115 Å for PTMO-30-1000, PTMO-30-2000, and PTMO-54-1000, respectively (Table I). The mean-square fluctuation in electron density $\langle \rho^2 \rangle$, is also listed in Table I for the three samples. For different urea content and constant soft-segment molecular weight (PTMO-30-1000 and PTMO-54-1000), $\langle \rho^2 \rangle$ increases with increasing urea fraction as expected. However, for the same composition but with different soft-segment molecular weight, PTMO-30-2000 shows a higher $\langle \rho^2 \rangle$ value than PTMO-30-1000, strongly implying better phase separation. This directly supports the earlier conclusion of Sung et al. based on their mechanical and thermal studies. The improvement in the domain texture of PTMO-30-2000 over that of PTMO-30-1000 could be attributed to increasing the thermodynamic incompatibility of the hard and the soft blocks due to the higher soft-segment molecular weight. That is, the Flory–Huggins χ parameter is molecular weight dependent and increases as the soft-segment molecular weight increases.[7]

A second area of interest is that of the effect of altering the morphology and the material by using ethylenediamine as the chain extender rather than butanediol. We have attempted to shed some light on this topic by determining the interfacial thickness of the domains using the SAXS method of Ruland.[8] Our analysis (see Table I) does indeed suggest that the diamine promotes somewhat better phase separation in that the boundary thickness values are somewhat less than those for the butanediol-containing systems. Specifically, earlier work of one of the authors[5] showed that the latter systems of equivalent hard-segment contents tend to provide interfacial thickness values on the order of 7–12 Å when the SAXS data are analyzed in an identical manner. However, one must be cautious to readily attribute major differences in properties between these two extenders to this interfacial or "mixing" argument alone. Specifically, there is also an inherent difference in molecular flexibility of the two extenders that may well contribute to property difference. This flexibility difference can be indirectly noted from the work of Bonart et al.,[9] who found that the hard-segment T_g based on MDI and diamine systems decreases from 187 °C when using ethylenediamine as an extender and to 179 °C for butylenediamine. In another study, Critchfield et al.[10] found that for a systematic series of linear aliphatic glycol extenders ranging in methylene content from 2 to 12, the modulus of the associated 2000 M_n poly(caprolactone)–MDI-based urethane passed through a minimum with seven methylene groups (1,7-heptanediol). Their explanation for this observed change in mechanical stiffness was based on changes in both phase separation and intermolecular interactions. Therefore, a significant point of argument may also be associated with the major change in flexibility, i.e., due to the increase in the first few methylene units. We suggest that the work of Sung et al. and their explanation may need to be modified by this consideration.

In summary, we believe that the SAXS results presented here lend more direct support to several of the earlier conclusions of Sung et al. regarding the effect of soft-segmented molecular weight on phase separation. However, some modification in thought may be useful to help explain the effect of the chain extenders on properties used in these same studies.

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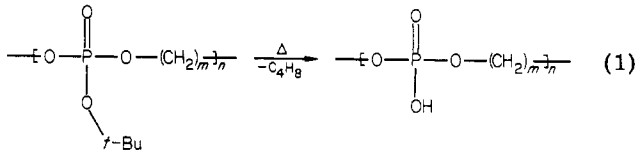
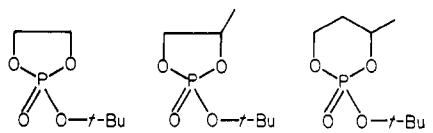
Novel Synthesis of Acidic Polyesters of Phosphoric Acid by Thermal Elimination of Isobutylene from Poly(alkylene *tert*-butyl phosphates)

The synthesis of high molecular weight poly(alkylene phosphates) is valuable for entry to functional polymers having a backbone analogous to the backbone of polynucleotides. There is also much interest in specific physical properties, e.g., hydrophilicity, inflammability, and thermal stability.[1] Synthetic routes reported so far are limited to (1) the synthesis of poly(ethylene phosphate) by removal of the quaternary ammonium salt with cation exchange resins from the polysalt of poly(2-methoxy-1,3,2-dioxaphospholane 2-oxide) and (2) the oxidation of poly(1,3,2-dioxaphosphorinane 2-oxide) with nitrogen dioxide.[2]

