

Synthesis & Characterisation of Hydroxy Terminated Polyepichlorohydrin & Polyglycidylazide

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ABSTRACT

Polyglycidylazides with molecular weight more than 2000 and 100,000 have been synthesized by reacting polyepichlorohydrin (PECH) diol with sodium azide in dimethyl sulphoxide. The conversion of the chloropolymers to azide polymers was above 90 per cent as estimated by fast neutron activation analysis. PECH of \bar{M}_n around 2000 was synthesized by activated monomer polymerization of epichlorohydrin using boron trifluoride-ethylene glycol complex as catalyst while aluminium triethyl-ethylene glycol complex was employed as catalyst to get PECH of \bar{M}_n more than 100,000. The polymers were characterized by various spectral analyses, fast neutron activation analysis and molecular weight measurement. The PECH diols and their corresponding azides of \bar{M}_n greater than 2000 and 100,000 cured readily with toluene diisocyanate using triethylamine and dibutyl tin dilaurate as catalysts.

1. INTRODUCTION

Polyglycidylazide (PGA) with two -OH groups per molecule is an important material for preparation of fuel-rich ram rocket propellants^{1,2}. It is also used as an energetic fuel-binder for composite rocket propellants³. In recent years, azide polymers and their copolymers have been used with the addition of HMX to make smokeless composite modified cast double base propellants⁴. Therefore, it was thought worthwhile to standardize a synthetic method for obtaining a viscous PGA diol of molecular weight around 2500 for ease of mixing with other ingredients of the cure system on one hand and an ultrahigh molecular weight PGA diol for higher energetics in burning, on the other. PGA diol is synthesized by reacting polyepichlorohydrin (PECH) diol with sodium azide in dimethyl sulphoxide (DMSO) to convert the -CH₂Cl groups to -CH₂N₃ groups. Thus, the magnitude of molecular weight of PGA diol depends upon that of PECH diol.

This paper reports the synthesis of PECH diol of low molecular weight on the basis of available data in patents and open literature for polymerization of epichlorohydrin (ECH), using boron trifluoride-ethylene glycol (BF₃-EG) complex as catalyst^{5,6}. The synthesis of ultrahigh molecular weight PECH diol using aluminium

triethyl-ethylene glycol [Al(C₂H₅)₃-EG] complex as catalyst was novel and involved modification of an available method⁷. However, both the methods were based on activated monomer polymerization with controlled addition of monomer to the polymerization reactor. Conversion of PECH diol thus obtained to PGA diols by reacting with sodium azide in DMSO was effectively followed by fast neutron activation analysis (FNAA) of nitrogen and chlorine in the final products.

2. EXPERIMENTAL DETAILS

2.1 Synthesis of Low Molecular Weight PECH Diol

Polymerization of ECH in the presence of ethylene glycol (EG) and BF₃-EG complex as catalyst was carried out using the procedure described by Biedron *et al* with some modifications. EG (31 g) was placed in a 2 l three-necked flask fitted with an effective stirrer, dropping funnel, thermometer and a condenser thermostated in a water bath at 20 °C. BF₃-EG complex was prepared by passing gaseous BF₃ through EG until the expected increase in weight was reached. To the reaction vessel, 100 ml of methylene chloride was added with continuous stirring followed by 1.5 g BF₃-EG complex (0.01 mol pure BF₃). This was followed by

addition of 790 g of ECH slowly at the rate of 2-3 drops per minute. Stirring was continued for a period of 70 hr. Addition of 100 ml of methylene chloride after each addition of 200 ml of ECH facilitated effective stirring. After complete addition of ECH, the reaction mixture was stirred at 20 °C for 2 hr. To neutralize the catalyst, 25 g of anhydrous calcium oxide (*CaO*) was added to the reaction mixture and stirred for 2 hr at 60 °C. The stirring was continued for another 1 hr at 90 °C. *CaO* was filtered off under vacuum using a G₃-Schott sintered glass filter. The remaining solvent in the resin was distilled off under vacuum with efficient bubbling of air.

\bar{M}_n (VPO), 2065; *OH* per molecule 2;

ν_{CH_2Cl} , 750 cm^{-1} , Yield 95 per cent

2.2 Synthesis of Low Molecular Weight PGA Diol

A mixture of 92.5 g (1 mol) of PECH diol, excess of sodium azide (80 g, 1.2 mol per mol of PECH) and sufficient DMSO was stirred at 100 °C for 11 hr. The precipitated *NaCl* was filtered off and most of DMSO was distilled off under vacuum and unreacted *NaN₃* was removed by filtration. PGA diol was further purified by extracting the polymer with dimethylformamide (DMF), and distilling off DMF under vacuum from a hot water bath with efficient bubbling of air in the polymer solution. PGA diol with following properties is obtained:

\bar{M}_n (VPO), 2150; *OH* per molecule, 2 per cent conversion (Fast neutron activation analysis), 92 per cent Yield, 70 per cent ; $\nu_{CH_2N_3}$, 2100 cm^{-1} .

