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The Average Molecular Structure of Base-Catalyzed Low-Mole Adducts of Propylene Oxide to Glycerin

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Synopsis

The average structure of low molecular weight base-catalyzed propylene oxide adducts of glycerin have been studied rather extensively using gas chromatographic and HNMR techniques. HNMR analysis of the trifluoroacetyl derivatives of individual adducts provide a useful technique for distinguishing internal isopropoxy units from terminal isopropoxy units. It can also be used to estimate the degree of initiation at the secondary hydroxyl site of the glycerin starter. A surprising amount of initiation at the secondary hydroxyl site was found for the three-mole adducts and the four-mole adducts are very highly initiated at this site. Concentrations of the possible contributing structures in fractions of a typical low-mole weight polyol are tabulated. The higher adducts are envisioned as consisting of three propagating chains of nearly equal length and reactivity.

INTRODUCTION

Propylene oxide adducts of glycerin, particularly those ranging in the 2000 to 5000 average molecular weight range are widely used in the manufacture of flexible and semiflexible foams that are used for furniture upholstery, bedding, automotive interiors, and many other diverse applications. Despite their wide use, there still remains much to be learned about the structure of these polyether polyols and the effect of such structure upon the properties of the finished products.

The propylene oxide adducts of glycerin are generally prepared by a base-catalyzed reaction. A modification of the mechanism for the oxyethylation of an alcohol as proposed by Satkowski and Hsu[1] to include the propylene oxide addition reaction can be depicted as follows:

$$ROH + MOH \rightleftharpoons ROM + H_2O$$

$$ROM \rightleftharpoons RO^- + M^+$$

$$CH_3{-}CH(\text{—}O\text{—})CH_2 + RO^- \rightarrow CH_3{-}CH(O^-){-}CH_2{-}OR + M^+ \rightleftharpoons CH_3{-}CH(OM){-}CH_2OR$$

$$CH_3{-}CH(OM){-}CH_2{-}OR + R'OH \rightleftharpoons CH_3{-}CH(OH){-}CH_2OR + R'OM$$

The point to be emphasized with the presentation of this mechanism is the highly specific manner in which the oxirane ring of propylene oxide opens in the base-catalyzed additions to yield secondary hydroxyl groups. Analysis for primary hydroxyl content on a wide range of base-catalyzed polyether polyols by differential reaction rate methods,[2] confirmed by other methods,[3,4] indicates that only about 2%, even less in some cases, of the oxirane ring opens in such a manner as to yield primary hydroxyl groups.

The purpose of this investigation has been to study the mode of addition of propylene oxide in the base-catalyzed reaction of propylene oxide with glycerin in the early stages of initiation. In this regard, we have specifically addressed ourselves to the question of whether these adducts can best be described as consisting primarily of molecules with three equally growing chain branches or as essentially linear molecules with very limited initiation and propagation at the secondary hydroxyl site of the glycerin starter.

NIAX Polyol LG-650 (product of Union Carbide Corporation), a 3-mole propylene oxide adduct of glycerin, was chosen as a representative low molecular weight adduct to serve as a model system. The HNMR spectra of the trifluoroacetyl derivatives of this product and its gas chromatographic fractions have provided the basis for our studies.

EXPERIMENTAL

A gas chromatographic procedure was developed to separate each of the adducts of LG-650 with respect to molecular weight. Figure 1 shows a chromatographic profile of LG-650 with the 1-, 2-, 3-mole adducts, etc., labeled accordingly. Instrument parameters employed to obtain this chromatogram are as follows: instrument, F and M Model 500; column, 18″ by 1/4″ copper tube packed with 20% SE-30 silicone rubber on 60/80 Chromosorb W; injection port temperature, 385°C; column temperature, programmed from 100°C to 380°C at 11°C/min; flow rate, 100 cc of helium per min; sample size, 1.5 μl (50% solution in methanol).

Sample sizes were increased to 40 μl and effluents representing the 2-, 3-, and 4-mole propylene oxide adducts of glycerin, the major components in LG-650, were repeatedly trapped at the exit port of the chromatograph until enough sample was available in each case to prepare the trifluoroacetyl derivatives.

