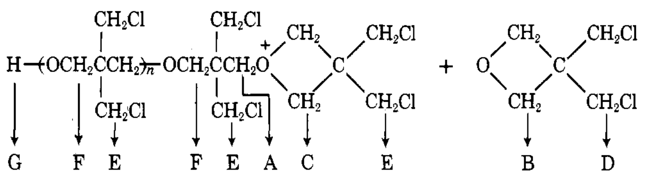
Table VII
Spectral Assignments in the Polymerization Mixture of Bis(chloromethyl)oxetane in CH_2Cl_2



Signal	Chem Shift in ppm (from Me_4Si)
A	4.56
B	4.41
C	4.31
D	3.91
E	3.60
F	3.47
G	10.8–2.9

protons and D to the chloromethyl protons. On polymerization both signals are shifted upfield, but due to the relief of ring strain the oxetane proton signals are shifted further (F) than the chloromethyl protons (E). A solution of poly[bis(chloromethyl)oxetane] shows, therefore, two sharp singlets of equal intensity, one at 3.60 ppm, the other one at 3.47 ppm.[11] The low degree of polymerization of the illustrated example causes the polymer peaks to become unequal in intensity, since the chain methylene groups which are α to an oxonium ion are shifted downfield, and the chloromethyl signal appears correspondingly stronger. Peak C (4.31 ppm), which has twice the intensity of peak A (4.56 ppm), was assigned to the ring methylene groups of the growing chain end, while peak A was assigned to the straight-chain methylene group adjacent to the oxonium ion. Signal G, finally, is due to the exchangeable hydroxyl proton (Table VII).

From Table VI it is seen that 40% of the monomer is consumed within the first 5 min. The initial ring opening and formation of tertiary oxonium ions is so fast at 0° that in contrast to five-membered cyclic ethers, no molecular weight maximum could be detected. After the free acid is consumed, the subsequent ring opening is much slower, and almost 6 hr are necessary for 60% of monomer to be consumed.

---

[11] Jeol Spectrum, No. 184, Sadler Corp., Philadelphia, Pa.

Sequence Analysis of Ethylene Oxide–Propylene Oxide Copolymers by Carbon-13 Nuclear Magnetic Resonance

E. B. Whipple* and P. J. Green

Union Carbide Corporation, Tarrytown Technical Center, Tarrytown, New York 10591.

Received July 28, 1972

ABSTRACT: The chain carbon-13 spectra of ethylene oxide–propylene oxide copolymers are assigned in terms of dyad and triad sequences. Ambiguities in the derivation of sequence distribution from nmr intensities are discussed. In the base-catalyzed copolymers examined, the distribution and tacticity of propylene oxide units are approximately random, but the monomer units are directionally oriented. A rather high probability of chain termination by propylene oxide groups is also noted.

Despite the fact that practical limitations have forced a very heavy emphasis on protons, nuclear magnetic resonance techniques have proved an extremely valuable method for the characterization of polymer structures.[1] The advent of fast Fourier transform methods[2] now makes it practical to extend these methods to carbon-13, where the expanded chemical shift range, longer relaxation times, isotopic dilution, and more direct involvement of the nuclei in the critical bonding features of organic molecules promise an extension considerably beyond the resolution available in proton magnetic resonance studies. Poly(propylene oxide) provides a case in point.[3-5] The present study considers the carbon-13 spectrum of a slightly more complicated copolymer system containing both ethylene oxide and propylene oxide units. Only the main-chain carbons are considered, since the methyl group spectrum shows no resolvable structure and consequently yields little information not available from other sources. With the application of proton decoupling, the carbon-13 spectrum is reduced to one sharp line for each unique chain carbon environment in the molecule, the criterion of uniqueness being defined by the chain length over which structural features affect the chemical shifts. A typical spectrum, shown in Figure 1, shows a multiplicity of lines indicative of the fact that the amount of structural information available is rich. The gross features of this spectrum can be reduced, moreover, to four main bands that are indicated in the figure. Our main concern in this study is to assign these bands to structural features, to relate these features to chemical parameters such as monomer sequencing and tacticity, and to indicate some of the ways in which this information conveys diagnostic information about the polymerization. We have not

---

[1] F. A. Bovey, "High Resolution NMR of Macromolecules," Academic Press, New York, N. Y., 1972.

[2] T. C. Farrar and E. D. Becker, "Pulse and Fourier Transform NMR," Academic Press, New York, N. Y., 1971.

