

## The Determination of Adjacent Oxypropylene-Oxyethylene Units in Propylene Oxide-Ethylene Oxide Adducts by Infrared Spectroscopy

U. H. GIBSON and Q. QUICK, *Research and Development Department, Union Carbide Corporation, Chemicals and Plastics, South Charleston, West Virginia 25303*

### Synopsis

A study of several base-catalyzed propylene oxide-ethylene oxide adducts of glycerin and certain model compounds has shown that an infrared absorption band at  $10.30 \mu$  can be associated with a structural entity represented by an oxyethylene unit attached to an oxypropylene unit at the secondary position. Coupled with other information such as total oxyethylene content and primary hydroxyl content, this finding has proved most useful in differentiating average molecular structure for commercial polyether polyols used in the manufacture of polyurethanes.

### INTRODUCTION

Polyols made by the base-catalyzed addition of propylene oxide to glycerin and certain other trifunctional starters are widely used in the manufacture of flexible polyurethane foam. These polyols are frequently modified to meet specific needs, such as improved processing or improved physical properties of the foam, by the incorporation of varying amounts of ethylene oxide into the molecule. The ethylene oxide can be added randomly by the use of a mixed-oxide feed or as blocks by the sequential addition of the two oxides. The blocks may occur adjacent to the starter, as internal blocks along the molecular chain, or as terminal blocks. In order to properly understand the effects of the oxyethylene upon these adducts, it becomes important to have appropriate analytical technology to evaluate molecular structure.

Chemical cleavage by various reagents<sup>1,2</sup> provides the basis for structural analysis of polyether polymers in many cases. Total oxyethylene content is sometimes determined conveniently by NMR analysis.<sup>3</sup> The ratio of primary to secondary hydroxyl groups is normally determined by differential reaction rates<sup>4</sup> and, more recently, by NMR analysis of the acetyl or trifluoroacetyl derivatives.<sup>5,6</sup>

The infrared spectra of commercial polyether polyols are in many cases quite similar, even though important structural differences are known to exist. Consequently, infrared spectroscopy has been used sparingly to

detect and measure structural differences which, nonetheless, may significantly affect foam properties. One exception is the use of the hydroxyl stretching band to determine molecular weight<sup>7</sup> whenever the functionality is known. Another is the reported use of the methyl C—H stretching and methylene C—H stretching vibrations<sup>8</sup> to determine the ratio of oxyethylene to oxypropylene in PLURONIC (Registered trade name of Wyandotte Chemicals Corporation) polyols.

Comparison of the infrared spectra of a wide range of base-catalyzed experimental polyether polyols produced in our own laboratories has resulted in the discovery of two absorption bands, one at 10.30  $\mu$  and the other at 11.30  $\mu$ , which can be correlated with the presence of certain oxypropylene-oxyethylene sequential arrangements. Through the study of certain model compounds, the former band has been related to a specific structural unit involving oxyethylene units adjacent to oxypropylene units. As a result, a possible infrared spectroscopic method for detecting and estimating the relative amounts of oxyethylene in random distribution in base-catalyzed mixed-feed propylene oxide-ethylene oxide adduct polyether polyols was indicated. The same infrared band provides valuable information about the positions of polyoxyethylene blocks in the case of block copolymers. This paper describes such a method and some of its applications to molecular structural analysis.

### EXPERIMENTAL

The random copolymer polyether polyols used in this investigation were prepared by reacting the desired ratio of mixed-feed ethylene oxide-propylene oxide to glycerin. In general, the reactions were carried out at 110–120°C and 60–70 lb pressure. Potassium hydroxide catalyst was added to the glycerin starter in the concentration range of 0.10–0.15% based on the final product. Block copolymers were prepared under the same conditions by alternately adding the ethylene oxide or propylene oxide to the glycerin starter. In each example, the number-average molecular weights of the adducts fall between 3000 and 4000.

Infrared spectra were recorded for each of the experimental polyols scanned neat in a 0.030-mm permanent-mount sodium chloride cell on either the Beckman IR-5A or IR-12 spectrophotometers. Because of better resolution and overall instrument stability, the best quantitative results are obtained with the Beckman IR-12 spectrophotometer.

