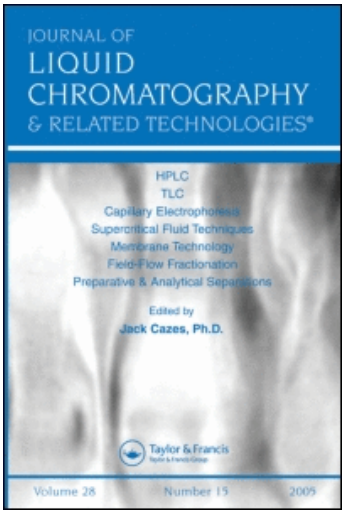

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ON-STREAM HPLC DETERMINATION OF RESIDUAL ETHYLENE OXIDE AND PROPYLENE OXIDE IN GLYCEROL BASED POLYOL SYNTHESIS

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ABSTRACT

A simple automated HPLC scheme was developed to monitor synthetic polymerization reactions on-stream. Chromatographic conditions that affect the separation of the reaction species from the reaction product and base catalyst using high-performance aqueous gel permeation chromatography were also studied. Reactor samples are automatically drawn from the reaction vessel through a micro-loop sampling valve/actuator assembly and transferred to the chromatographic system via stainless steel tubing without interruption of the mobile phase flow. The resulting chromatograms, monitored by a refractive index detector, of reactants and products are continuously measured at intervals during the reaction automatically and unattended. Application of this system for the reaction of propylene oxide and ethylene oxide to high molecular weight polyols is presented.

INTRODUCTION

A method for on-stream monitoring of ethylene oxide (EO) and propylene oxide (PO) is desirable to follow the loss of these epoxides during the synthesis of base catalyzed EO-capped poly(oxypropylene). Direct on-stream analysis by gas chromatography is considered unsuitable because the reaction mixture contains potassium hydroxide catalyst and polymer that could foul the injection port and column of a gas chromatograph. Headspace gas chromatography has been used for analyzing alkaline polymerization samples for propylene oxide [1], but it is not amenable to on stream monitoring. Titrimetric and spectrophotometric techniques are also used to determine propylene oxide; however, these analyses would be difficult to put on-stream. In a recent review outlining the advantages of online process liquid chromatography, Mowery [2] has pointed out the suitability of this technique for streams containing strong bases or polymers. On-stream HPLC, therefore, should be suitable to detect propylene oxide and ethylene oxide in the alkaline polymer mixtures encountered in poly(oxypropylene) synthesis reactors.

A simple scheme is described here that uses an aqueous gel-permeation column, a refractive index detector, and a Valco sampling valve to separate PO and EO in the presence of the KOH catalyst and poly(oxypropylene) polymer. This on-stream HPLC technique has the advantage of eliminating any pre-treatment procedures by sampling directly into the mobile phase and requiring a minimum of operator effort. This paper describes the development of the chromatographic conditions, the design of the on-stream sampling system and some of the results obtained during the on-stream operation.

EXPERIMENTAL

Chromatographic procedures:

Analyses were performed on a Hewlett Packard 1084B liquid chromatograph. Injections were made with a Valco CV-6-UHPa-N60, 7000 psig injection valve equipped with a ten microliter injection loop. Two Polymer Laboratories PL-Aquagel P2 (30 cm X 7.7 mm i.d.) columns were connected in series, and were used for the chromatographic separations. The detector was a Waters Associates R-401 refractometer operated at 8X sensitivity. A flow rate of 1.5 ml/min was maintained and separations were performed at ambient temperatures. Chromatograms were recorded and peak areas were integrated using a Shimadzu CR-3A integrator. Samples were injected directly onto the HPLC without any dilution after they were withdrawn from the reactor.

Gel Permeation Chromatography:

Molecular weights of some polyols were determined by gel permeation chromatography. These analyses were performed on a Waters Associates GPC-201 liquid chromatograph using a WISP sample injector and an R-401 refractive index detector. Separations are performed on two 30 cm Toya-Soda GMH-6000 columns connected in series and eluted with tetrahydrofuran at 1 ml/min. Number average molecular weights are determined with a Chromatix GPC-2 software package which uses universal calibration. The method uses polypropylene glycol standards from 425 to 3000 MW avilable from Scientific Polymer Products, Inc.

