# Tetrahydrofuran—propylene oxide copolymers: 1. End-group analysis by $^{13}C$ n.m.r. and the mechanistic inferences

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The boron trifluoride catalysed copolymerization of tetrahydrofuran and propylene oxide in the presence of 1,4-butanediol leads to linear, difunctional copolymers. The $^{13}C$ n.m.r. spectra of these copolymers are exceptionally informative in that the compositions, the molecular weights and the types of end-groups can all be obtained independently from both regions of the spectrum. The types of end-groups were identified by an off-resonance and a gated decoupling technique. No tetrahydrofuran end-groups were found. Only propylene oxide end-groups with a 2:1 ratio of secondary alcohol to primary alcohol were observed, regardless of the composition or the molecular weight of the polymer. The propylene oxide end-groups of the copolymer are considered to be formed by initial propagation reactions. These reactions are the attack of either monomer on the protonated propylene oxide to open the oxirane ring and form a cyclic oxonium ion. Attack on protonated tetrahydrofuran is thought not to lead to initiation. 1,4-Butanediol serves as a chain transfer agent and thereby regulates the molecular weight of the copolymer. Polymerization stops when all propylene oxide has been consumed because no new chains can be initiated by the remaining tetrahydrofuran.

## INTRODUCTION

Boron trifluoride etherate catalyses the copolymerization of tetrahydrofuran (THF) and propylene oxide (PO) in the presence of a glycol or water. The materials produced could have terminal hydroxy groups originating from either of the comonomers. In such polymers, a terminal THF unit would afford only a primary alcohol as an end-group while a terminal PO unit could afford either a primary alcohol or a secondary alcohol depending on how the epoxide ring opened. Determining both the hydroxyl content and the nature of the group bearing the end-group is necessary for the complete characterization of THF/PO copolymers.

The quantitative analysis of the end-groups of hydroxy-terminated polyethers has been used as a method of determining either the molecular weight or the functionality of the polymer. Phthalation[1] or acetylation[2] are acceptable methods for these determinations. The difference in reaction rates of primary and secondary hydroxyl groups with acetic anhydride has been used[2,3] to estimate the proportions of each of these alcohols as end-groups in homopolymers and copolymers of propylene oxide. For a routine analysis, we sought a method of analysis which would be quicker, more reliable and subject to less interpolation than the acetylation techniques developed.

Several recent spectroscopic methods have been reported for the end-group analysis of polymers by n.m.r. An analysis of the end-groups of hydroxy-terminated polybutadienes[4] was successful using either $^{13}C$ or $^{1}H$ n.m.r. Similarly, the primary and secondary alcohol content of propylene oxide/ethylene oxide copolymers was determined[5] both by $^{1}H$ n.m.r. after derivatization of the hydroxy-terminated polymer with trichloroacetyl isocyanate and by $^{19}F$ n.m.r. after derivatization of the polymer with trifluoroacetic anhydride.

Rather than being additionally concerned about the quantitative conversion of the end-group alcohols to the derivative, we sought the direct analysis of the end-group and $^{13}C$ n.m.r. seemed to be the most reasonable tool to use. As with any end-group analysis, the accuracy of the method should be greatest with the low molecular weight polymers Therefore, the many samples of difunctional THF/PO copolymers we prepared for this study had low molecular weight, i.e. $M_n < 6000$, and were ideal for this determination.

## EXPERIMENTAL

### *N.m.r.*

$^{13}C$ n.m.r. spectra were obtained with a JEOL PFT 100 spectrometer operating at 25.15 MHz. In addition to the usual random noise proton decoupled spectra, an off-resonance decoupling and a gated decoupling technique were used. Most of the polymers studied had sufficiently low molecular weight, so the spectra were run on neat liquids at 50°C.

Spin–lattice relaxation time, $T_1$, measurements were made on several of these polymers. The longest $T_1$ in the THF/PO copolymers at 26°C is 1.4 sec and arises from the methyl carbon of the poly(propylene oxide) end-group. A 90° pulse of 28 $\mu$sec and repetition times of 8–12 sec were used to ensure complete relaxation of all nuclei between pulses.