The trifluoroacetylation reagent was prepared by diluting Eastman-grade trifluoroacetic anhydride with toluene dried over molecular sieves (20% solution). Aliquots of this reagent calculated to provide at least a twofold excess of trifluoroacetic anhydride were reacted with a composite sample of LG-650 and with each of the collected fractions. The reaction mixtures were allowed to stand at room temperature for 1 hr. Completeness of reaction was confirmed in all cases by observing the complete disappearance of the hydroxyl stretching band (2.90 μ) from the infrared spectra of the reaction products. Excess reagent, solvent, and by-products

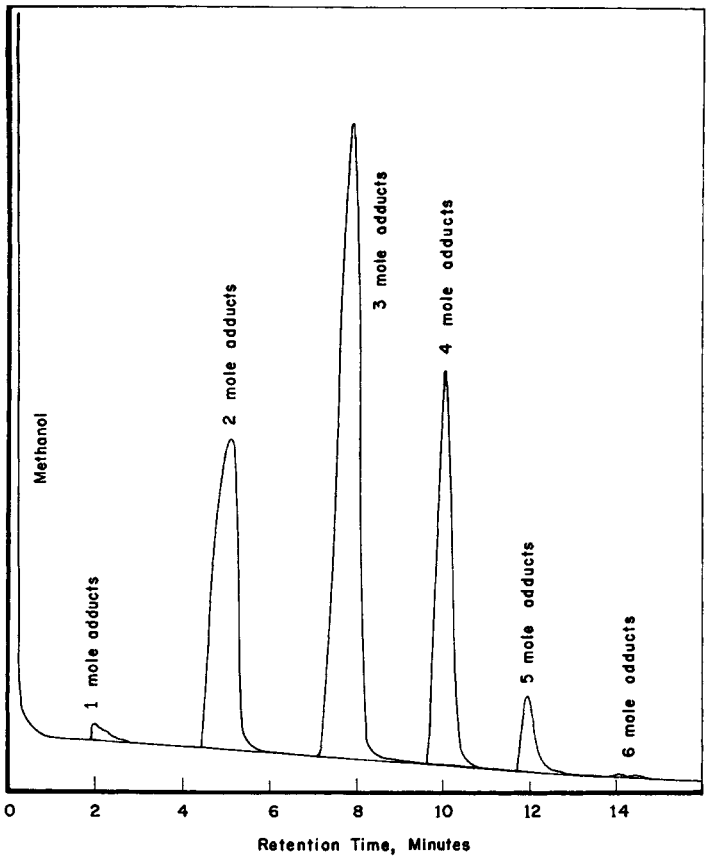
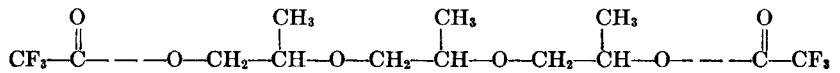


Fig. 1. Gas chromatographic profile of "NIAX" polyol LG-650.

were removed by stripping at reduced pressure and the trifluoroacetic ester residues were reserved for HNMR analysis. The HNMR spectra were recorded on the Varian A-60 spectrometer using approximately 20% solutions in deuterated chloroform containing tetramethylsilane (TMS) as an internal reference.

DISCUSSION

A better understanding of the assignments to be made for the various signals in the HNMR spectra of the trifluoroacetyl derivative of the propylene oxide adducts of glycerin can best be obtained by examining in detail the spectrum of the TFA derivative of tripropylene glycol. This product, not a base-catalyzed adduct, can be expected to have a distribution of both primary and secondary terminal isopropoxy units as well as one internal isopropoxy unit:



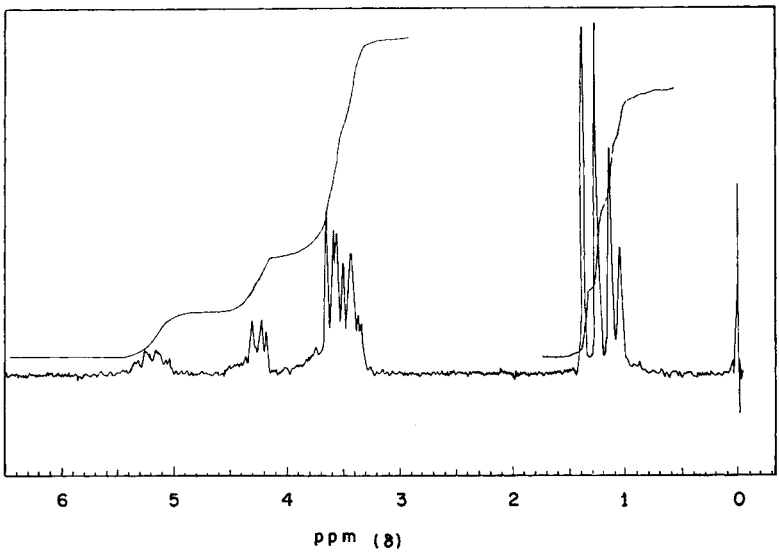


Fig. 2. HNMR spectrum of trifluoroacetyl derivative of tripropylene glycol.