Reagents:

Acetonitrile, methanol, and tetrahydrofuran were EM Science Omnisolv grade obtained from Bodman Chemical

Co., Media, Pa. Distilled de-ionized water was passed through a Millipore Milli-Q water purification system prior to use. Propylene oxide and glycerol were gold label grade obtained from Aldrich Chemical Co., Milwaukee, Wisconsin and were used without further purification. Ethylene oxide was obtained from Air Products Specialty Gases, Allentown, Pa.

RESULTS AND DISCUSSION

A high performance aqueous gel permeation chromatography procedure has been developed for the on-stream analysis of propylene oxide or ethylene oxide in polyol synthesis streams. In these reactions propylene oxide is reacted with a 350 molecular weight triol in the presence of potassium hydroxide until a higher molecular weight polyol (e.g. 5000 MW) is formed. In some instances, this polyol is then capped by reaction with an additional portion of ethylene oxide. HPLC is a logical choice to analyze for the unreacted epoxides; however, the caustic nature of the samples precludes the use of conventional silica-based HPLC columns. Recently several manufacturers have marketed resin-based reverse phase columns. These columns are much more tolerant of caustic mobile phases and should be tolerant of the moderate amount of potassium hydroxide present in polyol synthesis samples.

Several attempts were made to separate propylene oxide and polyols using a Hamilton PRP-1 column. These experiments employed a refractive index detector and several peaks were always observed in the solvent front portion of the chromatogram. In order to move propylene oxide away from these interferences, a significant amount of water was required in the mobile phase. In such mobile phases, however, the polyol products were not soluble. The option of removing potassium hydroxide from the samples by solid phase

extraction was considered to be not practical for on-stream analysis.

To overcome the problems and constraints described previously, an aqueous gel-permeation chromatography column, PL Aquagel, was chosen for the analysis. Initial experiments were conducted with 10% water- 90% acetonitrile mobile phase. This mobile phase was found to be compatible with the column, and would solubilize propylene oxide, polyol, and potassium hydroxide. As shown in Figure 1, a reasonable separation was achieved between propylene oxide and a 3500 MW polyol. Since the resolution was not complete, a tangent skim method of quantitation was used. Linear calibration was achieved for samples in the 1 - 20% concentration range for propylene oxide. Even at the 2% level, statistical analysis of 6 replicate injections showed 5% relative standard deviation. Expected interferences such as propylene glycol, potassium hydroxide, and low molecular weight polyol were found not to interfere. An analysis time of 20 minutes is possible with two 30 cm PL-Aquagel columns in series. A shorter analysis time is possible with a single column; however, at a price of poorer resolution and poorer quantitation of propylene oxide at low levels.

Figure 2 illustrates the on-stream configuration used in these studies. The on-stream approach eliminates any pre-treatment of the sample and minimizes operator manpower needed to perform the analysis. The reaction mixture is automatically picked up from the reaction vessel through an electrically actuated Valco injection valve. Using a sampling frequency of approximately 20 minutes, it was possible to obtain sufficient data to study the kinetics of propylene oxide decay during a two to three hour run. When the Shimadzu integrator is used to drive the sampling valve, the entire analytical procedure can be carried out unattended.