[3] K. C. Ramey and N. D. Field, *J. Polym. Sci., Part B*, **2**, 461 (1964).

[4] N. Tane, N. Oguni, and S. Watanabe, *J. Polym. Sci., Part B*, **6**, 577 (1968).

[5] J. Schaefer, *Macromolecules*, **2**, 533 (1969).

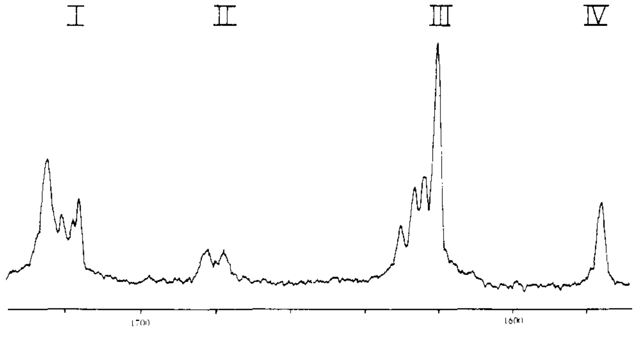
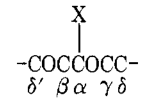


Figure 1. Carbon-13 nmr spectrum of chain carbon atoms in poly(ethylene oxide-propylene oxide) showing four main bands (sample 2 in Table III).

emphasized the quantitative aspects at this stage beyond the point of establishing the assignments and drawing some of the more obvious structural conclusions.

Assignments

Conceptually, an ethylene oxide-propylene oxide copolymer can be generated by methyl substitution on arbitrary, nonadjacent carbon atoms in a poly(ethylene oxide) chain. The amount of information that can be derived about this substitution from nmr spectroscopy will depend on the extent to which it is felt along the backbone chain. For long, unsubstituted chains, all the carbon atoms and attached protons are virtually equivalent. If a substitution shifts the immediately affected CH group away from the rest, or if the substituent itself is observable, one can determine the number of positions substituted. On this basis, the methyl to methylene-methine proton distribution has long been used to measure ethylene oxide:propylene oxide ratios. If the effect of substitution extends to the β position, no new information is derived, since substitution on adjacent carbon atoms is logically excluded. If the effect is felt as far as the γ position, then information about dyad sequences can be derived. At the δ position, triad sequences begin to be discernible. In analyzing these spectra, therefore, it is instructive first to consider the number of chain positions over which a methyl substitution is felt. This is easily done by observing a copolymer containing a small number of randomly sequenced propylene oxide units, each of which should be widely separated from the others. Such a spectrum, shown in Figure 2, contains a strong line obviously due to the ethylene oxide sequences, and three smaller, equally intense lines reflecting substituent effects felt at the α, β, and γ positions. One should, therefore, be able to interpret the gross features of the more general spectrum in Figure 1 in terms of dyad sequences. It further simplifies matters to consider at the outset only the four main bands into which this spectrum can be divided, ignoring for the moment the fine structure in each band.



$$\begin{array}{c} -\mathrm{COC}\overset{\overset{\displaystyle \mathrm{X}}{|}}{\mathrm{C}}\mathrm{OCC}- \\ \delta'\ \beta\alpha\ \gamma\delta \end{array}$$

It is clear from Figure 2 that carbon atoms with no substitution as close as two chain positions away give rise to lines in band III, while the three possibilities containing one substituent within this range give two lines in band I and one in band IV. The spectrum of poly(propylene oxide) falls entirely in bands I and II. Since each segment in poly(propylene oxide) must contain either α or β substitution, this spectrum requires that monosubstitution at the α and β position shifts the backbone carbon resonance downfield to band I, while γ substitution shifts it upfield to band IV. Band II must consequently arise from combined substitution at the α or β and the γ positions. The effects of carbon substitution derived in this manner (α = −4.3 ppm, β = −4.6 ppm, γ = 1.9 ppm) are about half as large as the additive values determined by Grand and Paul[6] for hydrocarbon chains. The band assignments for all possible substituted segments are listed in Table I.