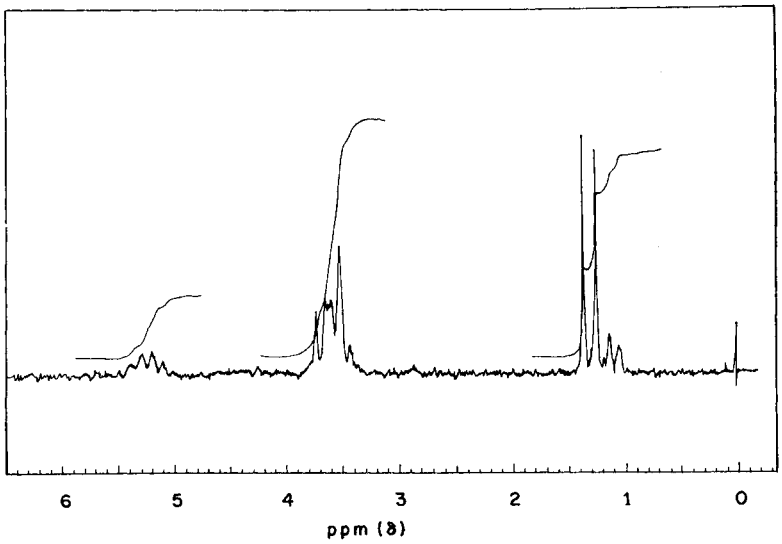


Fig. 3. HNMR spectrum of trifluoroacetyl derivative of "NIAX" polyol LG-650.

In the spectrum (Fig. 2), the methyl resonance attributed to the terminal secondary unit is centered at 1.3 ppm, while that for the terminal primary unit is centered at 1.2 ppm but is mostly obscured by the 1.3-ppm signal and the unsymmetrical doublet near 1.1 ppm. The methyl resonances of both terminal units are shifted downfield from the normal position for the methyl resonance of polyoxypropylenes (near 1.1 ppm) by the influence of the strongly electronegative trifluoroacetyl groups. Accordingly, the

doublet centered near 1.1 ppm is assigned to the internal isopropoxy unit which is too far removed to be appreciably influenced by the trifluoroacetyl groups. In all cases, the methyl resonances appear as doublets because of coupling with the adjacent methine protons. Since the base-catalyzed propylene oxide reactions produce very few primary hydroxyl-terminated structures, we would not expect significant contributions from these in our present study.

The HNMR spectrum of the trifluoroacetyl derivatives of NIAX Polyol LG-650 is shown in Figure 3. The methyl resonance doublet centered near 1.3 ppm, relative to TMS, is assigned to the methyl groups of the terminal isopropoxy units, while the doublet centered near 1.1 ppm is assigned to the internal isopropoxy units.

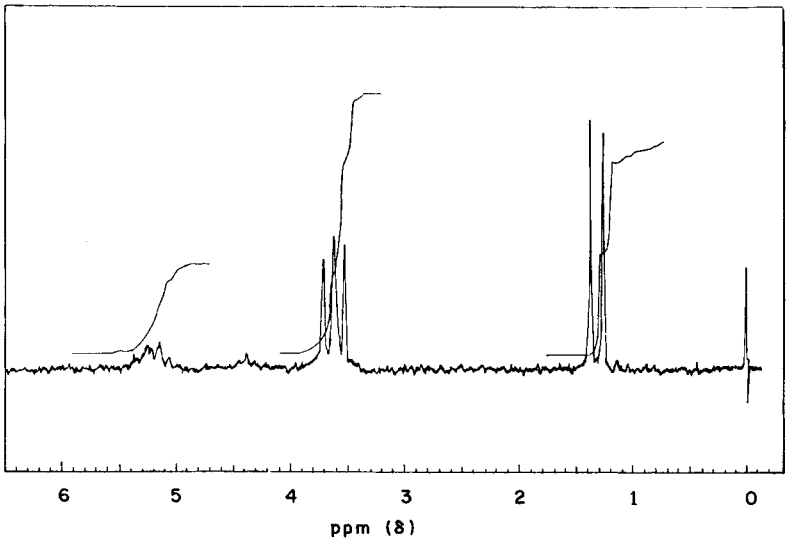


Fig. 4. HNMR spectrum of trifluoroacetyl derivative of two-mole propylene oxide adduct of glycerin.