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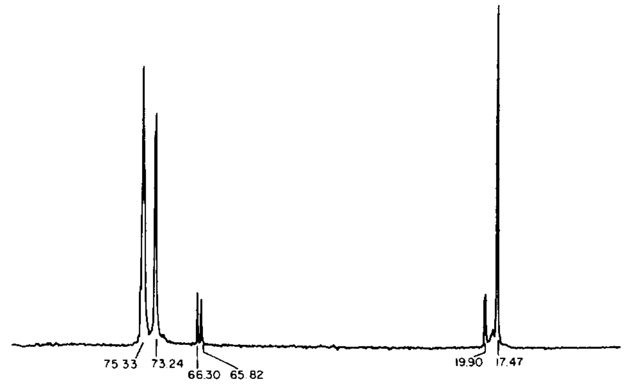


*Figure 1* $^{13}C - \{^1H\}$ n.m.r. spectrum of neat Niax PPG 1025 at 50°C. Peak positions are referenced to TMS. Twenty scans with pulse repetition time of 12 sec and pulse width of 28 μsec (90° tip angle)

Nuclear Overhauser Enhancement (*NOE*) factors were measured and found to vary by no more than 17% at the extreme. Most were within 10% of each other. In the calculations of composition and molecular weights corrections were made for *NOE*.

### *Materials*

Niax Polyol PPG 1025 (hydroxyl no. 113.2) was obtained from Union Carbide Corp. Polymeg (hydroxyl no. 111.1) was obtained from The Quaker Oats Co.

For polymerizations, tetrahydrofuran, 1,2-dichloroethane (both Fisher Scientific Co.), propylene oxide (Eastman), and 1,4-butanediol (MC & B) were found to contain sufficiently small amounts of water that each could be used without further purification. Boron trifluoride etherate was distilled from calcium hydride and excess diethyl ether at reduced pressure. Portions were stored under nitrogen for short periods.

### *Copolymer preparation*

The THF/PO copolymers were prepared according to the basic procedure described by Hammond *et al.*[6]. The polymerizations were carried out in a 1-gallon stainless steel reactor with circulating antifreeze as the coolant. Tetrahydrofuran, propylene oxide (a total of 1000 g of monomers), 1,4-butanediol and 1,2-dichloroethane (1000 ml) solvent were charged to the reactor under nitrogen and allowed to equilibrate at 0°C.

Boron trifluoride etherate (0.08 mol % of the monomers) in 1,2-dichloroethane was then added to initiate polymerization. The reaction was allowed to proceed 16–18 h and was terminated with water. The polymer solution was washed three times with distilled water, dried with magnesium sulphate and concentrated with a rotary evaporator. The molecular weight of the copolymers was controlled by the amount of 1,4-butanediol added[6]. The composition of the copolymer was controlled not only by the ratio of monomer charged but also by the molecular weight of the final polymer formed at a constant monomer charge[7].

## RESULTS AND DISCUSSION

To clarify the various $^{13}C$ n.m.r. peak assignments, several homopolymers were first examined. Some features of the spectra of these materials are important enough to warrant separate consideration.

### *N.m.r. of poly(propylene oxide)*

The $^{13}C - \{^1H\}$ (proton-decoupled) Fourier transform n.m.r. spectrum at 80°C of a neat sample of a commercial poly(propylene oxide), Niax PPG 1025, is shown in *Figure 1*. Peak positions are referenced to TMS. The peaks at the high field side (right side) are due to methyl carbons, and the small peak (which is a doublet) at 19.90 ppm is the methyl carbon of the end-groups. The two tall peaks at 75.33 and 73.24 are main chain methine and methylene carbons, respectively. The two smaller peaks at 66.30 and 65.82 are end-group carbons. The $^{13}C$ n.m.r. number-average molecular weight, $\bar{M}_n$, was calculated to be 918 from this assignment. The $\bar{M}_n$ calculated from the hydroxyl number is 991.

*Figure 2a* is the down-field portion of *Figure 1* on an expanded scale. *Figure 2b* is the spectrum of the same region run in the gated decoupling mode with *NOE* included. Four interesting features are observed in this spectrum.

(a) The end-groups are essentially all secondary OH's as evidenced by the large doublet splitting of the two peaks at 66.30 and 65.82 ppm. If primary OHs were present, a certain amount of triplet splitting due to the $CH_2$ coupling would have been observed.

(b) Both end-group peaks in *Figure 2a*, then, arise from methine carbons and must be sensitive either to the head and tail arrangement of the penultimate unit or to the steric placement of the penultimate methyl group. The latter explanation is probably correct for this polymer. The doublet structure of the end-group methyl carbon would presumably have the same explanation.

(c) The decoupling experiment shows that the large doublet peak at 73.2 ppm in *Figure 2a* is due to the main chain methylene carbons. The small splitting arises from differences in chemical shifts between meso and racemic dyad placements[8]. The approximately equal intensities of these two peaks, as well as in the end-group resonances, indicate random steric placements.