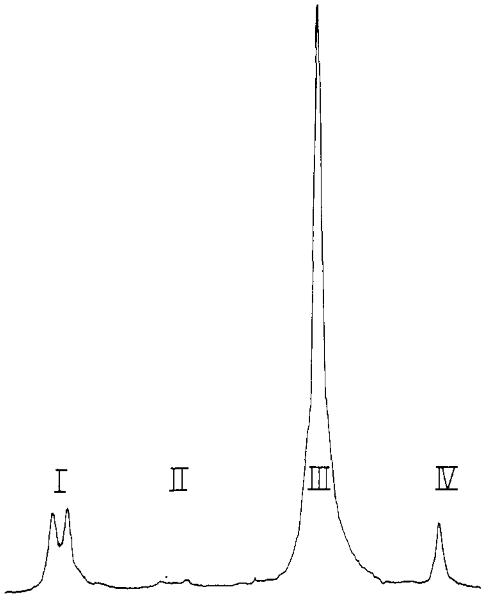


Figure 2. Nmr spectrum of chain carbon-13 in dilute copolymer (sample V in Table III).

Table I
Methyl Substitution and Band Assignments of Chain Carbons in Ethylene-Propylene Oxide Dyads

Band:	III	I		IV	II	
Substitution:	0	α	β	γ	$\alpha+\gamma$	$\beta+\gamma$
EE	2	0	0	0	0	0
$\mathrm{E}\overleftarrow{\mathrm{P}} = \overrightarrow{\mathrm{P}}\mathrm{E}$	0	1	0	1	0	0
$\overleftarrow{\mathrm{P}}\mathrm{E} = \mathrm{E}\overrightarrow{\mathrm{P}}$	1	0	1	0	0	0
$\overrightarrow{\mathrm{P}}\overrightarrow{\mathrm{P}} = \overleftarrow{\mathrm{P}}\overleftarrow{\mathrm{P}}$	0	1	0	0	0	1
$\overleftarrow{\mathrm{P}}\overrightarrow{\mathrm{P}}$	0	0	2	0	0	0
$\overrightarrow{\mathrm{P}}\overleftarrow{\mathrm{P}}$	0	0	0	0	2	0

Sequence Analysis

There are six possible dyad sequences in ethylene oxide propylene oxide copolymers. These are listed in the left hand column of Table I. Each dyad contains two carbon atoms whose substitution is uniquely specified within the present range of interest, and these are specified in the right-hand columns of Table I. The numbers in that portion of the table correspond to the matrix of coefficients of six linear equations in six unknowns relating the positions of neighboring methyl substitution to the dyad sequences. Inspection of this table quickly reveals that the set of equations are not linearly independent; *e.g.*, the sum of columns four and six equals column two. If, moreover, the numbers of carbon atoms bearing each allowed combina-

---

(6) D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, 86, 2984 (1964).

tion of neighboring substituents are to be determined from the intensities of the four main bands in Figure 1, then two pairs of columns in Table I must be combined as indicated to allow for the fact that certain combinations of substitution give lines in the same bands. This results in four independent equations in the six unknowns.

In slightly rearranged form, these equations read

$$2(A_{\mathrm{I}} - A_{\mathrm{II}}) = F_{\mathrm{E}\overleftarrow{\mathrm{P}}} + F_{\mathrm{E}\overrightarrow{\mathrm{P}}} + 2\Delta \qquad (1)$$

$$2(A_{\mathrm{I}} + A_{\mathrm{II}}) = F_{\mathrm{E}\overleftarrow{\mathrm{P}}} + F_{\mathrm{E}\overrightarrow{\mathrm{P}}} + 2F_{\mathrm{PP}} \qquad (2)$$

$$2(A_{\mathrm{III}} + A_{\mathrm{IV}}) = 2F_{\mathrm{EE}} + F_{\mathrm{E}\overleftarrow{\mathrm{P}}} + F_{\mathrm{E}\overrightarrow{\mathrm{P}}} \qquad (3)$$

$$2A_{\mathrm{IV}} = F_{\mathrm{E}\overleftarrow{\mathrm{P}}} \qquad (4)$$

where F is the fractional population of the subscripted dyad, A_{i} is the normalized area of the subscripted band in the nmr spectrum, and

$$F_{\mathrm{PP}} = F_{\overrightarrow{\mathrm{P}}\overrightarrow{\mathrm{P}}} + F_{\overrightarrow{\mathrm{P}}\overleftarrow{\mathrm{P}}} + F_{\overleftarrow{\mathrm{P}}\overrightarrow{\mathrm{P}}} \qquad (5)$$

$$\Delta = F_{\overleftarrow{\mathrm{P}}\overrightarrow{\mathrm{P}}} - F_{\overrightarrow{\mathrm{P}}\overleftarrow{\mathrm{P}}} \qquad (6)$$

The factor of two on the left-hand side of eq 1–4 results from the fact that each dyad contributes two carbon atoms to the total.