The ratio of internal to terminal isopropoxy units can be determined for the trifluoroacetyl derivatives of the composite sample of LG-650 by substituting the integrated areas into the following equation:

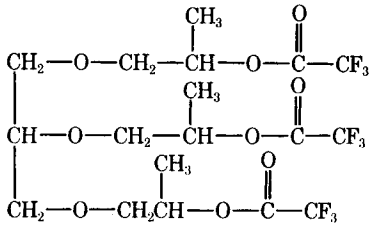
$$\text{per cent internal isopropoxy units} = \frac{x + 100}{x + y}$$

where x = area of 1.1 ppm doublet and y = area of 1.3 ppm doublet. Substituting in the equation, one obtains 18.5% internal isopropoxy units for the composite LG-650 sample.

Assuming that a mixture of isomers A and B, as shown below, would best represent the average molecular structure of LG-650, one must conclude that a relatively high degree of initiation, approximately 44% by inter-

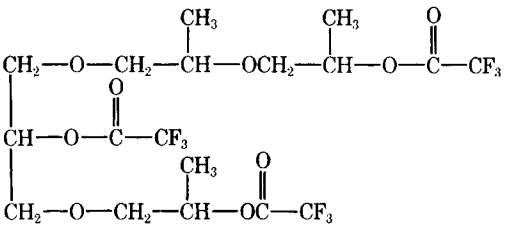
polation, has occurred at the secondary hydroxyl site on the glycerin starter.

A



no internal units

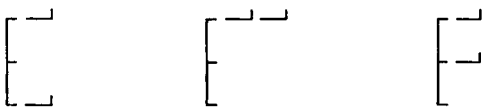
B



33% internal units

To obtain a more accurate picture of the mode of addition, one must consider not only the isomers shown here, but the other possible 3-mole adducts as well as the lower and higher mole adducts which are inevitably present.

HNMR spectra of the trifluoroacetyl derivatives of the isolated 2-, 3-, and 4-mole fractions are shown in Figures 4, 5, and 6, respectively. A small amount of internal isopropoxy structure, about 5.4% (Fig. 4), is indicated even for the 2-mole adduct. In this case, only three isomers will be considered, since the other isomers which can be drawn are not likely to be important contributors. Symbols representing the glycerin backbone and the isopropoxy units are drawn below to simplify the presentation of these structures. The system should be easily recognized and it will be noted that the trifluoroacetyl groups are omitted to conserve space:



I II III

Interpolation of the ratio of internal to terminal isopropoxy units for the 2-mole adducts indicates the presence of about 10% of isomer II, and/or its counterparts, and the remainder is presumed to be mostly isomer I. Because of the faster rate of addition of propylene oxide to the primary hydroxyl groups, isomer I would be expected to predominate and, in this respect, 10% of isomer I would appear to be unexpectedly high.

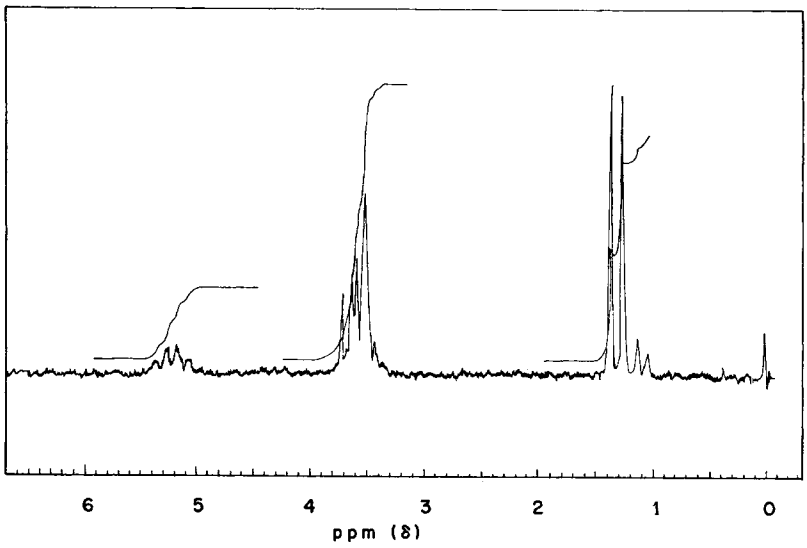
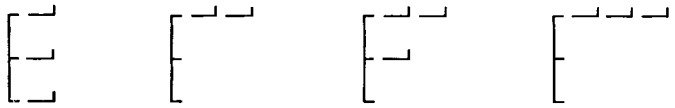


Fig. 5. HNMR spectrum of trifluoroacetyl derivative of three-mole propylene oxide adduct of glycerin.