(d) The decoupled spectrum also reveals that the large resonance at 75.33 ppm not only arises from the main chain methine carbons (the large doublet splitting) but also from sizable methylene resonance (the rather broad triplet pattern). This $CH_2$ resonance is probably due to the incorporation of ethylene oxide units in the chain. Proton n.m.r. also suggests this possibility. Additional evidence is that the integrated intensity of this composite peak at 75.33 ppm is about 30% greater than that of the methylene peaks at 73.2 ppm.

*Figure 3* is the $^{13}C - \{^1H\}$ spectrum of a poly(propylene oxide) prepared in this laboratory with a $BF_3{:}OEt_2$ catalyst

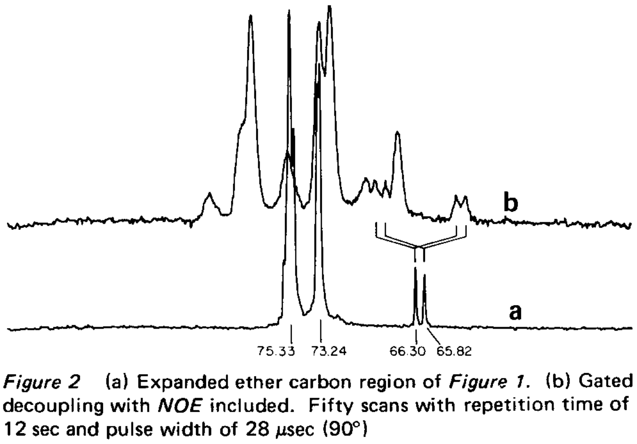


*Figure 2* (a) Expanded ether carbon region of *Figure 1*. (b) Gated decoupling with *NOE* included. Fifty scans with repetition time of 12 sec and pulse width of 28 μsec (90°)

(Sample A in *Table 1*). It is apparent from the main chain resonances that this polymer has several more structures than the polymer in *Figures 1* and *2*. This is more readily seen in *Figure 4* which is the ether carbon region on an expanded scale. *Figure 4a* is the decoupled spectrum and *Figure 4b* is the coupled spectrum in which the noise decoupler was shut off. By careful study of the spectrum, it can be seen that both main peaks contain methine and methylene resonances; therefore, head-to-head and tail-to-tail structures must be present.

For this paper the important features of this spectrum are the end-group patterns. The two peaks labelled '3' in *Figure 4b* are the central and the right satellite peaks of a $CH_2$ triplet, and the peak labelled '2' is the right half of a CH doublet. Thus, the end-groups consist of both primary and secondary OH groups. Integration of the resolved portions of the multiplets reveals that 38% of the end-groups are primary ($CH_2OH$) and 62% are secondary (CHOH). It is puzzling that the methylene and methine carbon peaks of the end-groups are so closely overlapped, but the coupled spectrum clearly shows that this is the case. The two small peaks on the left side of *Figure 4a* are the β carbons of the end-groups but are too overlapped with the large peaks to yield additional information. An n.m.r. $\bar{M}_n$ of 768 was calculated for this sample. The $\bar{M}_n$ determined by gel permeation chromatography (g.p.c.) is 723. This is supporting evidence that no end-groups are 'buried' under other peaks.

*N.m.r. of THF/PO Copolymers*

This series of tetrahydrofuran/propylene oxide (THF/PO) copolymers was prepared using $BF_3{:}OEt_2$ catalyst. The compositions were varied from 14 to 75 mol % PO, and the $\bar{M}_n$s ranged from 450 to 6000. The data for the $^{13}C$ n.m.r. analyses are listed in *Table 1*.

*Figure 5a* shows the ether carbon region of the decoupled spectrum of Sample H (see *Table 1*). In reading from left to right the peak assignments are as follows:

(1) The first grouping of peaks, including the broad peak at 73.22 ppm, are PO carbons. The peaks at 76.79 and 76.20 ppm are $CH_2$ and CH, respectively, β carbons of the PO end-

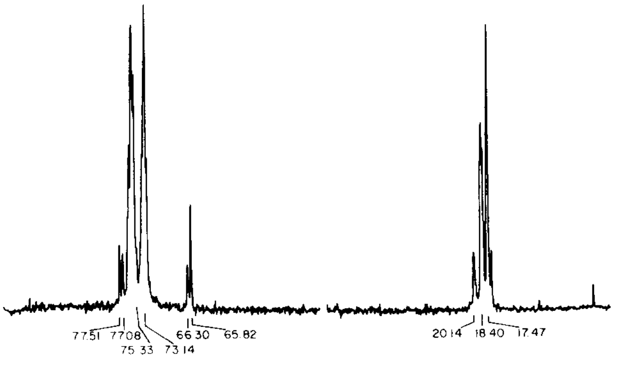


*Figure 3* $^{13}C-\{^1H\}$ n.m.r. spectrum of poly(propylene oxide) (Sample A) prepared with $BF_3-OEt_2$ catalyst. Spectrum obtained on neat liquid at 50° C. Twenty scans with repetition time of 12 sec and pulse width of 28 μsec (90°)