We report here a novel facile method for preparation of a series of poly(alkylene phosphates) by thermal elimination of isobutylene from poly(2-*tert*-butoxy-1,3,2-dioxaphospholane 2-oxide), poly(2-*tert*-butoxy-1,3,2-dioxaphosphorinane 2-oxide), or their alkyl-substituted polymers which were synthesized by ring-opening polymerization of the cyclic phosphate (reaction 1). Although the preparative methods for five- and six-membered cyclic phosphates are well established,[3] the physical and chemical properties of *tert*-butoxy derivatives such as 2-*tert*-butoxy-1,3,2-dioxaphospholane 2-oxide (**1**), 4-methyl-2-*tert*-butoxy-1,3,2-dioxaphospholane 2-oxide (**2**), and 4-methyl-2-*tert*-butoxy-1,3,2-dioxaphosphorinane 2-oxide (**3**)





1 **2** **3**

are relatively unknown due to their thermal instability. These compounds are now successfully prepared by oxidation of the corresponding cyclic phosphite with N_2O_4 at

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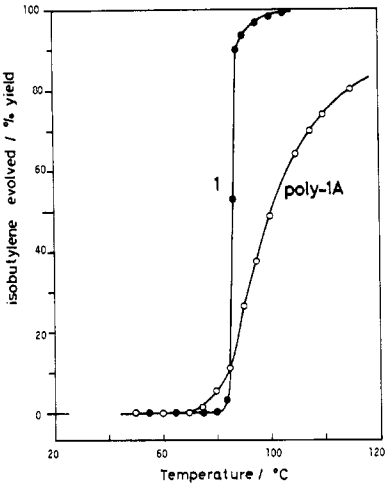
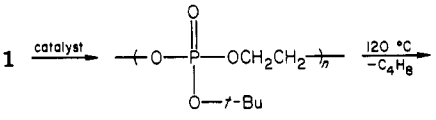


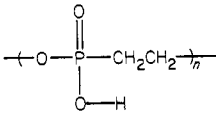
Figure 1. Mode of evolution of isobutylene for thermal degradation of 2-*tert*-butoxy-1,3,2-dioxaphospholane 2-oxide (1) and its polymer poly-1A obtained with Et_2Mg catalyst.

0 °C and purification by recrystallization in toluene–hexane below −20 °C (mp of **1**, **2**, and **3**: 28, 10–12, and 39 °C, respectively). The ^1H NMR data for 1 in $CDCl_3$ (δ(H(trans)) = 4.48, δ(H(cis)) = 4.39 ppm, $J_{PH(trans)}$ = 11.9, $J_{PH(cis)}$ = 8.3 Hz) are essentially the same as the well-defined spectral data of 2-ethoxy-1,3,2-dioxaphospholane 2-oxide[4] and are readily assigned to the twist-envelope conformation.[5] Compound **2** consists of trans and cis isomers in a 78:22 ratio as determined by ^1H NMR by reference to 4-methyl-2-methoxy-1,3,2-dioxaphospholane 2-oxide.[6] Heating of these compounds to 100–120 °C resulted in a unique thermal decomposition with rapid evolution of 1 equiv of isobutylene to produce a powdery polymeric product (its structure will be given in a separate paper). Decomposition temperatures are 85, 100, and 103 °C for **1**, **2**, and **3**, respectively. The observed elimination of isobutylene prompted us to examine the synthesis of poly(ethylene phosphate) from **1** to the following process: preparation of poly(2-*tert*-butoxy-1,3,2-dioxaphospholane 2-oxide) (poly-**1A**) at low temperatures followed by thermal elimination of isoobutylene at higher temperatures to give poly(ethylene phosphate) (poly-**1B**).

Thus, polymerization of **1** with diethylmagnesium (2 mol % to 1 in benzene) (reaction 2) was examined since al-



poly-**1A**



(2)

poly-**1B**

kylmagnesium-catalyzed polymerization[7] of 2-methoxy-1,3,2-dioxaphospholane 2-oxide is known to proceed at low temperature (20 °C). Benzene-insoluble polymer was obtained in 80% yield by reaction at 40 °C for 10 h. The molecular weight determined by gel permeation chromatography (using an HSG-15 column fitted on a Shimadzu-Du Pont Model 830 LGC with 1:1 methanol–water as eluent) was 25 000. The resulting polymer was dried at 20 °C and then heated at 150 °C at a rate of 10 °C/min in an argon atmosphere. Evolution of isobutylene begins at 78 °C (lower than the decomposition temperature of 1) and continues to 140 °C, as evidenced by gasometry (Figure