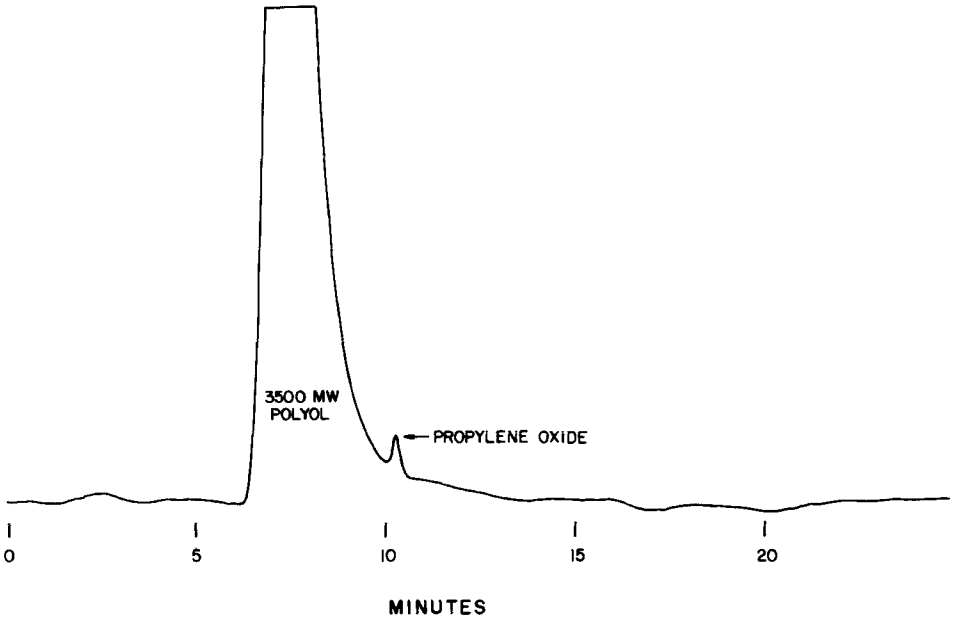

FIGURE 1. Separation of 3500 MW Polyol and Propylene Oxide. 2-Polymer Laboratories PL-Aquagel P2 Columns - 30 cm X 7.7 mm id, isocratic 90% acetonitrile - 10% water mobile phase, flow rate 1.5 ml/min.

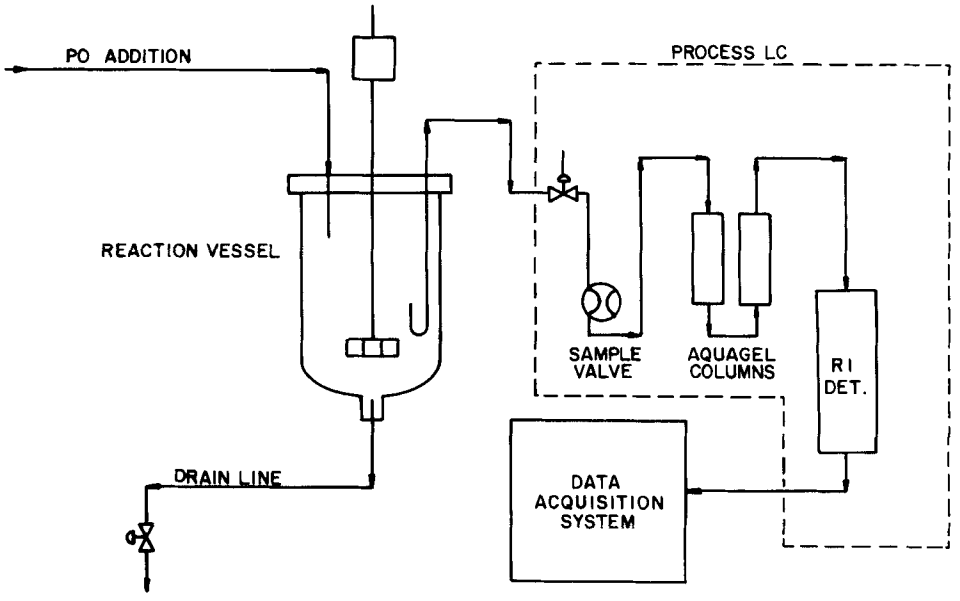

FIGURE 2. On-stream HPLC Configuration.