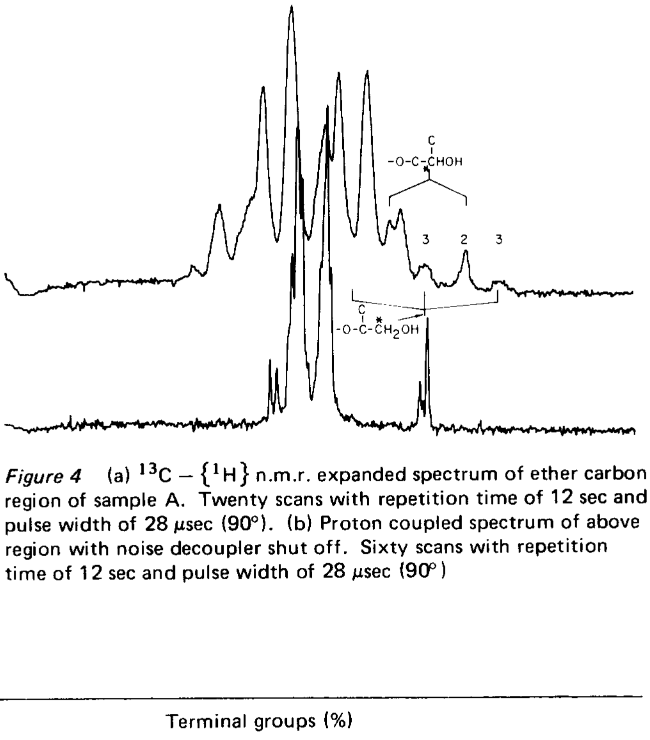


*Figure 4* (a) $^{13}C-\{^1H\}$ n.m.r. expanded spectrum of ether carbon region of sample A. Twenty scans with repetition time of 12 sec and pulse width of 28 μsec (90°). (b) Proton coupled spectrum of above region with noise decoupler shut off. Sixty scans with repetition time of 12 sec and pulse width of 28 μsec (90°)

*Table 1* $^{13}C$ n.m.r. analysis of THF/PO copolymers

| | | | | Terminal groups (%) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Ether carbons | | | Aliphatic carbons | | |
| | | $\bar{M}_n$ | | PO | | THF | PO[b] | | THF |
| Sample | Mol % PO[a] | G.p.c. | $^{13}C$ n.m.r.[a] | CHOH | $CH_2OH$ | $CH_2OH$ | CHOH | $CH_2OH$ | $CH_2OH$ |
| A | 100 | 723 | 768 | 61.5 | 38.5 | – | | | |
| B | 12.1 ± 1.4 | 5190 | 5170 ± 345 | – | – | – | 67.2 | 32.8 | 0 |
| C | 21.0 ± 0.6 | 2260 | 2650 ± 201 | – | – | – | 66.0 | 34.0 | 0 |
| D | 26.9 ± 2.9 | – | 2360 ± 30 | 66.0 | 34.0 | 0 | 62.0 | 38.0 | 0 |
| E | 31.7 ± 1.2 | 495 | 480 ± 28 | – | – | 0 | 45.2<br>(63.5)[c] | 26.0<br>(36.5)[c] | 28.8<br>(0) |
| F | 40.8 ± 2.1 | 2510 | 2540 ± 20 | – | – | 0 | 66.2 | 33.8 | 0 |
| G | 41.1 ± 0.7 | 877 | 785 ± 34 | – | – | 0 | 65.8 | 34.2 | 0 |
| H | 42.8 ± 4.2 | 944 | 1090 ± 100 | 64.8 | 35.2 | 0 | 65.9 | 34.1 | 0 |
| I | 45.5 ± 2.5 | 870 | 835 ± 20 | 64.5 | 35.5 | 0 | 64.8 | 35.2 | 0 |
| J | 47.0 | – | 903 ± 25 | – | – | 0 | 64.7 | 35.3 | 0 |
| K | 74.8 ± 1.8 | 875 | 897 ± 57 | 62.4 | 37.6 | 0 | 62.7 | 37.3 | 0 |

[a] These are the average values calculated from the ether and the aliphatic portions of the $^{13}C$ n.m.r. spectrum. The deviation between the two values is given; [b] the spectral peaks from which these data are taken are actually methyl carbon peaks on the end-groups. However, they are very sensitive to and reflect the position of attachment of the hydroxyl group; [c] the values in parentheses are calculated for the PO end-groups only