### DISCUSSION

Table I contains a general description of several experimental polyether polyols used to develop the infrared method of analysis described herein for the detection and estimation of oxyethylene in random distribution in both mixed-feed and sequential-feed propylene oxide-ethylene oxide adducts.

Figure 1 contains the superimposed infrared spectra of experimental polyols 1, 2, and 3. Differences will be noted in the absorption levels at  $10.30\ \mu$  and  $11.30\ \mu$ , in fact, a distinct absorption maxima is resolved at  $10.30\ \mu$  in the case of experimental polyol 3, a mixed-feed propylene oxide-ethylene oxide adduct. Slight increases in the absorption levels at both wavelengths for the capped polyol over that of the pure propylene oxide adduct will be discussed later. Kuroda and Kubo<sup>9</sup> have assigned bands near  $11.30\ \mu$  in the spectra of low molecular weight polyethylene glycols to the  $\text{CH}_2$  rocking

TABLE I  
Experimental Polyols Prepared by the Base-Catalyzed Addition  
of Propylene Oxide and Ethylene Oxide to Glycerine Starter

Experimental polyol	General description
1	Glycerin + propylene oxide to 56 hydroxyl number
2	Glycerin + propylene oxide to 50 hydroxyl number capped with 10% ethylene oxide to 45 hydroxyl number
3	Glycerin + mixed-oxide feed (14% ethylene oxide and 86% propylene oxide) to 47 hydroxyl number
4	Same as (3), except 11% ethylene oxide and 89% propylene oxide
5	Same as (3), except 20% ethylene oxide and 80% propylene oxide
6	Same as (3) except 35% ethylene oxide and 65% propylene oxide
7	Same as (3), except 50% ethylene oxide and 50% propylene oxide
8	Glycerin + 4 moles ethylene oxide ( $\sim 6.0\%$ ) attached directly to starter + propylene oxide to 56 hydroxyl number
9	Glycerin + propylene oxide + $\sim 6.0\%$ ethylene oxide + propylene oxide to 56 hydroxyl number
10	Glycerin + propylene oxide + $\sim 6.0\%$ ethylene oxide capping to 58 hydroxyl number

vibration. Absorption is also found at this wavelength in ethylene oxide-capped propylene oxide adducts. Consequently, the  $11.30\ \mu$  band is not suitable for the specific determination of oxyethylene in random distribution. Since mixed-feed adducts (e.g., polyol 3) would be expected to have a nearly complete random distribution of the oxyethylene units (i.e., few, if any, sequential oxyethylene blocks), some structural unit associated with this random distribution must give rise to the  $10.30\ \mu$  band. Conversely, adducts with oxyethylene in the form of blocks either fail to absorb at  $10.30\ \mu$  or are limited in their absorption for reasons yet to be explained.

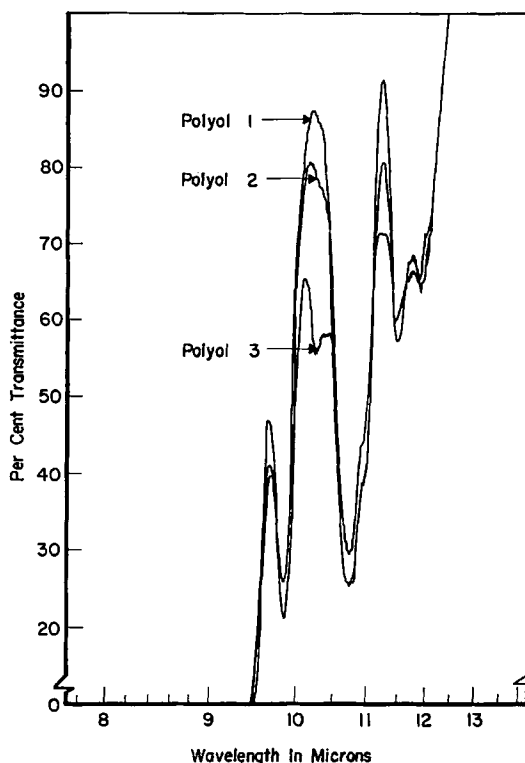
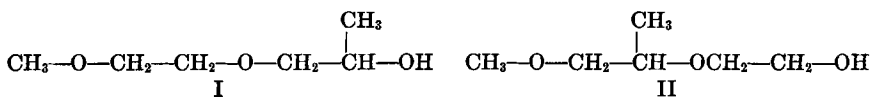


Fig. 1. Infrared spectra of experimental polyols.