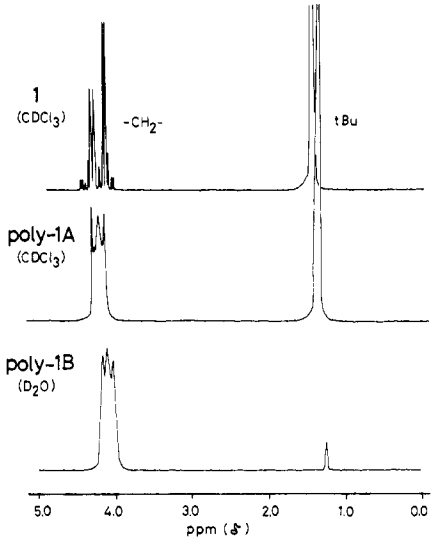
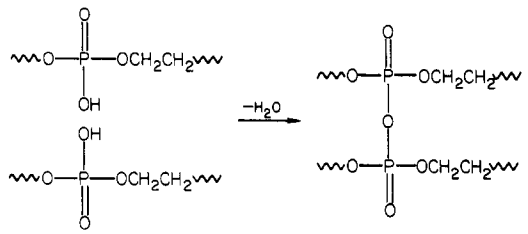


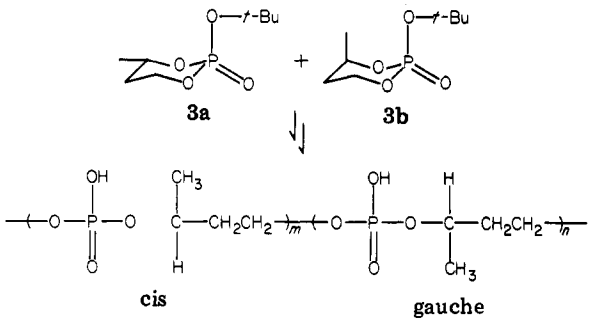
Figure 2. ^1H NMR spectra (100 MHz at 38 °C) of 1, poly-**1A** in $CDCl_3$, and poly-**1B** in D_2O.

1). The resulting colorless, rubberlike polymer is insoluble in organic solvents (chloroform, THF, benzene, acetone) but soluble in water. The ^1H NMR spectra of poly-**1A**, after heating, show quantitative elimination of isobutylene (95%) and formation of the expected linear poly-**1B**. The methylene proton signals of this polymer (Figure 2) are identical in chemical shift and signal pattern with that of the corresponding poly-**1B** reported by Penczek et al.[7] The two complex doublets are due to three- and four-bond ^{31}P–^1H coupling.

Characteristics of the present method lie in the facility of the procedure, complete conversion of poly(phosphate triesters) to anhydrous poly(alkylene phosphate), and no decrease in yield or degree of polymerization after elimination of isobutylene. These are caused by the absence of a hydrolysis process. It is important to note that the molecular weight of poly-**1B** increased on continued heating. The molecular weight of poly-**1B** which is obtained by heating poly-**1A** at 120 °C for 10 min is 28 000 and that of poly-**1B** obtained by heating for longer time (2 h) at 120 °C is 52 000, as evidenced by gel permeation chromatography (1:3 MeOH–water was used as an eluent). No difference was observed in the ^1H NMR spectra of these two polymers. Polymer heated for 10 h at 120 °C or kept at room temperature for 30 days in a sealed tube became insoluble in water. These results may be attributable to the condensation between the polymer chains to form a cross-linkage since such condensation is generally accepted in phosphoric acid chemistry.[3] The degree of cross-linkage for the water-insoluble polymer must not be extremely high because no significant change was observed in the IR spectra of these polymers in the region 1150–1300 cm^{-1}. Polymerization of **2** was carried out under the same reaction conditions and poly-**2** was obtained in 90% yield. Heating of poly-**2** at 130 °C for 20 min resulted in the quantitative release of isobutylene, giving a polymer with molecular weight 18 000 in 1:3 MeOH–H_2O.