2.3 Synthesis of High Molecular Weight PECH Diol

A five-necked round bottom flask was equipped with a stirrer, a thermometer, a nitrogen inlet (over surface of liquid), a reflux condenser and a rubber stopper for injecting ingredients with hypodermic equipment. The air in the flask was replaced with nitrogen by passing a fast stream of gas for 30 min. The reaction was carried out in an ice bath. Methylene chloride (100 ml) along with 16.1 ml of EG was added to the reaction flask with slow but continuous nitrogen sweeping. With the help of a hypodermic syringe, 20 ml of triethyl aluminium in *n*-hexane (1M) was injected to the reaction vessel with constant stirring. After about 30 min, 100 ml of ECH was added to the reaction mixture dropwise from a dropping funnel at the rate of 3 drops per minute. At the half way stage of ECH addition, 13 ml of triethyl aluminium in *n*-hexane was injected into the

reactor. Addition of ECH was continued at the same rate described earlier. The total time taken for the complete addition of ECH was 8 hr. The polymerization was stopped by the addition of 54 ml of anhydrous ethanol. Most of the polymer was in the form of a slurry, although a small amount was on the walls of the reactor. A fast stream of nitrogen was bubbled with constant stirring for 2 hr to take out the low molecular weight fractions from the reaction kettle.

The reaction mixture with 200 ml of dry diethyl ether was filtered, the filter cake was washed twice by slurring with 700 ml of diethyl ether followed by filtration. The ether-insoluble material was transferred to a beaker containing 80 ml of 10 per cent methanolic hydrochloric acid (100 ml methanol in 30.4 ml concentrated hydrochloric acid). The polymer was dissolved in the above solution. Then the polymer was precipitated out by using 10 per cent methanolic potassium hydroxide solution. After standing for 1.5 hr, the mixture was filtered and the solid was washed with methanol until it becomes neutral (four washes). The product was dried for 16 hr at 60 °C in an air oven to give 25 g of a white powder which was hydroxy-terminated, high molecular weight PECH.

2.4 Synthesis of High Molecular Weight PGA Diol

In 1 l capacity round bottom flask, 15 g. of high molecular weight PECH diol (synthesized using triethylaluminium-ethylene glycol complex), 75 g of sodium azide and 400 ml of DMSO were stirred at 100 °C on a water bath. The reaction was continued for 11-12 hr. After the contents of the flask were cooled to room temperature, they were filtered. The residue, which contained unreacted sodium azide, sodium chloride and PGA was washed with hot distilled water (3 washes). The polymer was recovered after filtration. It was washed with methanol (3 washes) and dried at 60 °C in an air oven.

The filtrate from the reaction mixture after conversion of PECH to PGA contained low molecular weight polymers dissolved in DMSO. Most of the DMSO was distilled off under vacuum. The polymer was precipitated using anhydrous ethanol. The solid was recovered after filtration and dried at 60 °C in an air oven.

\bar{M}_n 100,000; *OH* per molecule, 2 per cent conversion, 92 per cent (Fast neutron activation analysis); Yield 95 per cent

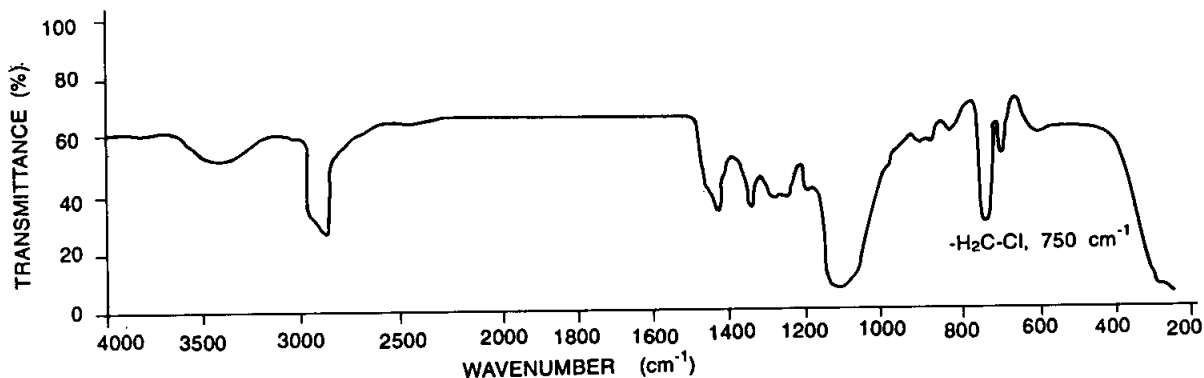


Figure 1. IR spectrum of PECH diol.