### Structural Unit Responsible for 10.30 $\mu$ Band

Several model compounds have been studied to determine the specific structural unit within the mixed-feed oxide adducts which give rise to the infrared bands at 10.30  $\mu$  and 11.30  $\mu$ . Two compounds in particular have been very enlightening in this regard. They are two of the four possible isomers derived from adding exactly 1 mole of propylene oxide and 1 mole of ethylene oxide to methanol:



The infrared spectra of these two compounds are shown in Figure 2. Model compound I contains a band at 11.30  $\mu$  but none at 10.30  $\mu$ . Possibly of equal importance in this case is the fact that three other bands appear between 10 and 12  $\mu$  in the spectrum of this compound which turn out to be the strongest bands in the rocking mode region. Model compound II contains bands at both 10.30  $\mu$  and 11.30  $\mu$ . Furthermore, these two bands represent the strongest bands found in the 10–12  $\mu$  region.

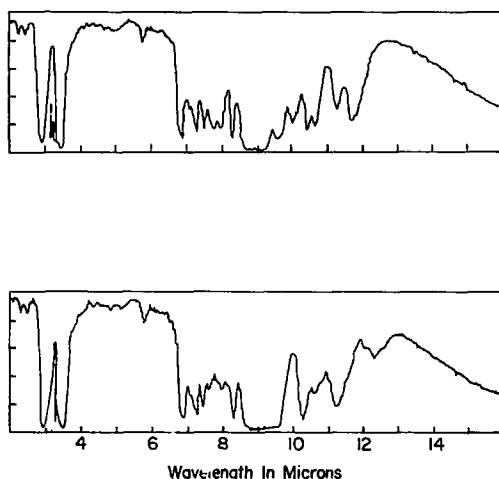
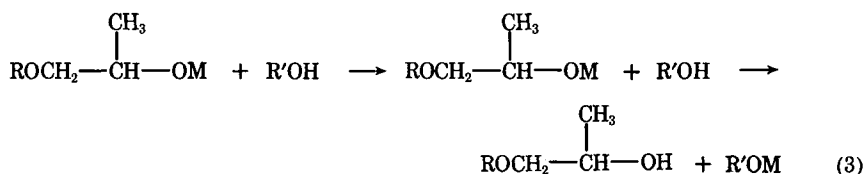
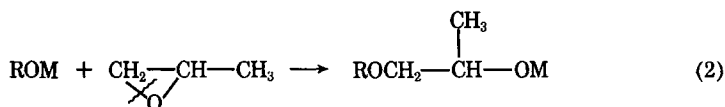
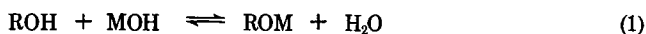


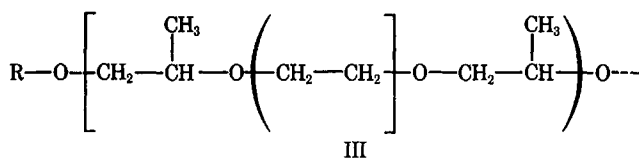
Fig. 2. Top: Infrared spectrum of model compound I (methoxyethoxyisopropanol). Bottom: Infrared spectrum of model compound II (methoxyisopropoxyethanol).

To show that the structural arrangement shown for compound II is a major contributor to the molecular composition of the mixed-feed propylene oxide-ethylene oxide adducts, one must consider the reaction mechanism for the base-catalyzed addition of propylene oxide to an alcohol starter. A condensed version of the reaction mechanism is shown in the following equations:



Cleavage of the oxirane ring occurs almost exclusively at the carbon-to-oxygen bond shown in eq. (2), resulting in the secondary hydroxyl terminated product as shown in eq. (3). The specificity of this reaction is reflected by the very low primary hydroxyl contents,<sup>6</sup> normally 2% or less, found for propylene oxide adducts varying over a wide molecular weight range.