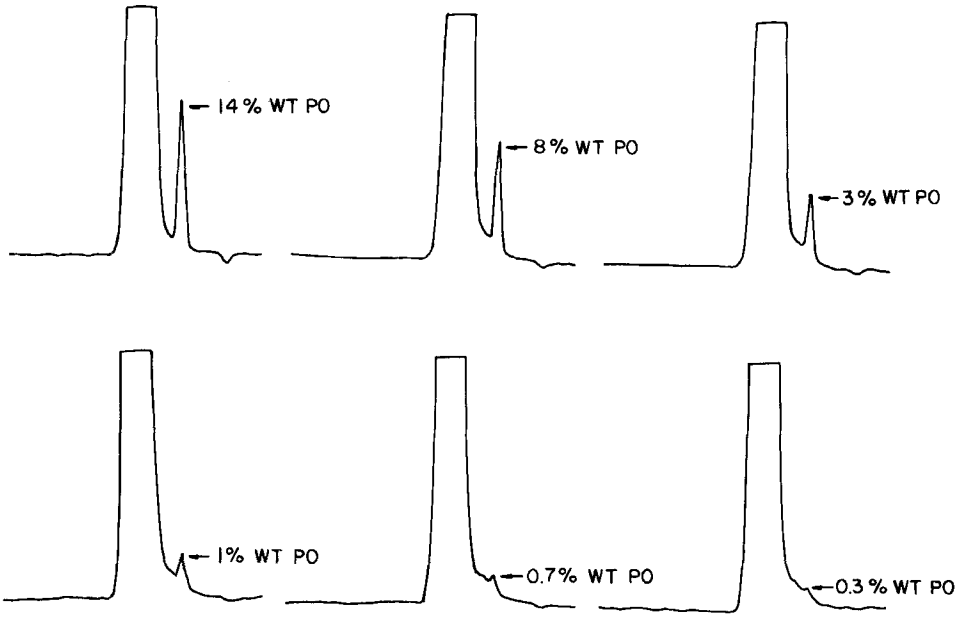

FIGURE 3. Chromatograms Showing Decay of Propylene Oxide Concentration with Time. Sampling Interval - 20 Minutes.

Figure 3 illustrates the resolving power of the method and its ability to track propylene oxide consumption with time. A polyol with a molecular weight of 350 - 500 was produced in this example. The decay curve resulting from the run represented in Figure 3 is shown in Figure 4. A comparison of propylene oxide concentration measured by LC against the calculated propylene oxide concentration determined by partial pressure in the reactor shows excellent agreement.

The HPLC conditions initially developed for this analysis worked well for synthetic samples which simulated actual reaction mixtures. When the analysis was applied to these actual reaction mixtures, poor