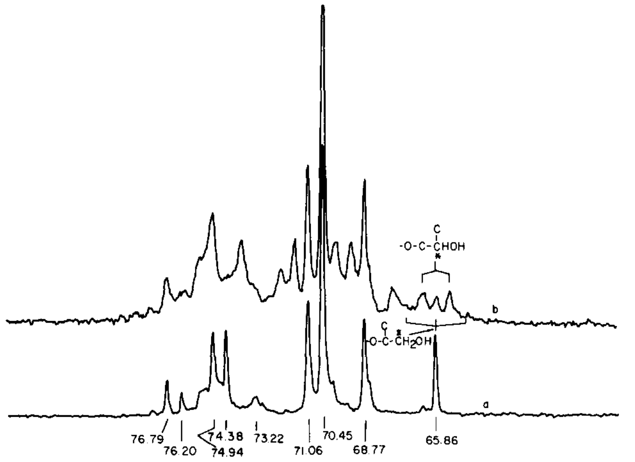


*Figure 5* (a) $^{13}C - \{^1H\}$ n.m.r. spectrum of ether carbon region of THF/PO copolymer (Sample H) prepared with $BF_3$—$OEt_2$ catalyst. Spectrum was run at 50° on neat sample. Twenty scans with repetition time of 12 sec and pulse width of 28 μsec (90°). (b) Single frequency off-resonance decoupled spectrum of the same sample. Shows triplet and doublet structure due to proton coupling in $CH_2$ and CH carbons of the end-groups. Fifty scans with repetition time of 12 sec and pulse width of 28 μsec (90°)

groups. The taller peaks at 74.94 and 74.38 are methylene and methine carbons of PO units attached to THF units.

(2) The next grouping which includes the peaks at 71.06, 70.45 and 68.77 ppm are all THF peaks. The two smaller peaks and the shoulders are also sequence distribution-related. A complete discussion of the sequence distribution in all of these polymers will be published later.

(3) The peak (and the small shoulder) at 65.86 ppm is due to the $CH_2$ and the CH of the PO end-groups, as in the homopolymer discussed above.

The rather startling feature of the spectrum of this polymer, and of all but one in *Table 1*, is that there are no THF end-groups – only PO end-groups. The $^{13}C - \{^1H\}$ spectrum (not shown) of a poly(THF) polymer, Polymeg, reveals there are two main peaks at 70.56 and 26.88 ppm and two end-group peaks at 61.52 ppm and at 29.97 ppm. Therefore, if there were THF end-groups in these polymers, two peaks would be observed near these latter two positions. None are observed. Using these assignments, the compositions and an n.m.r. $M_n$ can be calculated.

*Figure 5b* is a partly decoupled spectrum using an off-resonance decoupling technique. If the gated decoupling technique discussed with *Figure 2b* were used or if the noise decoupler were shut off as in *Figure 4b*, the satellite multiplet peaks from the THF resonances would obliterate the end-group patterns. In this off-resonance technique the offset and the power level of a single frequency proton-irradiation line is varied so that the desired partial coupling is achieved. The net effect is that the magnitudes of the multiplet splittings can be reduced to any amount desired. This is shown in *Figure 5b* in which the splittings are reduced, so there is no interference from the THF peaks. It is clearly seen that the sharp singlet PO end-group at 65.86 ppm in *Figure 5a* is really composed of a $CH_2$ carbon as evidenced by the triplet splitting and by a CH carbon as evidenced by the doublet splitting. Integration of these peaks reveals that 64.8% of the PO end-groups are secondary and 35.2% are primary, in good agreement with the results of the homopolymer (Sample A) in *Figure 4b*. These results and those of three other copolymers and the homopolymer (Sample A) are listed in columns 5 and 6 of *Table 1*.

*Figure 6* is the aliphatic portion of the spectrum of Sample H. The peaks at 27.11 and 26.70 ppm are due to the 'internal' methylene carbons of THF units. The remaining peaks arise from the PO methyl carbons which appear to be very sensitive to their environment. After the off-resonance work described above was completed on these polymers, it was observed that the peak intensities at 19.71 and 16.62 ppm are always in the ratio of 2:1 which correlates nicely with the off-resonance decoupling results. This indicates that these two peaks are from the methyl carbons on the secondary and primary end-groups, respectively. Chemical shift comparisons with model compounds confirm this assignment. This discovery makes it a simple matter to determine the relative amounts of primary and secondary OH end-groups without the need for decoupling experiments. The results of these measurements are listed in columns 8 and 9 of *Table 1*.