The ethylene oxide and propylene oxide fractions, which are independently measurable either from the proton resonance spectrum or by including the methyl ^{13}C line, are related to the dyad sequence population by eq 7 and 8, and hence provide no new information.

$$X_{\mathrm{E}} = \tfrac{1}{2}[2F_{\mathrm{EE}} + F_{\mathrm{E}\overleftarrow{\mathrm{P}}} + F_{\mathrm{E}\overrightarrow{\mathrm{P}}}] = A_{\mathrm{III}} + A_{\mathrm{IV}} \qquad (7)$$

$$X_{\mathrm{p}} = \tfrac{1}{2}[2F_{\mathrm{PP}} + F_{\mathrm{E}\overrightarrow{\mathrm{P}}} + F_{\mathrm{E}\overleftarrow{\mathrm{P}}}] = A_{\mathrm{I}} + A_{\mathrm{II}} \qquad (8)$$

There is also a logical restriction relating the dyad fractions in an infinite chain

$$\tfrac{1}{2}(F_{\mathrm{E}\overleftarrow{\mathrm{P}}} - F_{\mathrm{E}\overrightarrow{\mathrm{P}}}) = F_{\overleftarrow{\mathrm{P}}\overrightarrow{\mathrm{P}}} - F_{\overrightarrow{\mathrm{P}}\overleftarrow{\mathrm{P}}} = \Delta \qquad (9)$$

This follows from the fact that in any propylene oxide sequence the number of head-to-head and tail-to-tail dyads can differ at most by one, and the entry and exit dyads ($\mathrm{E}\overrightarrow{\mathrm{P}}$ and/or $\mathrm{E}\overleftarrow{\mathrm{P}}$) will differ by two or be the same depending on whether or not an unequal number of such linkages has occurred. However, this condition is also dependent on the set of equations already available, since combination of eq 1 and 4 gives

$$2(A_{\mathrm{I}} - A_{\mathrm{II}} - 2A_{\mathrm{IV}}) = F_{\mathrm{E}\overrightarrow{\mathrm{P}}} - F_{\mathrm{E}\overleftarrow{\mathrm{P}}} + 2\Delta = 0 \qquad (10)$$

Equations 7 and 10 provide two independent checks on the validity of the assignments in Table I and the reliability of population data inferred from carbon-13 intensities. Some experimental results are collected in Table II. The monomer fraction inferred from eq 7 and 8 compare favorably with those derived from proton resonance measurements, confirming the main assignments in this study. The data in column 8 of Table II are not, however, internally consistent with eq 10, since they show a small, but consistently positive residue. This point will be considered in detail later on.

It is possible to make an approximate analysis of the gross monomer sequencing by introducing the reasonable assumption that the numbers of head-to-head and tail-to-tail propylene oxide dyads are equal. In this approximation, Δ is assumed to vanish in eq 1, whereupon the set of eq 1–4 can be solved disregarding the orientations of monomer units within propylene oxide sequences. The assumption that $\Delta = 0$ is true at both limits of the ethylene oxide:propylene oxide ratio, and would be a valid approximation elsewhere provided, as chemical evidence indicates,[7] that head-to-tail propylene oxide addition is strongly preferred. This premise is questioned, however, by the observation of two clearly resolved components in band II of the carbon-13 spectrum, this being precisely the structure predicted by Table I when head-to-head propylene oxide dyads occur with about equal probability. (The head of a propylene oxide unit is herein considered to be the end bearing the methyl group.) The two lines observed in band II have, moreover, been assigned to inverted dyads in poly(propylene oxide).[5] It is therefore necessary to justify our neglect of differences in abnormal propylene oxide dyads on the basis that both are small.

Table II
Measured Band Intensities in Chain Carbons of Poly(ethylene oxide–propylene oxide)

Sample No.	X_{p}[a]	A_{I}	A_{II}	A_{III}	A_{IV}	$A_{\mathrm{I}} + A_{\mathrm{II}}$	$A_{\mathrm{I}} - A_{\mathrm{II}} - 2A_{\mathrm{IV}}$
I[b]	0.47	0.35	0.10	0.45	0.11	0.45	0.04
II[b]	0.44	0.35	0.10	0.46	0.10	0.45	0.05
III[c]	0.40	0.330	0.055	0.509	0.106	0.395	0.063
IV[c]	0.52	0.42	0.13	0.35	0.11	0.55	0.07
V[c]	0.17	0.18	0.04	0.73	0.06	0.22	0.02
Columns: 1	2	3	4	5	6	7	8

[a] Propylene oxide fraction measured from methyl group tc methylene + methine proton ratios. [b] Butoxide initiated, mol wt ~1800. [c] Diol, mol wt ~2600.

