Production of polyalcohols and polyethers from polyepoxides produced from metalloporphyrinic catalysis of *cis*-polybutadiene

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(Received 9 August 1993)

Polybutadiene polyepoxide, the product of the catalytic reaction of *cis*-polybutadiene with chloromanganese(III) teraphenylporphyrin in association with iodosylbenzene, was converted to polyalcohol and polyether when treated with anhydrous oxalic acid and acidified water, respectively.

(Keywords: polybutadiene polyepoxide; metalloporphyrinic catalysis; polyalcohols and polyethers)

Polyepoxides, polyalcohols and polyethers are being widely used[1] in advanced electronic technology. Polyalcohols are also good antifreeze agents for automobiles and serve as raw materials for the plastic furniture industry. We have already discussed[2-4] the catalytic transformation of polyene polymers to polyepoxides in an attempt to recycle polyene plastics.

In this study we report the novel conversion of polyepoxides, the products of our catalytic reaction, to polyalcohols and polyethers as the unexpected products of the action of anhydrous oxalic acid and acidified water respectively on the oxirane rings (*Figure 1*). We also report the *in situ* conversion of *cis*-polybutadiene to polyethers by the catalytic action of metalloporphyrins.

In an attempt to produce soap, the oxirane rings of *cis*-polybutadiene polyepoxide were treated with anhydrous oxalic acid. The product resulting from the opening of the oxirane rings was polyalcohol, instead of the expected esterification and the production of soap. For the above experiment, *cis*-polybutadiene (0.1 g) was converted[1-8] to polyepoxide by stirring with excess of iodosylbenzene[9] (1.65 g) in dichloromethane (15 ml) and the catalytic action of chloromanganese(III) tetraphenylporphyrin[10] (Mn(III)TPPCl) (0.03 g). The solid iodosobenzene was filtered off and anhydrous oxalic acid was added to the solution. The mixture was stirred for 2 h, the excess solid oxalic acid was filtered off and an aliquot of the solution was dried and its ^{1}H n.m.r. spectrum in chloroform was obtained. This spectrum did not show the peaks at 1.6 and 2.9 ppm that are characteristic of the polyepoxide. The appearance of a new peak at 3.6 ppm was observed, which disappeared on addition of a drop of deuterated water to the n.m.r. tube. This is a strong indication that this signal belongs to a hydroxy hydrogen. The spectra are shown in *Figure 2*.

In an attempt to produce polyalcohols, the oxirane rings of *cis*-polybutadiene polyepoxide were treated with acidified water. The acidic hydrolysis of the oxirane ring produced polyethers instead of the expected polyalcohols. For the latter experiments, the *cis*-polybutadiene polyepoxide solution was stirred overnight with acidified

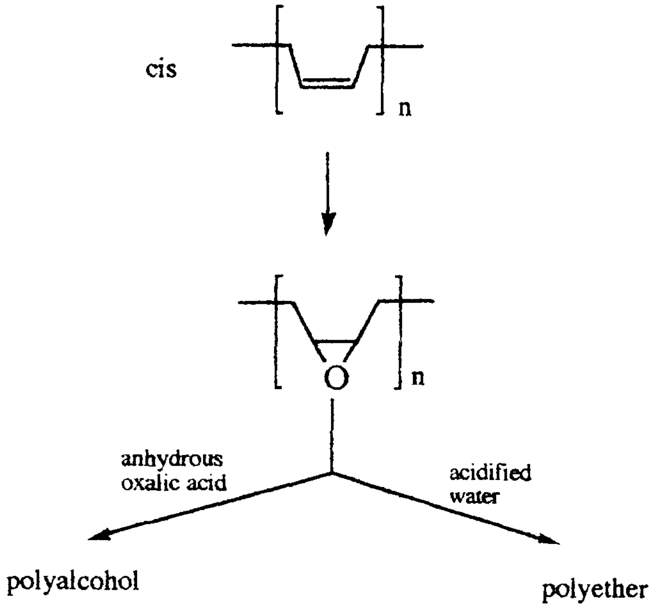

Figure 1 Conversion of polybutadiene polyepoxide, produced catalytically from *cis*-polybutadiene, to polyalcohol and polyether

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0032-3861/94/13/2857-02

water (15% HNO_3). The peaks of the ^1H n.m.r. spectrum of the polyepoxide disappeared and new peaks appeared. No changes in the spectrum were observed after the addition of D_2O to the sample in the n.m.r. tube.