Extending the reaction mechanism to include mixed propylene oxide-ethylene oxide adducts, the structural units shown in brackets and parentheses, compound III, would be produced in near equal ratio for products with a completely random distribution of the oxyethylene units:



However, it will be recalled that the structural unit shown in brackets corresponds to the structural arrangement for model compound II which exhibits an infrared absorption band at  $10.30 \mu$ . By contrast, the structural unit shown in parentheses, similar to the molecular arrangement of model compound I, does not exhibit an absorption band at  $10.30 \mu$ . Some mode of vibration associated with the structural unit shown in brackets, compound III, must account for the absorptions at  $10.30 \mu$  in the mixed oxide adducts. As previously mentioned, a band in the  $11\text{--}12 \mu$  region for polyethylene oxides has been assigned to a  $\text{CH}_2$  rocking mode. Therefore, it is most likely that a rocking mode within the oxypropylene unit accounts for the  $10.30 \mu$  band. Several investigators have assigned bands appearing in this general region for analogous isopropoxy structures to the  $\text{CH}_3$  rocking mode.<sup>10,11</sup> It should be pointed out, however, that the assignments for these rocking modes are difficult to correlate because of significant variations in frequency and relative intensity with minor changes in surrounding structure.

### Quantitative Analysis of Mixed-Feed Adducts

Partial infrared spectra of experimental polyols 4 through 7, all mixed-feed adducts of glycerin containing varying amounts of oxyethylene, are shown in Figure 3. There is a clear relationship indicated here between the absorbance at  $10.30 \mu$  and the contained amount of oxyethylene structure. Using the pure propylene oxide adduct of glycerin (polyol 1) as a baseline reference, the absorbance values were plotted versus the per cent by weight of ethylene oxide in the mixed feeds, Figure 4. A near-linear relationship exists up to about 25% to 30% oxyethylene. Between 40% and 50%, the curve flattens out and should, although no points are available above 50% oxyethylene, fall back toward zero absorbance with larger amounts of ethylene oxide in the mixed feed. Accordingly, an absorption band is not present at  $10.30 \mu$  in the spectra of pure polyethylene glycols. Apparently, a maximum exists for the calibration curve somewhere between 40% and 50% oxyethylene, but there are not enough points to locate the maxima precisely. Since 44% by weight of oxyethylene in the mixed feeds would represent a 1:1 molar ratio, the true maxima might be expected to fall near this point.

Results for oxyethylene in random distribution are shown in Table II for two polyether polyols prepared specifically for the purpose of evaluating the infrared method. In addition, Table II contains results for several commercial polyols along with the total amount of oxyethylene present as determined by  $\text{H}^1\text{NMR}$  analysis.<sup>3</sup> Except for the capped polyol, each of

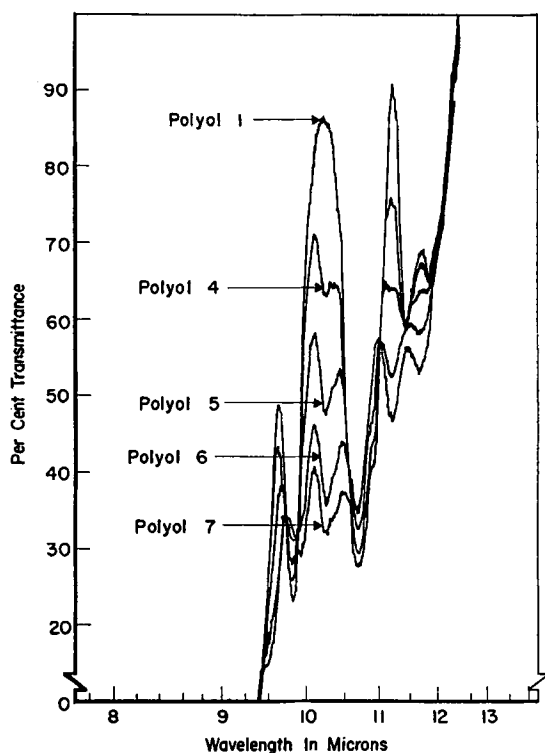


Fig. 3. Infrared spectra of experimental polyols.