Schaefer[5] has reported off-resonance proton-decoupling experiments in poly(propylene oxide) which show the lines corresponding to band I to be due to methine carbons and those in the region of band II to arise from methylene carbons. On the basis of these results and analogy to trimethylene glycol, he deduced tentative assignments that differ from those in Table I; namely, that α and $\alpha + \gamma$ sequences occur in band I, while β and $\beta + \gamma$ sequences occur in band II. The effect of these assignments in our spectra would be to replace eq 1 with 11, while leaving eq 2–4 unaltered. Insertion of the condition (9) in eq 11 would then predict

$$2(A_{\mathrm{I}} - A_{\mathrm{II}}) = F_{\mathrm{E}\overrightarrow{\mathrm{P}}} - F_{\mathrm{E}\overleftarrow{\mathrm{P}}} - 2\Delta \qquad (11)$$

$$2(A_{\mathrm{I}} - A_{\mathrm{II}}) = 2\Delta - 2\Delta = 0$$

which the data in Table II clearly do not support. Moreover, undecoupled spectra of our copolymers show the presence of both methylene and methine carbons in band I. One can reconcile all the *direct* evidence in the two studies (*i.e.*, our intensity data and Schaefer's decoupling results) only by excluding significant numbers of head-to-head and tail-to-tail propylene oxide sequences. In this event, β sequences would be excluded from band I and $\alpha + \gamma$ sequences excluded from band II in poly(propylene oxide), leaving only methine carbons in the former and methylene carbons in the latter.

A second line of evidence is found in the fine structure within the bands. In addition to the doublet structure in band II, on scale expansion fine structure is seen in two other main bands of Figure 1. This fine structure could result either from steric effects in the propylene oxide se-

---

(7) C. E. Price, R. Spector, and A. M. Tumolo, *J. Polym. Sci., Part A1*, 5, 407 (1967).

Table III
Triad Sequences in Band II of ^{13}C Spectrum

Triad	Structure $\delta'\quad\beta\ \alpha\quad\gamma\ \delta$	δ Substitution[a] 0	δ	δ'	$\delta+\delta'$
EEE	C-C-O-$\underline{\mathrm{C}}$-$\underline{\mathrm{C}}$-O-C-C	2	0	0	0
$\mathrm{EE\overrightarrow{P}} = \mathrm{\overleftarrow{P}EE}$	C-C-O-$\underline{\mathrm{C}}$-$\underline{\mathrm{C}}$-O-C-$\overset{\vert}{\mathrm{C}}$	1	1	0	0
$\mathrm{\overrightarrow{P}EE} = \mathrm{EE\overleftarrow{P}}$	C-$\overset{\vert}{\mathrm{C}}$-O-C-$\underline{\mathrm{C}}$-O-C-C	0	0	1	0
$\mathrm{\overleftarrow{P}E\overleftarrow{P}} = \mathrm{\overrightarrow{P}E\overrightarrow{P}}$	$\overset{\vert}{\mathrm{C}}$-C-O-$\underline{\mathrm{C}}$-C-O-$\overset{\vert}{\mathrm{C}}$-C	0	0	0	1
$\mathrm{\overleftarrow{P}E\overrightarrow{P}}$	$\overset{\vert}{\mathrm{C}}$-C-O-$\underline{\mathrm{C}}$-$\underline{\mathrm{C}}$-O-C-$\overset{\vert}{\mathrm{C}}$ $\delta\ \ \gamma\quad\ \alpha\ \beta\quad\ \delta'$	0	2	0	0

[a] Entries made in right-hand columns only for α-, β-, and γ-unsubstituted sequences.