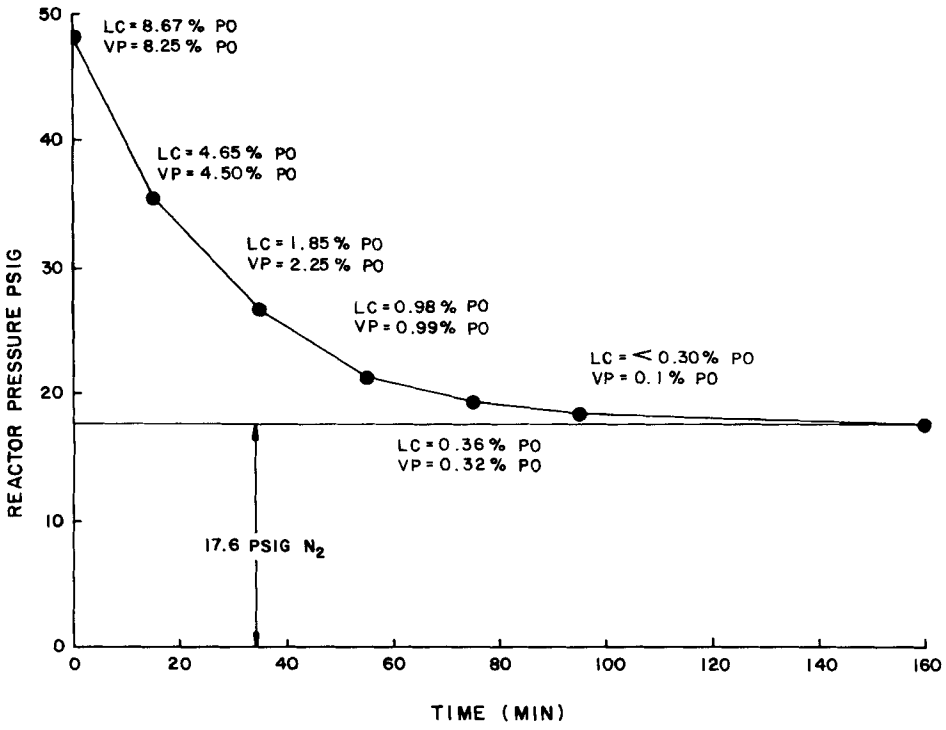

FIGURE 4. Comparison of Propylene Oxide Concentrations Determined by HPLC and Vapor Pressure. LC values are PO concentrations determined by HPLC, VP values are calculated from vapor pressure. 17.6 psig N_2 represents constant backgroud pressure of nitrogen applied to the reactor.

peak shapes and lack of resolution between propylene oxide and low MW polyols resulted. It was observed that the reactor samples were not completely soluble in the 90:10 acetonitrile/water mobile phase. Since the polyol solubility was adversely affected by the water present, the mobile phase was changed to 100% acetonitrile. This change caused the higher molecular weight polyols to elute after the lower molecular weight propylene oxide, a result unexpected for gel

permeation chromatography. There was some concern that this behavior might be caused by the high viscosity of the neat samples being injected onto the column, leading to a viscous fingering effect[3]. Even when the samples were significantly diluted (e.g., 1:10), the same effect was still observed. This meant that the polyols were probably retained longer on the column by an adsorption mechanism caused by the removal of water from the mobile phase.

A test of the solubility of four reactor samples ranging in molecular weight from 400 to 3800 revealed that 90% methanol - 10% water was satisfactory to dissolve all the samples. Other tests were conducted in which 0.05M KH_2PO_4 was substituted for water in order to neutralize any potassium hydroxide in the samples; however, this neutralization was found to be unnecessary. Tests in the laboratory then showed that the 90% methanol - 10% water mobile phase could sucessfully resolve propylene oxide from product polyols that ranged from 400 to 3800 MW.

Although the new mobile phase worked sucessfully in the laboratory, the analysis did not resolve propylene oxide and polyols when it was used in the on-stream application. Dilution experiments showed that the resolution improved as dilution increased from 1:1 to 16:1. Due to the pragmatic limitations imposed by on-stream dilution, the injection volume was reduced from 25 microliters to 10 microliters, which had the same effect on resolution as dilution. The analysis has now been used sucessfully for several series of pilot runs.

For some polyol kinetic studies it is desirable to measure ethylene oxide, either alone or in addition to propylene oxide. Figure 5 demonstrates the separation of both ethylene oxide and propylene oxide from a 3800 MW polyol. The on-stream method is thus suitable for the determination of either oxide singly or both oxides together.

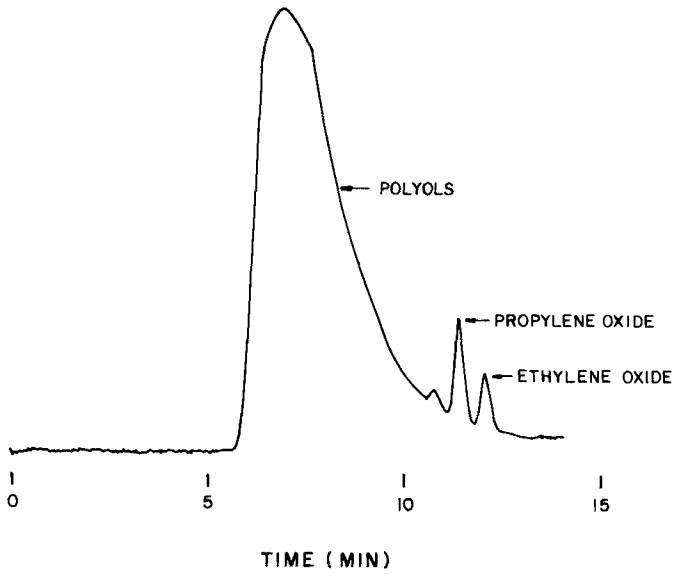

FIGURE 5. Separation of Propylene Oxide and Ethylene Oxide. Conditions same as FIGURE 1 except mobile phase is 90% methanol - 10% water.

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