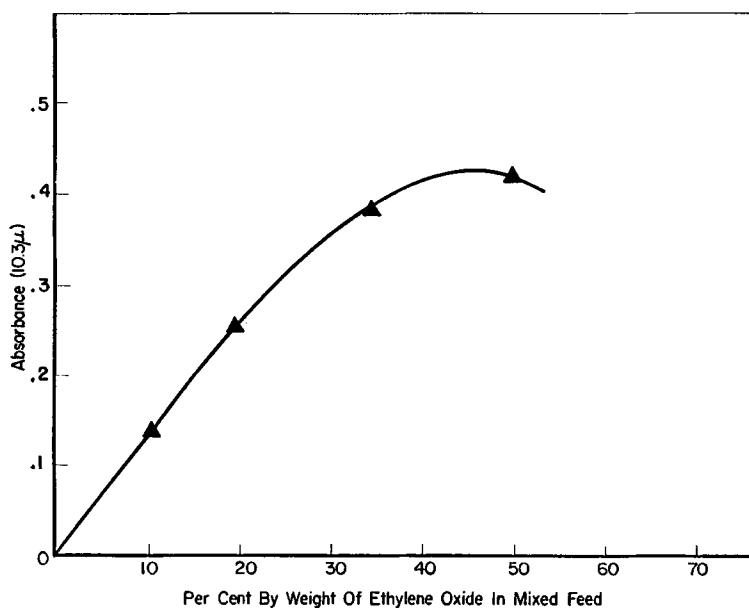


Fig. 4. Calibration curve for oxyethylene in random distribution in mixed-feed ethylene oxide-propylene oxide adducts of glycerin.

these products are either known or presumed to be mixed-feed adducts. Results are slightly higher than expected and the deviation appears to increase with increasing total oxyethylene content. This is believed to result from background absorption at the analytical wavelength due to oxyethylene structure in general, e.g., polyethylene glycols show more absorption at  $10.30 \mu$  than polypropylene glycols. It should be possible to correct for this effect in both block copolymers and mixed feed adducts containing relatively high amounts of oxyethylene structure by the use of a more suitable baseline reference.

### Block Propylene Oxide-Ethylene Oxide Adducts

The level of absorption at  $10.30 \mu$  in the infrared spectra of certain block propylene oxide-ethylene oxide adducts, coupled with  $H^1NMR$  analysis for total oxyethylene content and the ratio of primary to secondary hydroxyl groups by differential reaction methods, has proved a valuable tool for locating the positions of the oxyethylene blocks. The following rules are applicable when making these assignments:

1. *Terminal Oxyethylene Blocks.* For base-catalyzed adducts, only the initial oxyethylene unit adding to the polyoxypropylene chains will yield the structural unit responsible for the absorption at  $10.30 \mu$ . Consequently, the absorption will reach a maximum upon complete capping and will be a function of molecular weight and functionality, but not necessarily a function of the length of the oxyethylene blocks. In Figure 1, the increase in the absorption level at  $10.30 \mu$  for the capped polyol over that of the pure propylene oxide adduct can be attributed to this initial unit. In this case, the absorption is not sufficiently strong to be resolved into a distinct absorption band. High primary hydroxyl contents will always characterize this type of polyether polyol.

TABLE II  
Determination of Random Oxyethylene Units in Mixed  
Ethylene Oxide-Propylene Oxide Adducts of Glycerin

Sample	Ethylene oxide in mixed feed <sup>a</sup>	Total oxyethylene by NMR	Infrared analysis for random oxyethylene
Experimental polyol 1	6.0	—	6.1
Experimental polyol 2	12.0	—	12.8
Commercial polyol 1	14.0	—	14.5
Commercial polyol 2 <sup>b</sup>	—	10.6	11.3
Commercial polyol 3 <sup>b</sup>	—	15.0	16.8
Commercial polyol 4 <sup>c</sup>	—	10.0	2.3, 2.9

<sup>a</sup> All values are expressed in weight per cent.

