Metalloporphyrins catalyse *cis*-polybutadiene to polyepoxide

M. J. Tornaritis and A. G. Coutsolelos*
Laboratory of Inorganic and Coordination Chemistry, Department of Chemistry, University of Crete, PO Box 1470, Heraklion, GR-714 09 Crete, Greece
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cis-Polybutadiene has been transformed to the corresponding polyepoxide, a polyalcohol precursor, with chloro- or acetato-manganese(III) tetraphenyl porphyrin [Mn(III)(TPP)Cl, Mn(III)(TPP)OAc], acting as a catalyst in association with two different oxygen donors, sodium hypochlorite and iodosylbenzene.

(Keywords: epoxidation reaction; catalysis; metalloporphyrin; polyene polymer; polyepoxide)

The epoxidation[1,2] reaction of double bonds, is highly relevant to the catalytic transformation of any polymeric material having carbon–carbon double bonds. For example, this could be the first step in the degradation and recycling of polyene plastics. Also, the polyepoxides, as polyalcohol precursors, might be finally transformed to small molecular weight alcohols. In addition, polyepoxides could also be reacted with dicarboxylic acids to produce soaps.

In this study we report the novel transformation of polymer to polyepoxide with metalloporphyrin acting as a catalyst in association with an oxygen donor (*Scheme 1*). The large number of cycles per unit catalyst and the low price of the oxygen donors may make this catalysis suitable for industrial use.

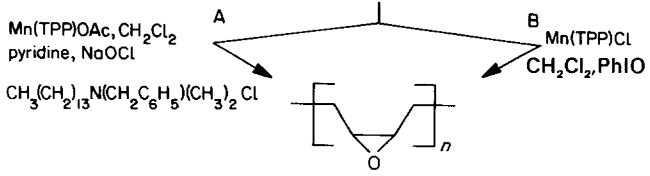
The *cis*-polybutadiene ($M_w = 200\,000$–$300\,000$) was obtained from Aldrich. The catalyst was acetato[3]- or chloro[3,4]-manganese(III) tetraphenyl porphyrin and the oxygen donor was sodium hypochlorite (Aldrich commercial grade, chlorine 5% minimum, $d = 1.097$ g cm^{-1}) or iodosylbenzene[5].

Following the 'conventional' method developed by Meunier *et al.*[6,7] for the epoxidation of olefins with sodium hypochlorite, *cis*-polybutadiene (0.21 g, ~4 mmol) (*Figure 1A*) was dissolved in methylene chloride (30 ml). To the solution acetato-manganese(III) tetraphenyl porphyrin (0.036 g, ~0.051 mmol) benzyldimethyltetradecylammonium chloride (0.04g, ~0.0099 mmol) and pyridine (0.1 ml, ~1.2 mmol) was added. Sodium hypochlorite (40 ml) was then introduced into the round-bottomed flask (*Scheme 1A*). The reaction mixture was stirred and after 7 h the two layers were separated. The organic layer was dried with anhydrous sodium sulphate and the solvent was evaporated. The ^{1}H n.m.r. spectrum was then obtained from the residue (*Figure 1B*). This spectrum clearly shows peaks at 3.1 and 1.8 ppm which are attributed to the –CH– and –CH$_2$– groups of the polyepoxide. The lack of significant peaks at 5.3 and 2.2 ppm belonging to the –CH– and –CH$_2$– groups, respectively, of the polyolefin indicate that the reaction was complete.

The molecular ratio of metalloporphyrin to double bonds of the polyolefin in the reaction was 1.3:100. This leads to the conclusion that, even under the mild conditions of the experiment, 1.3% catalyst is an excess.

In addition to the above aqueous–CH$_2$Cl$_2$ biphasic system, a solid (iodosylbenzene)–CH$_2$Cl$_2$ system can convert *cis*-polybutadiene to polyepoxide. For the latter conversion, *cis*-polybutadiene (0.15 g, ~2.78 mmol) was dissolved in methylene chloride (14 ml) and chloromanganese(III) tetraphenylporphyrin was added to the solution. Iodosylbenzene (1.2 g) was introduced to the reaction mixture and the mixture was stirred overnight (*Scheme 1B*). The ^{1}H n.m.r. spectrum (*Figure 1C*) obtained from the epoxidation reaction with iodosylbenzene clearly shows the signals of the polyepoxide produced. Also observed were multiple peaks in the 7–8 ppm range which are due to the phenyl ring hydrogens of iodobenzene, derived from iodosylbenzene. (The solid iodosylbenzene is not soluble in the reaction solvent or in the chloroform or benzene used to dissolve the n.m.r. samples.) The lack of any other peak indicates the complete transformation of the starting polymer to polyepoxide.