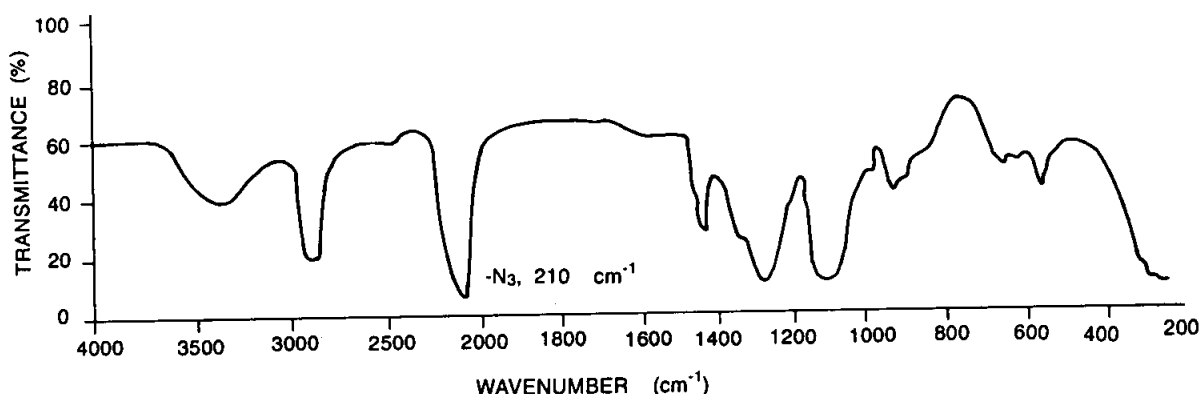
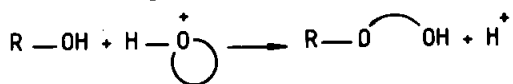


Figure 2. IR spectrum of PGA diol.

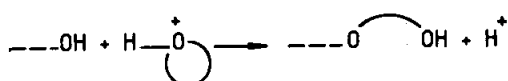
3. RESULTS & DISCUSSION

Polymerization of ECH in the presence of EG and BF_3 -EG complex as catalyst has been described by Biedron *et al*⁶ who proposed an activated monomer mechanism (AMM) for the polymerization process. The mechanism involves the concept of living polymerization that has no termination and transfer. In AMM, an activated or protonated or positively charged monomer molecule inserts into a growing polymer chain having an $-OH$ group at the growing end.

The initiation process is as follows :



Propagation



This mechanism leads to a polymer which has strictly two $-OH$ groups at the two ends. Here $\bar{M}_n =$