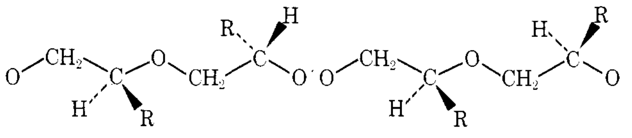
quences or from substituent effects over longer sequence lengths. In the case of band III, four lines are observed under higher resolution which, since no asymmetric centers are included within the substitutional segment, would clearly seem to result from triad sequences. There are two nonequivalent δ positions available, and one might therefore expect to observe as many as four lines corresponding to methyl substitution on neither, either, or both of the two carbon atoms available. This interpretation is in accord with rough quantitative considerations. The triad sequences which give rise to absorption in band III are detailed in Table III, where the number of carbon atoms corresponding to each type of δ substitution are listed for each sequence. The first four rows in the table correspond to "normal" triad sequences, while the fifth involves a tail-to-tail sequence. (Insertion of ethylene oxide units between propylene oxide groups can, for the purpose of discussing orientation of the latter, be disregarded.) The distribution of intensity among the four lines in band III clearly depends on whether or not this sequence is allowed. Assuming, as the dyad sequence analysis bears out, that the monomer distribution is approximately random, one can calculate the proportion of each sequence from the ethylene oxide:propylene oxide ratio. If one further assumes an orderly progression of chemical shifts from cumulative substituent effects, then one would predict the following trends as the monomer ratio is varied. If abnormal additions ($\mathrm{\overleftarrow{P}E\overrightarrow{P}}$ triads) are excluded, the lowest field component (all δ-substituent shifts being to lower field) due to $\mathrm{\overrightarrow{P}E\overrightarrow{P}}$ triads would decrease fastest with increasing ethylene oxide content, while the two middle lines due to traids containing a single propylene oxide unit would decrease at the same, somewhat slower rate. If, on the other hand, abnormal additions are appreciable, then all lines would vary at different rates, with one of the intermediate lines changing most rapidly. The experimental results agree with the first alternative, giving added evidence that abnormal additions do not occur significantly.

One consequence of our straightforward assignment of fine structure in band III to δ substitution is that one might also expect to resolve two lines in band IV and four lines in band II, according to the possibilities enumerated in Table IV. In neither case is this observed. Any rationale of this behavior admitting abnormal additions is necessarily devious, involving nonadditive combinations of substituent effects in the γ and δ positions. However, the absence of fine structure in band IV is a simple and direct consequence of the exclusion of abnormal ($\mathrm{\overrightarrow{P}E\overleftarrow{P}}$) sequences. Similarly, all the triad sequences in band II except for the $\mathrm{E\overleftarrow{P}\overleftarrow{P}}$ also involve abnormal additions, so that no fine structure in this band would originate from δ' substitution.

Table IV
Triad Sequences in Bands II and IV of the ^{13}C Spectrum

Sequence	Structure	Substitution
Band IV		
$\mathrm{EE\overleftarrow{P}}$	CCOC$\underline{\mathrm{C}}$O$\overset{\vert}{\mathrm{C}}$C	γ
$\mathrm{\overleftarrow{P}E\overleftarrow{P}}$	$\overset{\vert}{\mathrm{C}}COC\underline{\mathrm{C}}O\overset{\vert}{\mathrm{C}}$C	γ
$\mathrm{\overrightarrow{P}E\overleftarrow{P}}$	C$\overset{\vert}{\mathrm{C}}O\underline{\mathrm{C}}\underline{\mathrm{C}}O\overset{\vert}{\mathrm{C}}$C	$2(\gamma+\delta')$
Band II		
$\mathrm{E\overrightarrow{P}\overleftarrow{P}}$	CCOC$\underline{\overset{\vert}{\mathrm{C}}}O\overset{\vert}{\mathrm{C}}$C	$\alpha+\gamma$
$\mathrm{\overleftarrow{P}\overrightarrow{P}\overleftarrow{P}}$	$\overset{\vert}{\mathrm{C}}COC\underline{\overset{\vert}{\mathrm{C}}}O\overset{\vert}{\mathrm{C}}$C	$\alpha+\gamma$
$\mathrm{\overrightarrow{P}\overrightarrow{P}\overleftarrow{P}}$	C$\overset{\vert}{\mathrm{C}}O\underline{\mathrm{C}}\underline{\overset{\vert}{\mathrm{C}}}O\overset{\vert}{\mathrm{C}}$C	$\alpha+\gamma+\delta'$ $\beta+\gamma+\delta'$
$\mathrm{E\overleftarrow{P}\overleftarrow{P}}$	CCO$\overset{\vert}{\mathrm{C}}\underline{\mathrm{C}}O\overset{\vert}{\mathrm{C}}$C	$\beta+\gamma$

One is therefore led to conclude that the main doublet which is observed in band II must be due to the methylene carbon in isotactic and syndiotactic head-to-tail propylene oxide dyads. Schaefer[5] has shown that only the



isotactic PP dyad   syndiotactic PP dyad

lower field member of this doublet persists in crystalline poly(propylene oxide), and on the basis of this evidence it can be assigned to the isotactic dyad. The steric sequencing in the polyethers studied in this report appears to be slightly weighted in favor of isotactic dyads.