In another experiment, *cis*-polybutadiene (0.2 g) in dichloromethane (30 ml), sodium hypochlorite (50 ml), benzenedimethyltetradecylammonium chloride (0.02 g), pyridine (0.05 ml) and acetomanganese(III) tetraphenylporphyrin (0.02 g) were stirred for 4 h. From an aliquot of the organic layer the ^1H n.m.r. spectrum in $CDCl_3/C_6D_6$ 1/1 was obtained. Peaks at 1.25 and 2.65 ppm proved the formation of polyepoxide (63% with respect to the polyene polymer). The solution was continuously stirred overnight and the ^1H n.m.r. spectrum in $CDCl_3/C_6D_6$ 1/1 was taken. The polyepoxide and polyene polymer peaks disappeared and new peaks appeared at 1.55 and 2.75 ppm. A possible mechanism for this could be the *in situ* basic catalysis of the oxirane rings to polyethers due to excess of pyridine in the solution.

Contrary to its polyepoxide and polyene polymer precursors, the polyalcohol produced seems to precipitate from its chloroform solution on addition of benzene. The solubility and the structure of the new polymers are under examination as well as their thermal and dielectric constants, which are expected to be different from their precursors.

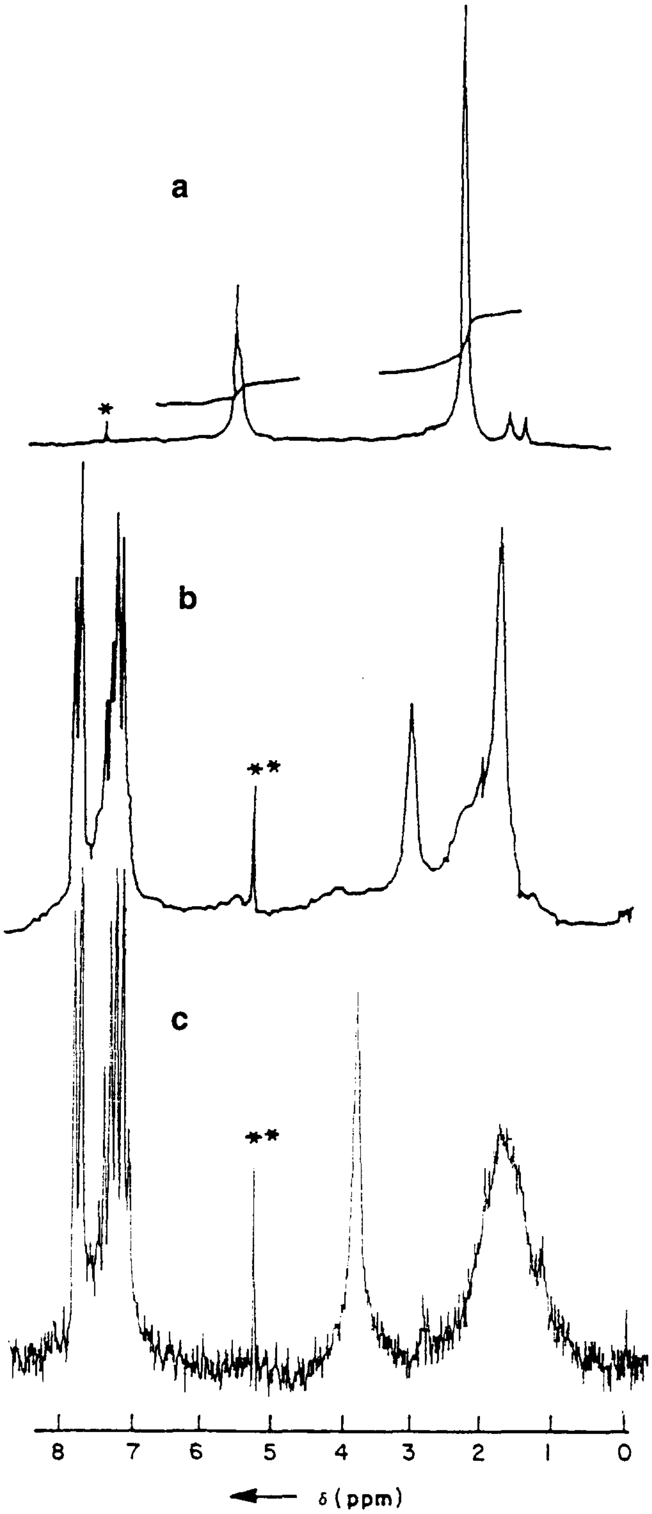

Figure 2 The 80 MHz ^1H n.m.r. spectra of: (a) *cis*-polybutadiene; (b) the polyepoxide product in the reaction mixture of the epoxidation reaction of porphyrinic complex with PhIO (*$CHCl_3$, **CH_2Cl_2); and (c) the polyalcohol product in the reaction mixture of *cis*-polybutadiene polyepoxide and anhydrous oxalic acid

ACKNOWLEDGEMENTS

This research was supported by Greek General Secretary of Research and Technology through Grant No. 89ED237 and the Special Research Account of the University of Crete through the Research Commission (No. 149).

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