Application of this type of reaction to the polymer obtained from **3** is of the utmost importance because the sequence of six atoms present in the polymer backbone is very close to that of a natural polynucleotide. Polymerization of **3** by 1:0.9 $AlEt_3$–H_2O catalyst (2 mol % to **3**) in benzene at 40 °C successfully produced a benzene-insoluble polymer (50% yield) which changed to a colorless powdery polymer when it was dried at 20 °C for 5 h. Heating of this polymer at 130 °C for 20 min resulted in the evolution of isobutylene to give poly(4-methyl-2-hydroxy-1,3,2-dioxaphosphorinane 2-oxide) (poly-**3B**) quantitatively. The molecular weight determined by GPC was 25 000. Chemical shifts and proton signal intensity ratios of the ^1H NMR spectrum of poly-**3B** clearly indicate the formation of the expected poly(methyl propylene phosphate). The determination of the microstructure of the polymer cannot be made at present because the starting monomer **3** consists of two stereoisomers in an 11:9 ratio, as evidenced by ^1H NMR. The preference of the alkoxy group to be axially disposed has been generally accepted for 4-alkyl-substituted six-membered cyclic phosphates[8] and hence the stereoisomers **3a** and **3b** are considered as the thermodynamically stable phosphates. The chemical shift difference between the two methyl proton signals is 2.2 Hz (in 100-MHz NMR), in accord with the value (2.4 Hz) observed for the corresponding stereoisomers of 4-methyl-2-methoxy-1,3,2-dioxaphosphorinane 2-oxide.[6] The methyl group in the resulting polymer also appeared as two doublets in a 1:1 ratio whose chemical shift difference is 2.3 Hz. On the basis of these facts, it is most likely that poly-**3B** has a ca. 1:1 cis–gauche sequence (with respect to OH and Me groups) in the polymer backbone although it is not clear from this work whether the ring opening occurs with retention of configuration or with inversion. Since the chiral carbon or phosphorus in the polymer chain is apart from the neighboring chiral carbon atoms by six bonds, the observed chemical shift difference seems too large to attribute it to the tacticity (disyndiotactic, threo or erythro diisotactic, or atactic) or sequence regulation (head-to-head or head-to-tail). Accurate microstructural analysis should be done starting from a single diastereomer of **3** (though no preparative method is yet known).



Aqueous solutions of both poly-**1B** and poly-**3B** (0.1 g/mL) showed strong acidity (pH 1.5), as was observed for low molecular weight poly(ethylene phosphate) prepared by a condensation method.[9] Both poly-**1B** and poly-**3B** are stable in water in the pH range 1.5–12.0 but hydrolyzed rapidly in 6 N HCl or 6 N NaOH aqueous solution.

The introduction of a *tert*-butoxy group into mononucleotides of cyclic phosphate structure, some of which have been separated into diastereomers,[10] is likely to be valuable in the polymerization of nucleotides to polymers analogous to poly-U, poly-A, etc.

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Effect of Matrix Molecular Weight on Diffusion of a Labeled Molecule in a Polymer Melt[1]

A basic tenet of recent theories[2-4] of molecular motion in entangled solutions and melts of linear polymers is that a given molecule in such systems moves curvilinearly (reptates) within effectively fixed surroundings; the topological environment of such a molecule is generally represented as a "tube",[5] defined by the locus of its entanglements with neighboring chains. Direct experimental support for the reptation picture has come in particular from translational diffusion studies in polymer melts; in these the diffusion coefficient $D(M,P)$ of deuterated polyethylene (DPE) chains of molecular weight M, diffusing in a protonated polyethylene (PPE) melt of fixed high molecular weight P, was measured.[6] The results showed

$$D(M,P) \propto M^{-2.0} \qquad (M \ll P) \tag{1}$$

in accord with the inverse-square relation expected for curvilinear motion in a fixed network.[7] In a real polymer system, however, one expects the "tube" about any given molecule to rearrange with time,[8] as it is itself defined by the mobile neighbors of that molecule. A consideration of the problem[8-10] indicates that for M smaller than, or comparable with, P, the "tube" relaxation time, τ_{tube}, is much longer than τ_{rep}, the time taken for a molecule to reptate right out of a "tube": in this case a molecule will move at all times within effectively fixed local surroundings.

To investigate more directly how the environment of a given molecule in an entangled melt changes with time, I have extended previous measurements[6] on translational diffusion in a polyethylene melt (where M varied and P ($\gg M$) was fixed) to the case where the *matrix* molecular weight P varies for a fixed labeled diffusant M. The diffusants were again DPE fractions, while the matrix consisted of PPE fractions. Molecular characteristics are given in Table I.

The experimental procedure for measuring $D(M,P)$ is a scaled-down version of the technique previously described[11] and is based on IR microdensitometry. The scaling down is essential since only small amounts of the PPE fractions were available (except for HDPE1). Briefly,

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