Further supporting evidence that these assignments are correct is given by the fact that copolymer compositions and an $\bar{M}_n$ can also be calculated from this portion of the spectrum, and they agree closely with the calculations from the ether region. The values for mol % PO and $^{13}C$ n.m.r. $\bar{M}_n$ in columns 2 and 4, respectively, are the averages of the measurements from the two portions of the spectra. The deviations of the two measurements are also listed.

Proton n.m.r. results are not listed in *Table 1*, but the values for mol % PO by $^{13}C$ n.m.r. and by $^1H$ n.m.r. agree well within 1% for all samples in the Table. It is seen that there is also good agreement between the $^{13}C$ n.m.r. $\bar{M}_n$ and that from g.p.c.

As mentioned previously, only one copolymer (E) in the Table exhibits THF-like end-groups. This copolymer has a very low molecular weight and was obtained by low conversion of the monomer to polymer. Sample E is, therefore, an exception since all of the other polymers included in *Table 1* were carried to complete conversion of the PO. The spectrum of sample E is shown in *Figure 7*. In addition to the features pointed out previously, this spectrum shows THF-like end-groups at 61.61 and at 29.70 ppm. These peaks are actually due to end-groups of partly reacted 1,4-butanediol which was used as a chain-transfer agent in the preparation of these copolymers. They appear only in spectra of polymers prepared at less than 50% conversion. A THF/PO copolymer was prepared utilizing 1,6-hexanediol (rather than

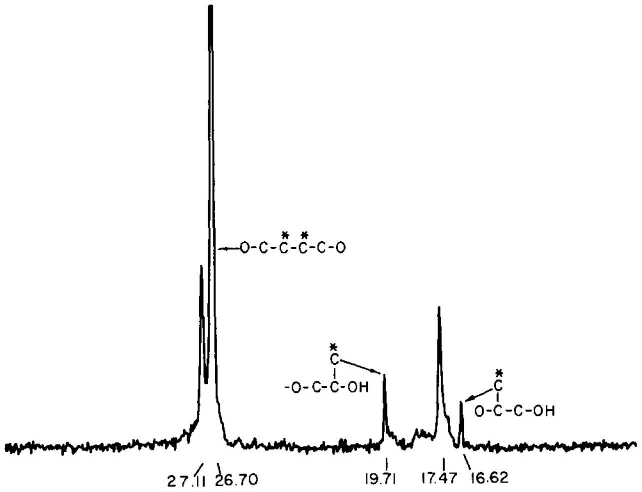


*Figure 6* $^{13}C - \{^1H\}$ n.m.r. spectrum of the aliphatic region of sample G. Fifty scans with repetition time of 12 sec and pulse width of 28 μsec (90°)

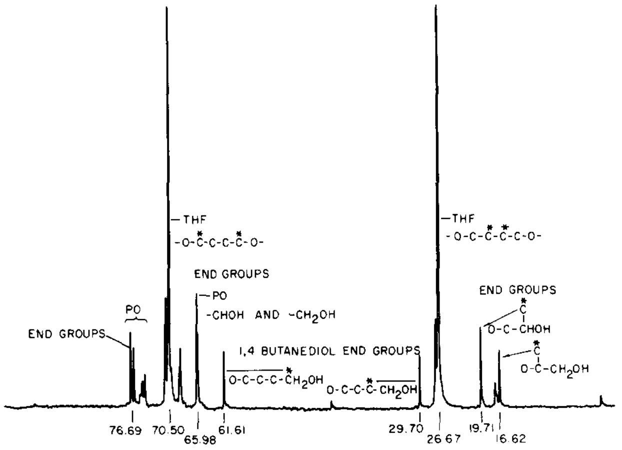


*Figure 7* $^{13}C - \{^1H\}$ n.m.r. spectrum of low molecular weight (495) THF/PO copolymer (sample E). Spectrum obtained on neat sample at 50°C. Twenty scans with repetition time of 12 sec and pulse width of 28 μsec (90°)

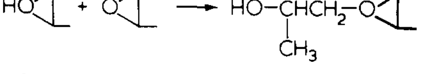
1,4-butanediol) and the polymerizate was sampled several times during the reaction. The diol does enter into the polymer chain end, and end-groups attributable to it are detectable by $^{13}C$ n.m.r. up to approximately 50% conversion. Above 50% conversion only PO end-groups are observed.

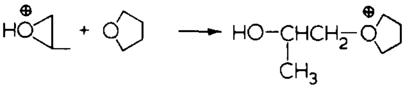
From the last six columns of *Table 1*, then, we have compelling evidence that THF/PO copolymers prepared with $BF_3{:}OEt_2$ catalyst have only PO end-groups. These PO end-groups always form in the approximate ratio of two secondary OH end-groups to one primary OH, regardless of the molecular weight and of the composition.

