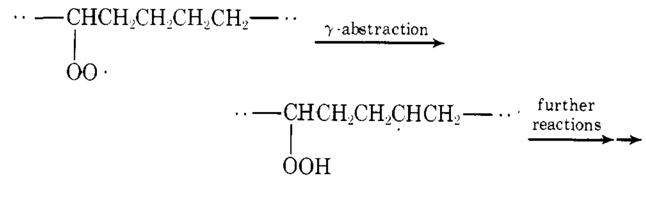
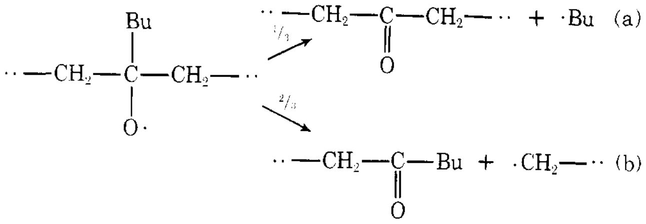
Over 80% of the oxygen consumed can be accounted for by the known products observed.[16] However, it appears at present that this scheme is not complete, as there are products for which it does not account. For example, γ-lactone, also reported by Adams in the oxidation of polyolefins, may be formed either via intramolecular attack by the peroxyacyl radical[5] or alternatively via an intrachain "back-biting" scheme parallel to that suggested by Rust[17] and by Chien et al.[18]



In addition, it is important to reiterate that not all the observed peaks are as yet assigned. Some of these may represent products resulting from intrachain reactions initiated as above. Particularly conspicuous is a peak at 43.7 ppm, and two keto carbonyl resonances at 206.8 and 208.0 ppm. These appear to correspond to products not yet recognized in any published oxidation scheme. The resonance at 175.0 ppm is tentatively assigned to the carbonyl of peracid, -C(=O)OOH, generally accepted as an intermediate in the oxidation of aldehyde to carboxylic acid.

Our data also provide an estimate of the ratio of reactivity to oxidative attack of branch points compared to linear hydrocarbon chains. It is observed that the butyl C-2 carbon resonance intensity at 23.4 ppm (Figure 1b) decreases from 9.7 to 6.6 per 1000 CH_2 upon absorption of 53 ml g^{-1} of oxygen. Oxidative cleavage at an *n*-butyl (or longer) branch point is believed to occur as follows[15,18,19] (the tertiary alkoxy radical having been generated by steps parallel to those shown above):



Reactions (a) and (b) occur with statistical probability giving long-chain ketone and butyl ketone, which are indeed observable in our experiments. Model compound measurements show that in the *n*-butyl ketone group the butyl C_2 carbon resonance moves from 23.4 to 22.7 ppm, becoming coincident with the C_2 resonance of "amyl + long" branches, the intensity of which correspondingly increases upon oxidation. By comparing these results quantitatively with the overall production of oxidized structures, it can be shown (by calculations which we shall not detail here) that the reactivity ratio of branch points to linear chains is 9.8 ± 1.0, a result in good agreement with the value of 8 derived from model hydrocarbon oxidation studies.[15]

Preliminary studies of the photoxidation of low-density polyethylene, to be reported in detail later, indicate a substantial production of terminal vinyl groups together with a decreased appearance of oxygen-containing groups in the polymer chains as compared to thermal oxidation.