Discussion of Results

Having concluded that the fraction of abnormal additions is small, one can reasonably neglect Δ in eq 1 and solve the resulting set of four equations in four unknowns to obtain an approximate analysis of the dyad sequences. However, the failure, expressed in column 8 of Table II, of the experimental quantities on the left-hand side of eq 10 to vanish, as required by eq 9, will result in a consistent excess of ethylene to propylene tail ($\mathrm{E\overrightarrow{P}}$) over ethylene to propylene head ($\mathrm{E\overrightarrow{P}}$) dyads. One possible source of this discrepancy is the failure of eq 9 due to end-group effects on finite chains. If the addition to propylene oxide is highly directional, then each chain terminating in a propylene oxide group will have one or two (depending on whether the chain can propagate in both directions) extra $\mathrm{E\overrightarrow{P}}$ dyads. Equation 9 should therefore be modified to read

$$F_{\mathrm{E\overrightarrow{P}}} - F_{\mathrm{E\overleftarrow{P}}} = 2(F_{\mathrm{\overrightarrow{P}\overleftarrow{P}}} - F_{\mathrm{\overleftarrow{P}\overrightarrow{P}}}) + \frac{\beta}{n} = \frac{\beta}{n} - 2\Delta \quad (9')$$

where n is the degree of polymerization and $0 \leq \beta \leq 2$ is the average number of propylene oxide end groups per chain. With this modification, eq 10 now reads

$$2(A_{\mathrm{I}} - A_{\mathrm{II}} - 2A_{\mathrm{IV}}) = F_{\mathrm{E\overrightarrow{P}}} - F_{\mathrm{E\overleftarrow{P}}} + 2\Delta = \frac{\beta}{n} \quad (10')$$

Through observation of the proton resonance of propylene oxide groups in appropriate solvents such as pyridine it is possible to measure independently the fraction, X'_{p}, of these groups at hydroxyl-terminated chain ends. An ex-

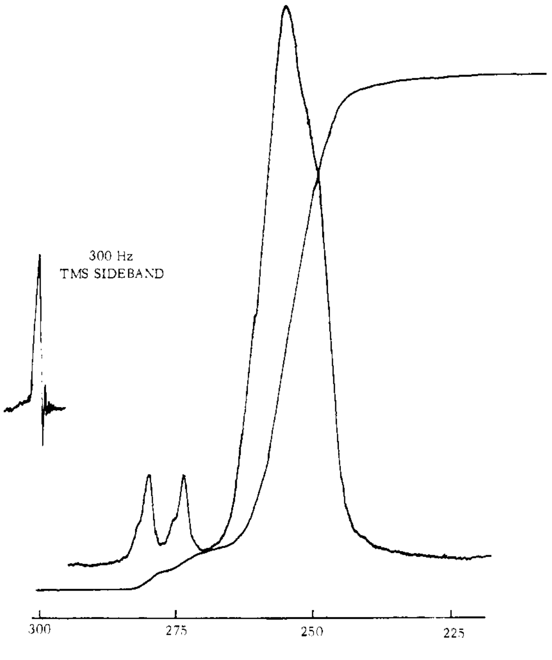


Figure 3. Pmr spectrum of methyl groups in sample IV of Table III, observed in pyridine solution to reveal end-group doublets.

ample is shown in Figure 3. One can therefore determine β/n independently from the relation

$$\beta/n = X'_P n_P/n = X'_P X_P$$

The results shown in Table V do indicate a surprisingly high probability of propylene oxide termination, values of β close to the maximum being obtained when values of n are estimated from the approximate molecular weights (Table II). Nevertheless, end effects are able to account for only one-third of the total discrepancies listed in column 8 of Table II.

