. The [222] compound was purified by freeze drying in benzene and sealed under high vacuum in tubes fitted with break seals. The same procedure was applied to the freshly redistilled dicyclohexyl-18-crown-6 compound (Aldrich Chemical Co.).

Polymerization. Polymerizations were carried out in glass apparatus sealed under high vacuum. Ligands were added to the catalyst solutions or suspensions just before adding the monomer, except for the benzene solution of the dianion of 1,1,4,4-tetraphenylbutane which cannot be obtained in the absence of [222]. The reaction mixtures were stirred at room temperature. After a period of time polymerization was stopped by addition of a small amount of hydrochloric acid in THF and the polymers were recovered after evaporation of the solvent. Intrinsic viscosities were measured in chloroform at 25 °C for polymers of β-propiolactone and in benzene at 30 °C for those of ε-caprolactone. Preliminary polymerization experiments were made in dry toluene or chloroform solution in air (Table I). β-propiolactone was freshly distilled and initiators and the [222] compound were dried before use.

It has been established[2] that a considerable increase in reactivity of anionic initiators can be brought about by complexation of macroheterobicyclic ligands of formula I. Moreover, use of these macrobicyclic compounds permits anionic polymerization of such monomers as styrene, hexamethylcyclotrisiloxane, and episulfides under conditions that ordinarily do not lead to polymers. We have now