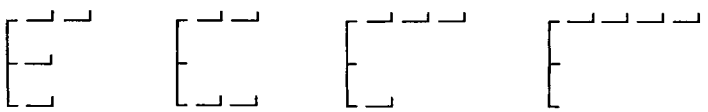
A ratio of 12.4% internal isopropoxy units is calculated for the 3-mole adducts (Fig. 5). Isomers IV, V, VI, and VII would be considered the most important contributors in this case:



IV V VI VII

Isomers V and VI contain one internal isopropoxy unit and isomer VII contains two. Interpolation of the 12.4% result for internal isopropoxy structure between 0% for isomer IV and 33% for isomers V or VI indicates that a minimum of 63% of isomer IV is present in the mixture. This is excluding any contribution from isomer VII, which, if present, would yield an even higher result for isomer IV. At any rate, it is quite apparent that a relatively high degree of initiation has occurred at the secondary hydroxyl site of the glycerin starter for the 3-mole adducts.

An HNMR spectrum of the TFA derivatives of the 4-mole adducts (Fig. 6) shows 27.1% internal isopropoxy structure and the isomers considered of major importance are shown below:



VIII IX X XI

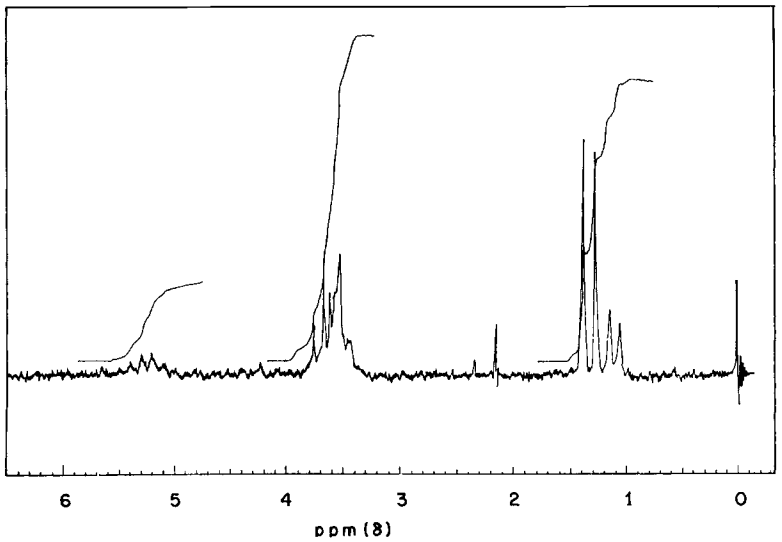


Fig. 6. HNMR spectrum of trifluoroacetyl derivative of four-mole propylene oxide adduct of glycerin.

Obviously, the 4-mole isomers will contain at least one (25%) internal isopropoxy unit, as illustrated for isomer VIII, and others will contain two (50%) or three (75%) units. Consequently, the 27.1% value for internal

TABLE I
Schematic Presentation of the Major Molecular Structures in NIAX Polyol LG-650

Moles of propylene oxide added				
1	2	3	4	5
>90%	90% + 10%	63% + 37% others minor	92% + 8% others minor	major isomers

isopropoxy units is interpolated to yield a minimum of 92% of isomer VIII for the 4-mole adducts. This excludes any contribution from isomer XI, which, if present, would make the result even higher.

In conclusion, these studies of the gas chromatographic fractions of the low-mole adducts of NIAX Polyol LG-650 have shown that a high degree of initiation occurs at the secondary hydroxyl site of glycerin in the early stages of the reaction. Table I summarizes the results estimated for the relative amounts of the major isomers. Although the 5-mole adducts were not examined, they would certainly be expected to show nearly 100% initiation at the secondary hydroxyl site.

Beyond the 5-mole adducts, the HNMR technique for monitoring the internal oxypropylene units, and hence, the degree of initiation at the secondary hydroxyl site of glycerin, would cease to be a practical method for studying the structure of the various isomers. Since all of the reactive sites become nearly equivalent at this point, neglecting any steric efforts due to spacial arrangements, one would expect further addition of propylene oxide to propagate equally on the three growing chains. Consequently, it is postulated that even higher mole weight adducts of glycerin can best be represented as branched-chain molecules consisting of three nearly equal segments. These conclusions do not take into account the effects that catalyst concentration, reaction temperature, or different base catalysts might have on these reactions. Such parameters could be significant in altering the mode of addition.

References

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