<sup>b</sup> Commercial polyols 2 and 3 are presumed to be glycerin started.

<sup>c</sup> Commercial polyol 4 is an ethylene oxide-capped product.



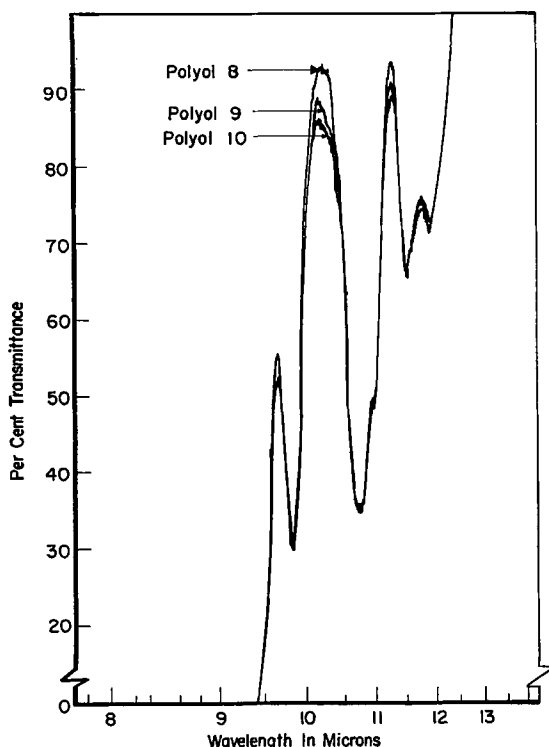


Fig. 5. Infrared spectra of experimental polyols.

2. *Internal Oxyethylene Blocks.* The relationship between internal oxyethylene blocks and the infrared absorption at  $10.30\ \mu$  should be the same as spelled out for the terminal oxyethylene blocks, but in this case the primary hydroxyl content will be low.

3. *Oxyethylene Blocks Attached to Starter.* The oxyethylene blocks attached directly to the glycerin starter and certain other common starters, excluding propylene glycol, will not contain the structural unit responsible for the absorption at  $10.30\ \mu$ .

Infrared spectra of all three types of block oxyethylene-oxypropylene adducts of glycerin have been recorded to confirm the relationships enumerated above. Infrared spectra of experimental polyols 8, 9, and 10 (Table I) are cited as appropriate examples (Fig. 5). Each polyol contains approximately 6.0% oxyethylene in the form of blocks located at the various positions indicated. Experimental polyol 8 does not contain appreciable absorption at  $10.30\ \mu$ , whereas polyols 9 and 10 exhibit readily discernible absorptions at this wavelength which are attributed to the structural units containing the initial oxyethylene group adding to the oxypropylene-terminated precursor. Although it might be expected that polyols 9 and 10 should absorb with identical intensities at  $10.30\ \mu$ , the slightly stronger

absorption exhibited by polyol 10 may, in this case, reflect a slightly better intermolecular distribution of the oxyethylene blocks. In addition to sequential feed adducts containing a single oxyethylene block, adducts with both internal and terminal blocks have been successfully characterized by correlation of the data outlined.

### CONCLUSIONS

In summary, not only can the 10.30  $\mu$  infrared band be used to distinguish mixed-feed propylene oxide-ethylene oxide adducts from sequential feed adducts and quantitatively estimate the relative amounts of oxyethylene present in random distribution in both cases, but also, with the aid of primary hydroxyl and total oxyethylene measurements, it can locate the positions of oxyethylene blocks in certain polyether polyols. Although all of the polyether polyols reported in this study were base-catalyzed adducts of glycerine, certain other functional fluids, brake fluids, surfactants, etc., manufactured from propylene oxide and ethylene oxide (UCON lubricants, PLURONICS, etc.) should lend themselves to similar evaluations of the nature of the oxyethylene distribution.

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