There are two other plausible soucces of small error, and the present accuracy of our data does not permit a clear-cut choice between them. The first possibility is a differential nuclear Overhauser effect[8] resulting from the proton decoupling. In order to explain the discrepancy with eq 10, this would have to take the form of a greater enhancement of the methine carbon resonance over the methylene carbon. Neither effect is consistent with measurements of the homopolymers which show equal NOE's for all carbons in poly(propylene oxide) which are slightly smaller (2.5 *vs.* 2.7) than that in poly(ethylene oxide).[9] Also, an effect of this type would be manifested in consistently erroneous values of the ethylene oxide:propylene oxide ratios derived from eq 8, leading one to expect the values in column seven of Table II to exceed those in column two. This does not consistently happen, leading one to infer that differential NOE's of either type are smaller than other errors in the measurements.

A second possible source of error is the improper assignment of band positions to the inverted propylene oxide dyads. Since their numbers are small, there is no direct evidence for the assignments of (α + γ)-substituted sequences to band II, and one might reasonably expect sufficient interaction between the two groups to void the simple additivity rule on which the assignment to this band is based. Although a matter of conjecture, it is pertinent to consider the effect of including α + γ sequences in either of the adjacent bands. This will alter eq 1-4, the result in each case being, together with eq 8 and 9, to yield a set of five equations in the six dyad populations plus one redundancy which serves as a consistency check. Introducing the assumption Δ = 0 again permits a solution in each case. A moment's reflection shows that moving a resonance from band II to band I will not affect the measured ethylene oxide:propylene oxide ratio, and will be doubly effective in reducing the terms in column 8 of Table II which involves the difference of these bands. Shifting lines from band II to and III will be less effective in bringing column 8 into line, and will diminish the agreement between column 7 and the monomer ratio. A somewhat better situation results from the first assumption, therefore, but in either case the discrepancies can be brought into line with reasonable numbers of inverted dyads. If the α + γ sequences occur in band I for example, then about 10% of the propylene oxide dyads are calculated to be of the head-to-head type.

Table V
End-Group Effects in Poly(ethylene oxide–propylene oxide)

Sample No.	$X_P{}'^a$	$X_P{}^b$	$X_P{}'X_P$	β/n^c
I	0.084	0.47	0.039	0.08
II	0.081	0.44	0.036	0.10
III	0.080	0.40	0.032	0.126
IV	0.074	0.52	0.039	0.13
V	0.126	0.17	0.021	0.06

[a] Measured from methyl end-group fraction (Figure 3). [b] Table II. [c] From eq 10′ and Table II.

For any assignment of the minor α + γ sequences, one derives a highly random monomer distribution from the data in Table II. One can therefore readily distinguish block from random copolymers and make an approximate analysis of the dyad sequence distribution, including the stereochemistry of propylene oxide dyads. To pursue the fine details, however, more must be learned about the relative magnitudes of nuclear Overhauser effects and the positions of some of the weaker lines. It does not at the present stage appear hopeless that carbon-13 nmr will prove to be a useful quantitative, as well as qualitative, structure tool.

Experimental Section

All ^{13}C spectra were run on a Brucker HFX-90 multinuclear spectrometer operating at 22.63 MHz ,and locked on an external ^{19}F resonance from C_6F_6. The spectrometer is equipped with a proton noise decoupler and a Fabritek 1070 fast Fourier transform system with a capacity of 4K, 18 bit words of data. The pulse system is capable of rotating the ^{13}C magnetization 90° in about 10 μsec in a single-coil rf configuration. Pulse widths of 8 μsec were normally employed for data scanning, with repetition periods of 4 sec, corresponding to a sepctrum range of 500 Hz and computer resolution of 0.25 Hz; 256 scans were accumulated over periods of 17 min each.

Samples were commercial grade materials provided by Dr. C. L. Schilling of the Union Carbide Corp., Tarrytown, N. Y., and were observed both as neat liquids and as ~20% solutions in CCl_4 or $CDCl_3$ in order to enhance resolution.

Proton spectra were recorded on a Varian HR-220 instrument operated by a Consortium at the Rockefeller University, and supported in part by NSF Grant No. GB12278 and grants from the Research Corp. and Sloan Foundation.

Acknowledgments. The authors express their appreciation to Mr. M. Ruta, who obtained most of the spectra on which this study is based, and to Mr. R. A. Thursack of Union Carbide Corp., South Charleston, W. Va., for a most helpful discussion involving the interpretation.

---

(8) E. G. Paul and D. M. Grant, *J. Amer. Chem. Soc.*, **86**, 2977 (1964).

(9) J. Schaefer and D. F. S. Natusch, *Macromolecules*, **5**, 416 (1972).