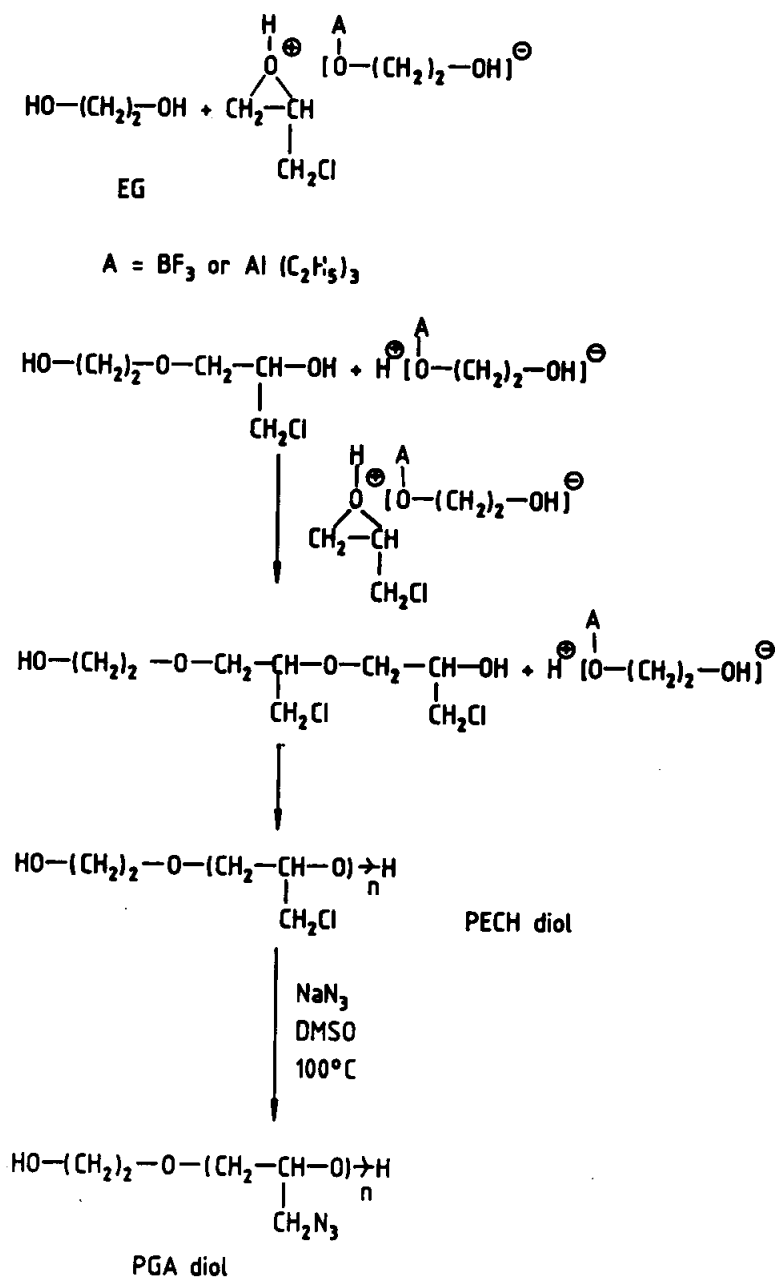
(ECH)/(EG). The direct proportionality of \bar{M}_n with the monomer concentration holds good up to a molecular weight of 2500 after which due to the formation of cyclic products, the linear relation does not remain valid. However, the cyclic products are derived due to the polymerization of ECH by conventional cationic polymerization mechanism with a cation at the end of the polymer during propagation. Such charged end can terminate by cyclizing with the terminal $-OH$ of the polymer at the other end. Thus the charged end polymerization mechanism which competes with the AMM can be suppressed by making the addition of ECH very slow so that the rate of addition of ECH equals the rate of its consumption by AMM while controlling the reaction temperature at 20 °C.

Ultrahigh molecular weight PECH diol was synthesized by following the AMM using $Al(C_2H_5)_3$ -EG complex in EG. Vandenberg⁷ described the synthesis of ultrahigh molecular weight (600,000 - 2000,000) PECH by polymerization of ECH in bulk by the use of $Al(C_2H_5)_3 \cdot 0.6 H_2O$ as catalyst. Such a polymer is unlikely

to possess 2 OH groups per molecule. Hence the catalyst was modified to fall in line with the concepts of Biedron described earlier by adding $Al(C_2H_5)_3$ in n-hexane (1 mol) to EG (1 mol). The rest of the procedure of the activated monomer polymerization described earlier was kept intact. Thus we succeeded in getting a high molecular weight solid polymer that cured readily with

toluene diisocyanate using triethylamine and dibutyl tin dilaurate as catalyst.

Both the PECH diols were converted to PGA diols by reacting them with excess sodium azide in DMSO at $100^\circ C$ for 11 hr. The scheme of reaction can be depicted as follows:



The conversion of PECH diol to PGA diol by the procedure described in the paper is almost quantitative, though the yield is around 70 per cent. The IR spectra of PECH diol and PGA diol are given in the Figs. 1 and 2 respectively. It can be seen that a strong peak at 750 cm^{-1} due to $-\text{CH}_2\text{Cl}$ (Fig.1) is completely absent in the spectrum of PGA diol, whereas a very strong peak due to $-\text{CH}_2\text{N}_3$ appears at 2100 cm^{-1} (Fig. 2). An attempt was made to quantitatively estimate the conversion by measuring the percentage of nitrogen in PGA diol, employing FNAA using 14.0 MeV neutrons to convert nitrogen to its radioactive isotope that decayed producing γ -energy with a peak at 0.511 MeV. Aluminium was used as the monitor. The details of the method have been described by Panda *et al* elsewhere⁸. Thus the percentage conversion was found to be 96.7 though 98 per cent conversion has been claimed in one of the papers⁵. The hydroxyl functionality measurement was based on the measurement of hydroxyl equivalent using acetic anhydride method as it was found to be the most suitable.

Conversion of PECH diol in the presence of excess sodium azide requires DMSO as solvent which penetrates into the blood stream through skin absorption much faster than other organic solvents. Thus DMSO is used as a solvent for calmatives^{9,10}. Further DMSO is known to undergo decomposition at its boiling point¹⁰. Hence precaution must be taken using handgloves and respiratory mask while working with DMSO. Distillation of DMSO should always be carried out at reduced pressure from a hot water bath. Polymers with pendant azide groups are photosensitive^{11,12} and can undergo decomposition and crosslinking when exposed to the visible and UV radiations^{11,12}. PGA diols therefore should be stored in the dark.

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