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(12) The spectra were obtained using a Varian XL-100 spectrometer modified for FT operation and interfaced with a Nicolet 1080 computer.[13] Proton ^{13}C couplings were eliminated using a noise-modulated decoupling field. The free induction decays were stored in 8K computer locations using a dwell time of 83 μsec (i.e., a spectral window of 6024 Hz). The pulse was located at the high-field end of the spectrum at 25.16032 MHz, the pulse width being 63 μsec for an approximately 90° pulse. Pulse intervals were 6 to 10 sec. Hexamethyldisiloxane (HMDS) was used as internal reference (2.00 ppm from TMS) and C_6D_6 as internal deuterium lock. At the observing temperature (110°), T_1 for the main chain carbons is ca. 1.4 sec.[9]
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(16) This estimate is based on the assumption that in the mechanism shown the formation of each ketone, alcohol, and hydroperoxide group consumes one O_2 molecule; each acid and lactone group two O_2 molecules; and each ester group three O_2 molecules. Thus for the sample consuming 53 ml of O_2 per gram of polymer, the material balance, corrected to the original polymer, is: polymer = 71.4 mmol of CH_2/g; O_2 = 2.37 mmol; carboxyl = 0.550 mmol × 2 = 1.100 mmol; ketone = 0.493 mmol × 1 = 0.493 mmol; hydroperoxide = 0.164 mmol × 1 = 0.164 mmol; secondary alcohol = 0.114 mmol × 1 = 0.114 mmol; γ-lactone = 0.079 mmol × 2 = 0.158 mmol; ester ≈ 0; total oxygenated groups = 2.039 mmol/2.37 mmol O_2 consumed = 86%. The oxygen unaccounted for presumably consists of volatiles other than H_2O, principally CO_2, and unidentified products.
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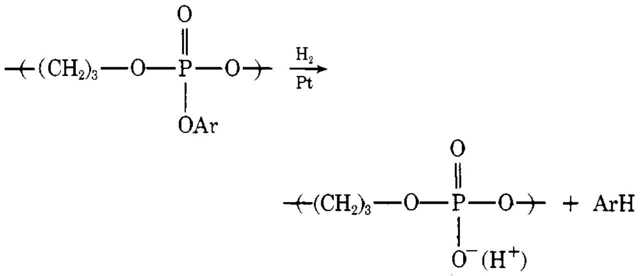
A New Class of Synthetic Polyelectrolytes. Acidic Polyesters of Phosphoric Acid, (Poly(hydroxyalkylene phosphates))

We have previously[1] discussed the possibility of preparation of the acidic polyesters of phosphoric acid (poly(hydroxyalkylene phosphates)), starting from polymers of 2-aryloxy-2-oxo-1,3,2-dioxaphosphorinanes. These monomers, with alkoxy[2,3] or aryloxy[4] substituents, can be polymerized by using cationic or anionic initiators, but the polymerization degrees are usually low, because of an extensive chain transfer to monomer. The proportion of the chain transfer vs. chain propagation is especially high for the six-membered dioxaphosphorinanes, because, as we have shown,[1] the reactivity of the exocyclic ester group is close to that of the ring. The six-membered dioxaphosphorinanes, according to our measurements,[1] are only slightly strained ($\Delta H^0_{ss} = -1.1$ kcal/mol and $\Delta S^0_{ss} = -5.5$ cal/(mol °K) for 2-methoxy-2-oxo-1,3,2-dioxaphosphorinane). Attempts to prepare poly(hydroxyalkylene phosphates) from poly(aryloxyalkylene phosphates) were not successful because the complete dearylation (e.g., by hydrogenation) was not possible.[4]



$$\left(-(CH_2)_3-O-\underset{OAr}{\overset{O}{\overset{\|}{P}}}-O-\right) \xrightarrow[\text{Pt}]{H_2} \left(-(CH_2)_3-O-\underset{O^-(H^+)}{\overset{O}{\overset{\|}{P}}}-O-\right) + ArH$$

In order to prepare high molecular weight acidic polyesters of phosphoric acid, related to the naturally occurring polymers, we have, therefore, used the following two new approaches, which led eventually to polyacids of ethylene and 1,3-propylene phosphates.

(a) The five-membered 2-methoxy-2-oxo-1,3,2-dioxaphospholane (**1**), much more strained than its six-membered counterpart, was polymerized first to the high molecular weight polyester and this converted into the corresponding polyacid via a polysalt, obtained in the reaction of a polyester with trimethylamine.

(b) 2-Hydro-2-oxo-1,3,2-dioxaphosphorinane (**2**) was polymerized first to the high molecular weight polyester (poly(*P*-hydro-1,3-propylene phosphonate)) and oxidized afterwards to the corresponding free polyacid (poly(hydroxy-1,3-propylene phosphate)).