The complete catalytic transformation of the *cis*-polybutadiene to polyepoxide with metalloporphyrins in



Scheme 1 Epoxidation reaction with (A) sodium hypochlorite and (B) iodosylbenzene

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* To whom correspondence should be addressed

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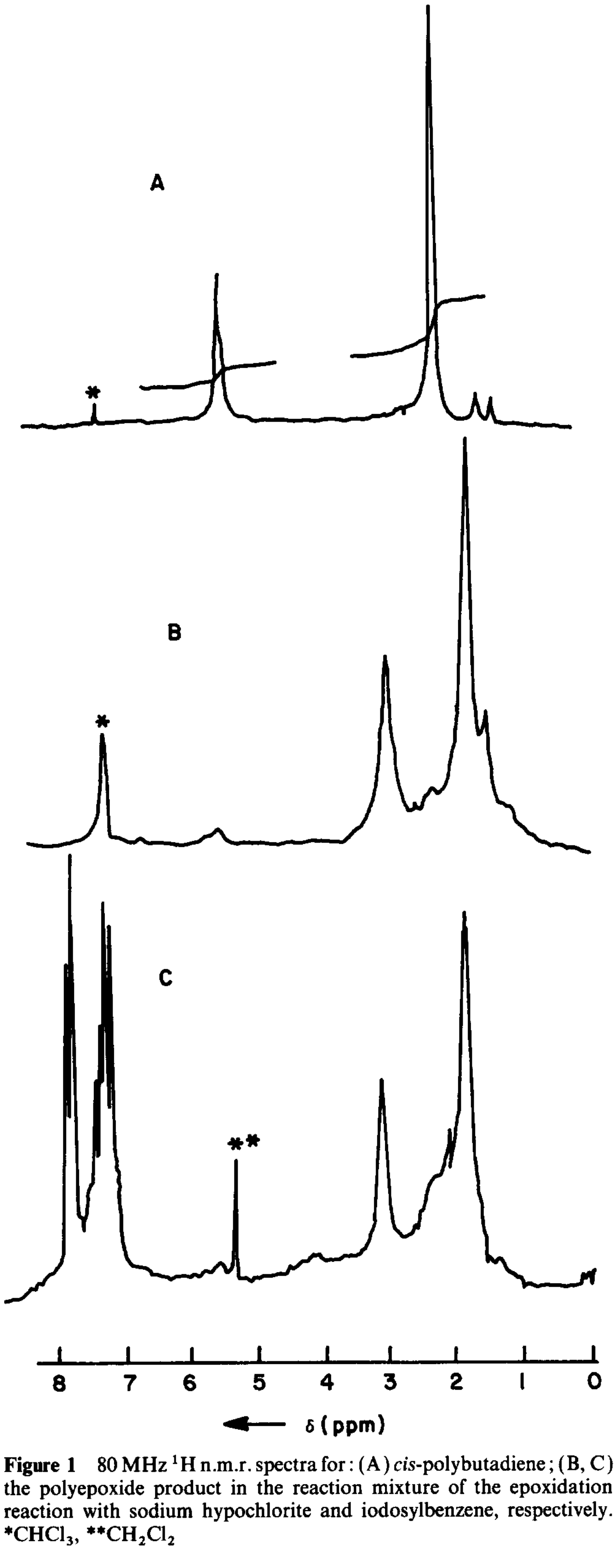

Figure 1 80 MHz ^{1}H n.m.r. spectra for: (A) *cis*-polybutadiene; (B, C) the polyepoxide product in the reaction mixture of the epoxidation reaction with sodium hypochlorite and iodosylbenzene, respectively. $^*CHCl_3$, $^{**}CH_2Cl_2$

association with an oxygen donor was followed easily by ^{1}H n.m.r. spectroscopy. Preliminary experiments in our laboratory with *cis*-polyisoprene (natural rubber) or *trans*-polyisoprene as substrate, show the complete transformation of the substrates to polyepoxides within a few hours. The above epoxidation of the polyene polymers involves very little cost and can be performed under mild conditions and could point a way towards solving some experimental problems associated with the disposal of plastic materials.

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