Table I[a]
Molecular Characteristics of Polyethylene Samples

protonated samples	$\bar{P}_w$ ($\equiv P$)	$\bar{P}_w/\bar{P}_n$
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	$\bar{M}_w$ ($\equiv M$)	$\bar{M}_w/\bar{M}_n$
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.

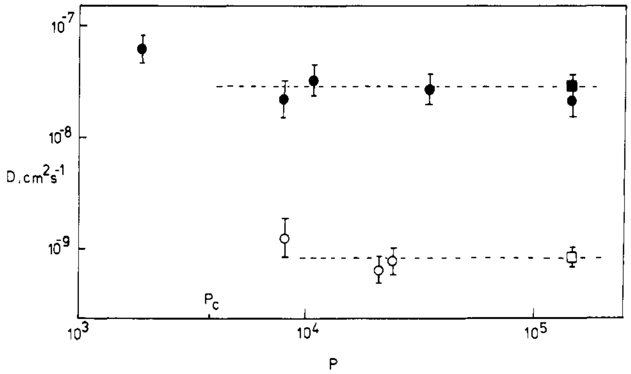

Figure 1. Variation of $D(M,P)$ with matrix molecular weight P at 176 ± 0.5 °C: (●) DPE1 (M = 3600); (○) DPE5 (M = 23 000). Each point is the mean of two or more independent experiments. (■, □) D values obtained in the study by Klein and Briscoe for DPE1 and DPE5, respectively.

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)

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

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

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

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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J. Klein

Polymer Department, The Weizmann Institute of Science
Rehovot, Israel

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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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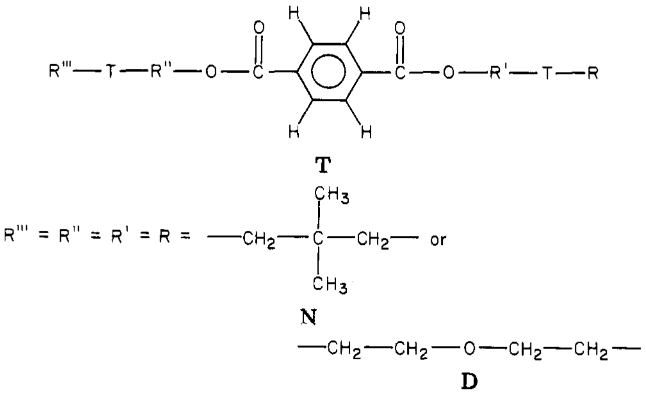
pentyl glycol (N) with terephthalic acid (T) show more resolved peaks in the aromatic region than would initially be expected. The fine structure reflects the abundance of chemical sequences involving diol units that are not only nearest but also next-nearest neighbors to the terephthalic acid of interest. A typical 600-MHz spectrum is shown in Figure 1.

There is no evidence of coupling effects in the spectra. For example, the spectra at 600 MHz are essentially identical with those at 400 MHz except for greater resolution. If the lower-field spectra were composed of overlapping spin–spin multiplets, very different spectra would appear at higher fields as the coupling patterns were pulled apart. All of the observed resonances can be accounted for in terms of different types of chemical sequences, each type giving rise to a single line, as explained below.

There are ten different possible types of chemical sequences involving diols that are nearest and next-nearest to a given terephthalic ring. We actually see evidence for nine separate signals. Assignments of specific sequences to the NMR resonances were made by observation of changes in peak intensity as the proportion of the two types of diols was varied. The final assignments are shown in Figure 1. The middle resonance is assigned to the central terephthalic acid protons of the two sequences N–T–N–T–D–T–D and D–T–N–T–D–T–N.



The changes in intensity with composition that we observed confirm that, for each of the sequences, only a single resonance results from all four of the protons in any given aromatic ring, in spite of the fact that the aromatic protons in some of the rings are chemically nonequivalent. Integration of the peak areas was consistent with a random distribution of the chemical sequences assigned to the various NMR peaks.

The extreme number of bonds which separate the observed terephthaloyl protons from at least some of the sites that control their chemical shifts suggests that the effects are transmitted "through space". This implies that at least some moieties in the polymer chain allow it to fold back on itself. In adjacent portions of the folded chain, chemical shift changes result from the shielding effects of the aromatic rings on the protons in the nearby chain segments.