Polymerization of 2-alkoxy-2-oxo-1,3,2-dioxaphospholanes has already been described[5] but the structure of the polymers was not established. According to our data, linear polyesters are formed in anionic, cationic, or coördinate polymerization.[6] On the other hand, polymerization of 2-chloro-2-oxo-1,3,2-dioxaphospholane leads to polymers of mixed structure of a polyester and polyanhydride (P–O–P).[7]

Polymers similar to our poly-**2** (e.g., poly(*P*-hydrohexamethylene phosphonate)) were previously prepared by a polycondensation technique.[8,9]

Preparation of Polyesters and Their Conversion into the Acidic Polyesters (Polyacids). Poly(hydroxyethylene phosphate). Poly-1 has been prepared by polymerizing the corresponding monomer (synthesized according to ref 10 and 11) with 0.5 mol % of $(i\text{-}C_4H_9)_3Al$ or $(C_5H_5)_2Mg$ used as initiators in CH_2Cl_2 solution. Polymerization has been carried out in the temperature range from −25 to 20°. The yields of polymers were quantitative according to NMR spectra. Molecular weights, measured by a high-speed membrane osmometry, gave values ranging from 3×10^4 to 10^5. Anal. Calcd for $(C_3H_7O_4P)_n$ [mol wt $(138.07)_n$]: C, 26.10; H, 5.11; P, 22.43. Found: C, 25.93; H, 5.34; P, 21.45.

Higher values for H and lower values than calculated for C and P are connected with the highly hydrophilic nature of poly-1 and difficulties in removing traces of water.

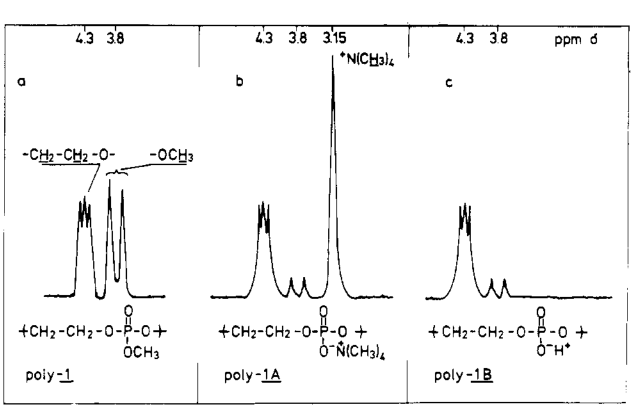
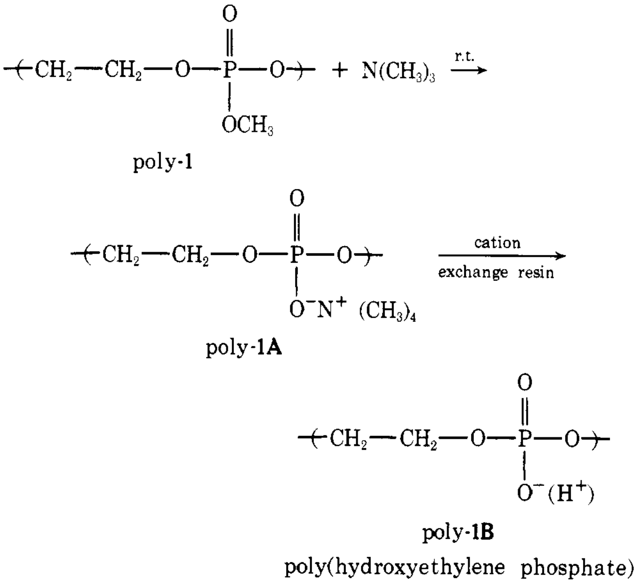


Figure 1. ^1H NMR spectra of (a) poly-**1**, (b) polysalt, and (c) free polyacid (poly(hydroxyethylene phosphate) in D_2O solution). The following lines are observed (from DSS, internal standard): $-CH_2-CH_2$ δ 4.3 m; $-OCH_3$ δ 3.8 d; $-N^+(CH_3)_4$ δ 3.15 s. In (b) and (c) absorption at δ 3.8 shows the residual $-OCH_3$ groups (10% of their starting concentration); according to (c) the $N^+(CH_3)_4$ groups are completely removed.

