

MICRO-SYNTHESIS OF DEUTERIUM LABELLED
PROPOXYLATED TRIMETHYLOLPROPANE POLYOLS

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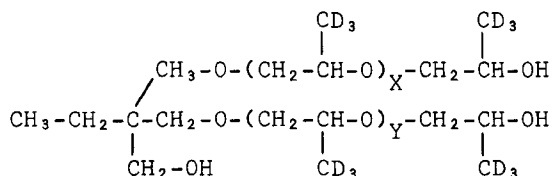
Summary

A method for preparing specifically labelled propoxylated trimethylolpropane polymers is described.

Key words: deuterated propoxytrimethylolpropane, polymer synthesis, propoxylation

Introduction

During the investigation of the thermal degradation of urethane polymers, it became apparent for the need of a deuterated polymer to serve as a mechanistic probe. Because of the amount of information (2,3,4) available on the thermal degradation of propoxylated trimethylolpropane-based urethanes, compound 1 was chosen as the model system.



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A common method for polymerizing propylene oxide with various di- and tri-alcohols has been described by Simons and Verbanc (5). Their method utilizing potassium hydroxide as a catalyst was conducted in sophisticated glassware not suited for adaptation to a micro-scale. In addition, a gas chromatographic (GC) analysis of the product from this type of synthesis indicated that polypropylene glycol was produced as a major impurity. The Simon-Verbanc method proved to be unsuitable for the synthesis of the suggested deuterated compound; therefore, a new method which was simple, adaptable to micro-scale and yielded products of high purity had to be defined.

Discussion

Figure 1 is an outline of the synthetic route used for the preparation of 1

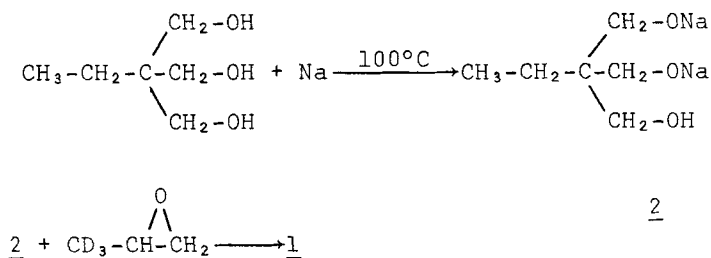


Figure 1. Synthetic Scheme for Propoxy-TMP

The formation of the trimethylolpropane (TMP) alkoxide initially involved 5 percent of the available hydroxyl hydrogens. Because of the relative reactivity of these hydrogens, this small percentage allowed for the eventual propoxylation of all the TMP molecules. It is estimated on the basis of GC results that 2.4 hydroxyl positions are eventually propoxylated.

The reaction sequence was run under vacuum utilizing the apparatus represented in Figure 2. The reaction has been run at pressures of less than 10^{-5} torr and at 0.1 torr with no observable change in product distribution. The reaction procedure in-

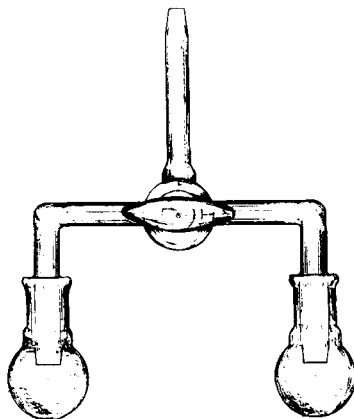


Figure 2. Glassware for micro-scale synthesis of Propoxylated Polyols.

involved charging the apparatus with sodium and TMP in flask A and the propylene oxide in flask B. After reducing the pressure on the entire system, the TMP and sodium were reacted at 100°C followed by addition of the propylene oxide.

Propylated TMP has been prepared by this method with a stoichiometric controlled mean molecular weight (\overline{MW}) range from 340 to over 1000. The procedure worked equally well for reactants in single gram quantity or 100 gram quantities. The product distribution from the micro-scale procedure was almost identical, with the exception of the polypropylene glycol when compared by GC, to KOH prepared polyol of 300 \overline{MW} . The polypropylene glycol observed from the KOH catalyzed reaction amounted

from 1.5-2.0 percent total weight while the amount of polypropylene glycol detected in the micro-scale product was less than 0.4%.

The reaction temperature of 100°C was initially selected, based on melting points and heating device limitations. Later, it was shown that variations in the reaction temperature from 95°C to 125°C had little effect on the reaction time or product distribution.

A high-purity, deuterated propoxy-TMP was prepared in excellent yield using this simple procedure. The loss of expensive propylene-3,3,3-d₃ oxide was also minimized by use of vacuum line techniques. We believe the procedure can be used for the preparation of small quantities of most propoxylated polymer systems.

Experimental

All glassware used in this synthesis was washed with chromic acid, rinsed with distilled water and then dried at 120°C overnight. All solvents were distilled prior to use.

Product distributions were measured on a Hewlett Packard Model 7620A gas chromatograph using a 3% OV-17 stainless steel column (1/8" x 5') with helium as a carrier gas. The peaks were integrated using a Hewlett Packard Model 3300 Laboratory Data System. Nmr spectra were obtained on a Varian Model A60A spectrometer. Chemical ionization mass spectra were recorded from probe samples on a modified Varian Model CH-7 spectrometer.

Deuterated proxylated trimethylpropane

A 3 mm³ piece of sodium and 1.55 g of trimethyl propane

(Aldrich Chemical Co.) were heated together with stirring in the apparatus illustrated in Figure 2 under 0.1 torr vacuum at 100°C until all gas evolution ceased (~2 hr). Previously degassed propylene-3,3,3-d₃ oxide (Merck & Co.) (3 ml. 2.6g) was then introduced through the 3-way stopcock to the TMP-sodium flask. After 2 hr all of the propylene oxide was consumed. Stirring and heating were continued for an additional 2 hr. The clear viscous liquid was then cooled to 60°C and opened to the atmosphere. Approximately 0.2 ml of 17% hydrochloric acid was then added to acidify the solution to pH 5 or 6 which caused the solution to turn cloudy due to the precipitation of sodium chloride. The mixture was dissolved in dichloromethane, neutralized with sodium bicarbonate and dried with anhydrous magnesium sulfate. Filtration of the mixture, followed by removal of the dichloromethane under vacuum, yielded 3.2 g of the deuterated propoxytrimethylolpropane.

The nmr spectra clearly indicated that the reaction had been accomplished with no scrambling of the methyl deuterium. Gas chromatography results indicated the following distribution of products:

dipropoxy	- 26.9%
tripropoxy	- 39.5%
tetrapropoxy	- 26.7%
pentapropoxy	- 6.9%

A \overline{MW} 315 was calculated from the results. Chemical ionization mass spectrometry of the product using isobutane as a reagent gas showed the correct molecular weights for the individual species. Polypropylene glycol content was less than 0.3% in the product.

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