The examination of these THF/PO copolymers by $^{13}C$ n.m.r. has proved to be very beneficial. From an analytical standpoint, direct observation of the terminal unit carbons allowed not only an independent determination of molecular weight but also an identification of the terminal units and the differentiation between primary and secondary alcohol end-groups.

### *Mechanistic considerations*

The finding that these THF/PO copolymers contain terminal units only from propylene oxide was not expected. The mechanism of the polymerization proposed by Hammond *et al.*[6] seemed quite reasonable; actually it is compatible with our findings. The results of the end-group analysis pointed out several features of the copolymerization which were not fully appreciated previously. After the pre-initiation and initiation steps, the possible initial propagation reactions suggested[6] are:


(1)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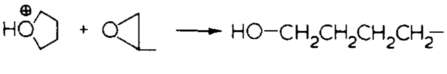
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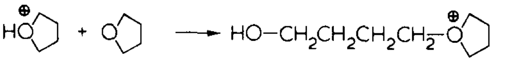
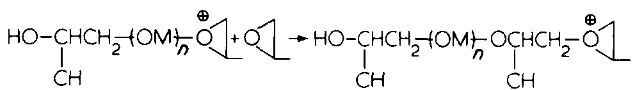

(4)

Attack of either monomer on the protonated PO, equations (1) and (2), leads to ring opening and to the formation of an hydroxyl-bearing terminal group. Of the two remaining possibilities, equations (3) and (4), the latter has been previously dismissed as an initial propagation reaction. Hammond *et al.*[6] have suggested that attack of THF on protonated THF, equation (4), leads to no reaction. This was inferred from the observation that homopolymerization of THF does not occur with the reaction conditions used[9]. In the homopolymerization of THF, a tertiary oxonium ion has been considered[10] to be necessary for propagation; the protonated THF, a secondary oxonium ion, must be too stable a species to undergo ring opening reactions. If this be the case, we can further exclude as an initial propagation reaction the attack of PO on protonated THF, shown in equation (3). The results of our end-group analysis support these arguments that neither of the reactions of equations (3) and (4) occurs. We therefore suggest that the ring opening reactions of PO shown in equations (1) and (2) represent all initiation reactions in these copolymerizations.

In the ring-opening reactions of PO, such as equations (1) and (2), all of the products have been depicted for the sake of simplicity as secondary alcohols. These reactions, of course, also give primary alcohols. The observed ratio of the secondary:primary alcohols in the end-groups was always 2:1. A similar reaction, the boron fluoride catalysed alcoholysis of propylene oxide[11], has been shown to give a mixture of hydroxy ethers. In this case, the secondary to primary alcohol ratio was dependent on the structure of the alcohol and on the temperature of the reaction. For example, ethanolysis at 20° and at 30°C gave secondary to primary alcohol ratios of 1.5:1 and 1.2:1, respectively. Our results are consistent with these, particulary when the temperature effect observed here and our reaction temperature are considered.

Subsequent propagation steps can occur according to the copolymerization equations 5–8: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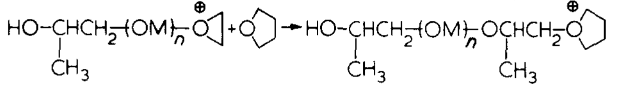
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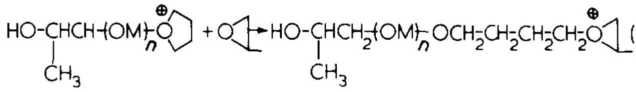
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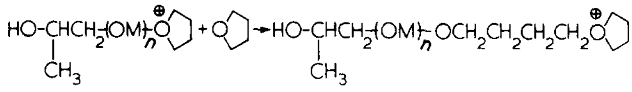
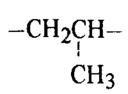

(8)

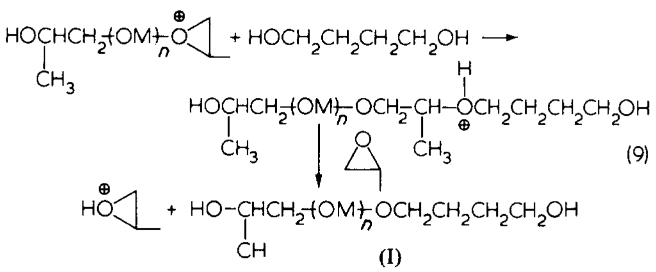
where M represents either propylene units,



$$-CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H-$$

or tetramethylene units, $-CH_2CH_2CH_2CH_2-$, or both. All four propagation reactions, including the attack of THF on the THF oxonium ion as in equation (8), must occur. That this reaction does indeed occur is borne out by the analysis of sample B from *Table 1*. This sample contains, on average, at least seven THF units for each PO unit excluding the terminal monomer units. This conflicts with the reports of Blanchard *et al.*[12,13] who present evidence that only two THF units can be adjacent to each other in these copolymers. Our analyses indicate that THF can add to itself in the growing chain but that it does not add to itself in an initial propagation step.