High molecular weight polymers were also obtained in the anionic polymerization of 1 with *t*-BuOK whereas cationic polymerization, initiated with tertiary oxonium salts or derivatives of triflic acid, leads to the low molecular weight oily products.

The ^1H NMR spectrum of poly-1 is given in Figure 1a.

The neutral polyester (poly-1) has been converted into the polysalt in a reaction of poly-1 with trimethylamine in water solution at 20°:



$$\left(-CH_2-CH_2-O-\underset{OCH_3}{\overset{O}{\overset{\|}{P}}}-O-\right) + N(CH_3)_3 \xrightarrow{\text{r.t.}}$$

poly-1

$$\left(-CH_2-CH_2-O-\underset{O^-N^+(CH_3)_4}{\overset{O}{\overset{\|}{P}}}-O-\right) \xrightarrow[\text{exchange resin}]{\text{cation}}$$

poly-**1A**

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

poly-**1B**

poly(hydroxyethylene phosphate)

According to the ^1H NMR spectrum the degree of dealkylation exceeds 90% (Figure 1b), and according to the titration data is equal to 88%.

The free polyacid (poly-**1B**) has been directly prepared from poly-**1A** by passing its water solution through the cation exchange resin Dowex 50W.

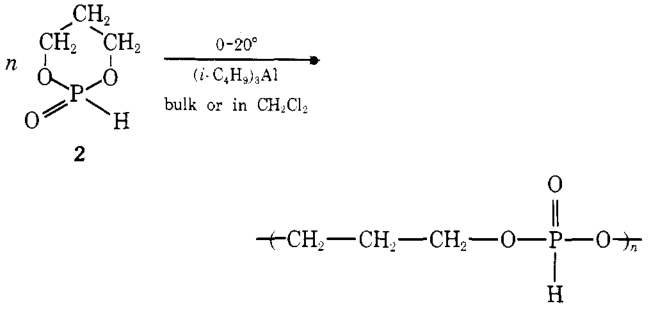
The degree of exchange of the $N^+(CH_3)_4$ cations in poly-**1A** by protons is, according to ^1H NMR (Figure 1c), practically quantitative. The detailed discussion of the ^1H, ^{31}P, and ^{13}C NMR spectra, confirming the shown above polymer structure, will be given in a paper which will be submitted to this journal shortly.

Poly-1 and poly-**1B** are colorless, hydrophilic, soluble in water, and highly elastomeric solid materials. Poly-**1A** is also water soluble, but in contrast with poly-1 and poly-**1B** has no elastic properties. Anal. Calcd for poly-**1B**

($(C_2H_5O_4P)_n$, 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

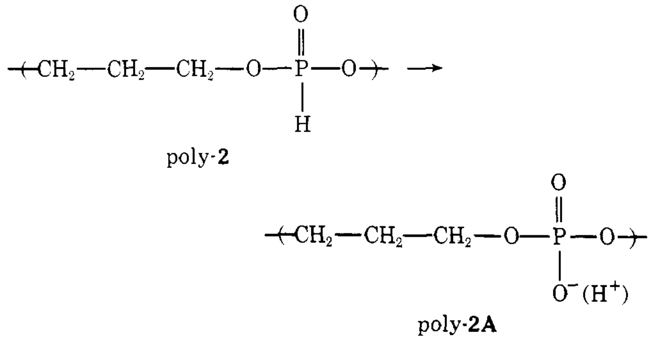
$$-\!\!\left(CH_2-CH_2-CH_2-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{|}}{P}}-O\right)\!\!-_n$$

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°:



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

poly-**2**

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

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) $\approx 6 \times 10^{-5}\ M^{-1}\ s^{-1}$ 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-