We do not expect nearby chain segments to approach each other closer than 5 Å. The standard formulas show that an aromatic ring in one chain segment placed, even somewhat off center, above an aromatic ring in the other segment shields all four protons essentially equally.[1] Thus, the accidental chemical shift equivalences are not surprising in this system. The ring protons in other polyesters do give rise to complex AA′BB′ patterns,[2] as expected.

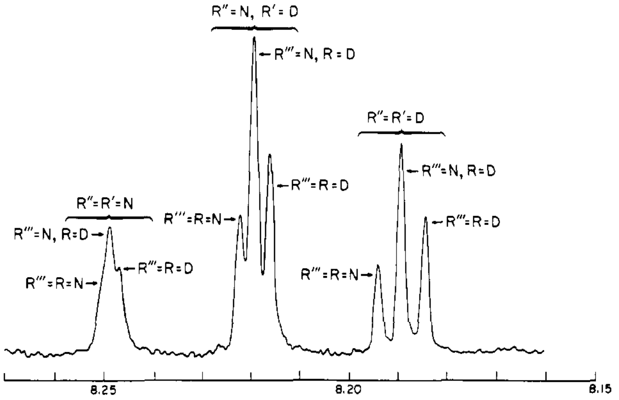


Figure 1. ^{1}H NMR spectrum taken at 600 MHz of the aromatic region of a polymer containing 55 mol % diethylene glycol and 45 mol % neopentyl glycol with terephthalic acid. The concentration was 10 mg/mL in trifluoroacetic acid. In other samples, all three resonances in the left-hand group are resolved.

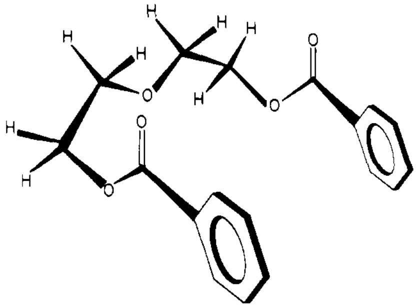


Figure 2. A conformation of diethylene glycol that allows for chain folding.

The most pronounced long-range chemical shift effects are associated with polymer sequences containing diethylene glycol (Figure 1). The diethylene glycol moiety does, in fact, allow for chain folding in the conformation shown in Figure 2. This conformation must be present in rather high concentration to account for the observed results, however, a condition which at first seems unreasonable because of the gauche conformations of the CH_2–CH_2 bonds. Nevertheless, work on small molecules has shown that polar, vicinal substituents on a two-carbon segment tend to stabilize such gauche configurations. The effect has been observed for both cyclic and acyclic molecules.[3] It is also relevant that polyesters containing ethylene glycol sometimes form crystalline phases with a gauche conformation of the ethylene unit.[4]

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P. M. Henrichs and J. M. Hewitt*

Research Laboratories
Eastman Kodak Company
Rochester, New York 14650

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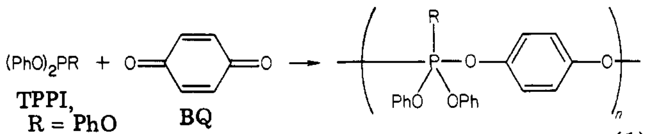
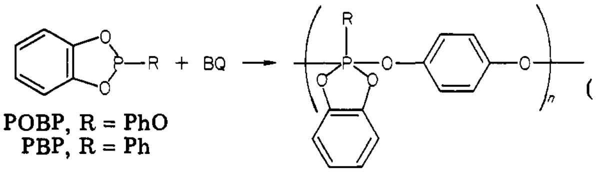
Polyphosphoranylation of *p*-Benzoquinone with Acyclic and Cyclic Phosphorus(III) Compounds Having Aryl and Aryloxy Groups

In a series of studies on the "no-catalyst alternating copolymerization via zwitterion intermediate", we have discovered a new alternating copolymerization in which cyclic phosphorus(III) compounds serve as nucleophilic monomers.[1-15] This communication reports alternating copolymerization between acyclic as well as cyclic phosphorus(III) compounds and *p*-benzoquinone (BQ). The acyclic phosphorus(III) compounds employed were triphenyl phosphite (TPPI) and diphenyl phenylphosphonite (TPPO) and the cyclic ones were 2-phenoxy- and 2-phenyl-4,5-benzo-1,3,2-phospholanes (POBP and PBP, respectively). The copolymerization gave polyphosphorane-type polymers 1 and 2, in which the phosphorus compounds served as nucleophilic monomers and BQ behaved electrophilically (*polyphosphoranylation*).



