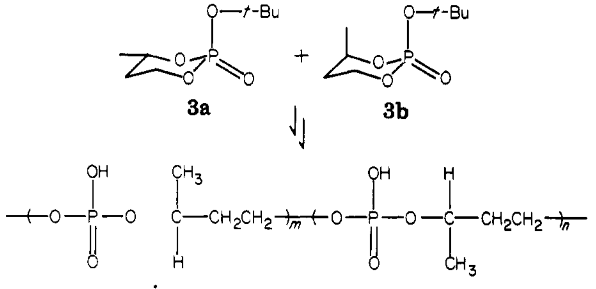
Application of this type of reaction to the polymer obtained from **3** is of the utmost importance because the sequence of six atoms present in the polymer backbone is very close to that of a natural polynucleotide. Polymerization of **3** by 1:0.9 $AlEt_3–H_2O$ catalyst (2 mol % to **3**) in benzene 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).



cis **gauche**

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

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

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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Table I[a]
Molecular Characteristics of Polyethylene Samples

protonated samples	$\overline{P}_w$ ($\equiv P$)	$\overline{P}_w/\overline{P}_n$
HDPE1 (i)	160 000	~16
PPE1 (ii)	36 000	1.9
PPE2 (ii)	25 000	2.1
PPE3 (iii)	22 000	3.1
PPE4 (ii)	11 000	2.1
PPE5 (iii)	8 500	2.4
PPE6 (iv)	2 000	1.1
deuterated fractions	$\overline{M}_w$ ($\equiv M$)	$\overline{M}_w/\overline{M}_n$
DPE1[b] (ii)	3 600	2.25
DPE5[b] (ii)	23 000	1.8

[a] Molecular weights and polydispersities were determined by gel permeation chromatography. Samples were very kindly donated and characterized as follows: (i) RAPRA, Shawbury; (ii) Dr. D. G. Ballard, ICI, Runcorn, Cheshire; (iii) Dr. R. Koningsveld, DSM, Geleen, Holland; sample (iv) was bought from Polymer Laboratories, Shawbury.

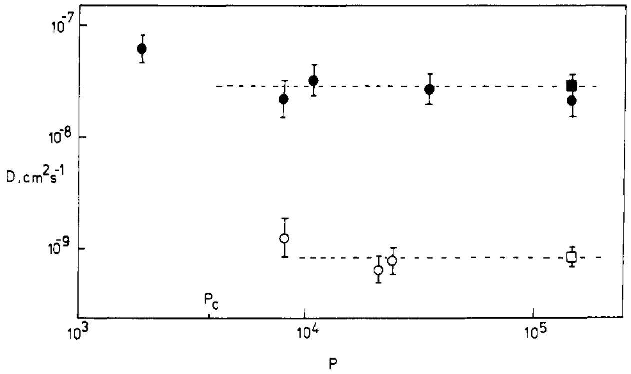

Figure 1. Variation of $D(M,P)$ with matrix molecular weight P at 176 ± 0.5 °C: (●) DPE1 (M = 3600); (○) DPE5 (M = 23 000). Each point is the mean of two or more independent experiments. (■, □) D values obtained in the study by Klein and Briscoe for DPE1 and DPE5, respectively.

the procedure is as follows: two thin rectangloids of the PPE ($\sim 1 \times 1 \times 0.01$ cm^3), one of which contains 2% (w/w) of the DPE diffusant, are placed side by side in a close-fitting PTFE frame, with the thin sides adjacent and in contact. The combination is sandwiched between glass plattens and heated; on melting, a coherent step function in the DPE concentration forms, which broadens in time with diffusion. Concentration profiles are measured in the usual way[11] to yield D. Details will be reported in the full paper.[12]

The results are summarized in Figure 1, where $D(M,P)$ is plotted against P for each value of M; within the estimated error, $D(M,P)$ is seen to be independent of P for $P \gtrsim 10^4$. For M = 3600 diffusing in P = 2000 (PPE6) there is a small but significant increase of D above its plateau value for high P.

Now it is argued elsewhere[10] that (for linear M,P)

$$D(M,P) \propto M^{-1}P^{-1} \qquad (P \lesssim P_c) \qquad (2)$$

$$D(M,P) \propto M^{-2}P^{0} \qquad ((M/P_c)^{1/2} < (P/P_c) > 1) \qquad (3)$$

$$D(M,P) \propto M^{-1/2}P^{-3} \qquad ((M/P_c) > (P/P_c)^2 > 1) \qquad (4)$$

where P_c is the molecular weight for onset of entangled behavior;[13] for polyethylene P_c = 3800. Equations 2 and 3 reflect the fact that at low P the matrix is "unentangled" and the diffusion of molecules within it becomes Rouse-like,[14] while at higher P it is "entangled" and tube renewal becomes slow relative to reptation (i.e., $\tau_{\text{rep}} \ll \tau_{\text{tube}}$). Equation 4 applies to a regime where diffusant molecules are very much longer than those of the matrix, and diffusion by "tube" reorganization becomes the faster process.[10] The present values of M and P fall in the regime of eq 3 (which includes $M = P$, i.e., a homopolymer): the observed plateau in D for $P \gtrsim (2\text{–}3)P_c$ is thus in agreement with this equation.

Within the range of molecular parameters described, therefore, these results strongly support the conjecture that the topological environment of molecules in a melt (the "tube" surrounding them) changes only slowly relative to the diffusional motion of the molecules themselves.

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Effects of Long Chemical Sequences on the ^{1}H NMR Spectrum of Polyesters

We have observed that the 400- and 600-MHz ^{1}H NMR spectra of copolyesters of diethylene glycol (D) and neo-

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