A transfer to hydroxyl has been suggested as a chain-terminating reaction[6]. This type of reaction would provide a second route to end-groups to the chain. Butanediol, or water[12], could serve as the source of the hydroxyl in the first stages of the reaction. An example of such a reaction is shown in equation (9):



This reaction accounts nicely for the incorporation of the added glycol into the chain, but it suggests an end-group other than propylene oxide. The new end-group in (I) is depicted as coming from 1,4-butanediol. This end-group would be indistinguishable from one arising from PO attack on protonated THF, as in equation (3). According to our $^{13}$C n.m.r. evidence, this type of chain end does not survive in detectable quantities to the end of the normal copolymerization. The consumption of hexanediol end-groups, *vide supra*, was shown to be complete by 50% conversion.

In order to explain the disappearance of the end-groups in (I) derived from glycol, we need only to assume that polymers such as (I) can also participate as chain transfer agents. These would thereby take the role of the 1,4-butanediol as in the reaction of equation (9). Conceivably all hydroxyl-containing materials could participate in this chain-transfer reaction. The PO end-groups, because of the pendant methyl on either the α- or β-carbon, would tend to be more sterically crowded than the straight chain THF-like end-group. Because of this, they would probably react at a slower rate in the chain-transfer reaction than would the THF-like end-groups. Such an agreement suggests that the THF-like end-groups would be more readily consumed than would the PO end-groups.

Hydrolysis by water quenching of the copolymerization is a third possible route to the formation of end-groups. In this case, water would attack the oxonium end-group with the concomitant opening of the ring. Any THF-based oxonium ions could lead to THF end-groups. The catalyst (i.e. $BF_3$:$OEt_2$) level used in all of these copolymerizations was constant at 0.08 mol % of monomers[6] In preparing 1000 $\bar{M}_n$ copolymers the 1,4-butanediol level was 4 mol % of monomers. If we assume that each alcohol group of the diol eventually is responsible for one end-group of the copolymer, then 0.08/4 x 2 or 1% of the chain ends bear oxonium ions at any one time. Therefore, at the most, only 1% of the end-groups present in the final 1000 $\bar{M}_n$ polymer can be accounted for by quenching the polymerization. This is certainly below our level of detection. Of the three possible routes to end-group formation which are considered here, the only one not excludable is end-group formation during the initial propagation reactions as shown in equations (1) and (2). Indeed, *all* end-groups are formed by these initial propagation reactions.

It has been reported that consumption of THF ceases when all of the propylene oxide has been consumed[9]. This observation can be accounted for readily by a chain-transfer reaction as in equation (9). Once all of the propylene oxide has been incorporated into polymer chains, there is but one reasonable alternative left for further reaction: the chain-transfer reaction in which the source of hydroxyl is a polymer chain end. If the same sequence of reactions were followed, the proton would transfer to THF, rather than to PO, as shown in the equation. It has been argued earlier that protonated THF does not lead to propagation under these reaction conditions. Hence, reaction stops.

## CONCLUSIONS

Copolymers of tetrahydrofuran and propylene oxide prepared with boron trifluoride etherate catalyst in the presence of 1,4-butanediol contain only propylene oxide end-groups by $^{13}$C analysis. The propylene oxide end-groups form in the ratio of two secondary hydroxyls to one primary hydroxyl, regardless of the molecular weight or the composition of the copolymers. The results indicate that all of the end-groups of the compolymer are formed by the initial propagation reactions which are the attack of each monomer on protonated propylene oxide. The protonated tetrahydrofuran is thought not to enter into the initial propagation reactions with either monomer. However, after the initial propagation reactions of protonated propylene oxide, all four propagation reactions of the conventional copolymerization scheme proceed. The 1,4-butanediol serves as a chain transfer agent. End-groups attributable to the chain transfer agent can be observed at conversions less than 50%. Beyond this point, chain transfer takes place with the polymeric alcohol end-groups. Polymerization stops when all propylene oxide has been consumed because no new chains can be initiated by the remaining tetrahydrofuran.

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