TPPI, R = PhO
TPPO, R = Ph

1a, R = PhO (1)
b, R = Ph



POBP, R = PhO
PBP, R = Ph

(2)

2a, R = PhO
b, R = Ph

Table I
Alternating Copolymerization of *p*-Benzoquinone with Phosphorus(III) Compounds[a]

sample no.	P(III) compound	temp, °C	time, h	polymer yield, %	polymer structure	polymer mol wt[b]
1	TPPI	130	38	32	**1a**	3200
2	TPPI	150	52	68	**1a**	6400
3	TPPO	150	52	62	**1b**	5900
4	POBP	150	48	43	**2a**	3800
5	PBP	150	58	72	**2b**	4100

[a] 3 mmol each of the monomers in 3 mL of benzonitrile. [b] Determined by vapor pressure osmometry in DMF at 55 °C.

The copolymerization of TPPI and BQ was carried out in benzonitrile. At temperatures higher than 130 °C the copolymerization took place without added initiator and alternating copolymer **1a** was obtained after work-up procedures excluding moisture. The product copolymer was a pale grayish powder soluble in polar solvents such as DMF, Me_2SO, and $CHCl_3$ but insoluble in diethyl ether, benzene, and water. Copolymerization results are given in Table I.

The structure of the copolymer was determined by ^{31}P NMR and IR spectroscopy as well as by elemental analysis. The ^{31}P NMR spectrum of the isolated copolymer **1a** shows a broad peak centered at δ -85.6 ppm, indicating that the copolymer is composed of a pentaphenoxyphosphorane-type structure.[16] Furthermore, absorption due to P=O stretching was not found in the IR spectrum. The results of the elemental analysis were in good agreement with the calculated values for 1:1 TPPI-BQ (Table II).

Similarly, copolymerizations of TPPO, POBP, and PBP with BQ were performed at 150 °C and gave phosphorane-type polymers **1b**, **2a**, and **2b** (Tables I and II). These copolymers were not so unstable to moisture in spite of the fact they contain a phosphorane unit which is usually very sensitive to moisture.

In the present copolymerizations, the phosphorus(III) monomers were converted to pentavalent phosphoranes, whereas BQ was reduced to the ether of hydroquinone. Thus, these copolymerizations offer additional examples of "redox copolymerizations".[5,7,9]

The hydrolysis of polymer **1a** took place readily at room temperature with an excess of water in benzonitrile. The ^{1}H-decoupled ^{31}P NMR of the reaction mixture showed several peaks between -15 and -18 ppm. This result is taken to indicate the production of a mixture of triaryl phosphates of several combinations of phenoxy and para-substituted phenoxy groups. Among these, the main product was triphenyl phosphate. These results show that the P-O bond cleavage occurred at all P-OAr, including that of the main chain. In the case of polymer **2b**, elim-

Table II
^{31}P NMR and Elemental Analyses of Alternating Copolymers

sample no.	structure	^{31}P NMR,[a] ppm	formula[b]	anal. calcd[b] C	calcd H	calcd P	found C	found H	found P
2	**1a**	-85.6	$(C_{24}H_{19}O_5P)_n$	68.90	4.58	7.40	68.78	4.31	7.52
3	**1b**	-69.5	$(C_{24}H_{19}O_4P)_n$	71.64	4.76	7.70	71.32	4.81	7.88
4	**2a**	-56.8	$(C_{18}H_{13}O_5P)_n$	63.54	3.85	9.10	63.46	3.78	9.04
5	**2b**	-40.0	$(C_{18}H_{13}O_4P)_n$	66.67	4.04	9.55	66.31	3.85	9.72

[a] ^{31}P NMR spectra were recorded without proton decoupling. Chemical shifts are negative upfield from external 80% H_3PO_4 standard. [b] Calculated for 1:1 composition.

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