# Enzymatic epoxidation of polybutadiene

**Ann W. P. Jarvie,* Nigel Overton and Christopher B. St Pourçain†**

*Division of Chemical Engineering and Applied Chemistry, Aston University, Aston Triangle, Birmingham, UK B4 7ET*

**An immobilised lipase isolated from *Candida antarctica* (Novozym 435) catalyses the selective epoxidation of polybutadiene.**

The use of enzymes in organic synthesis is becoming increasingly widespread. There are previous reports of the use of lipases in polytransesterification reactions, but their application to the modification of the backbone of synthetic polymers has not been explored.[1] We now report the enzyme catalysed epoxidation of a monophenyl terminated polybutadiene ($M_n \simeq$ 1300; 45% 1,2-vinyl, 35% 1,4-*trans*, 20% 1,4-*cis*) in a three phase system, under very mild conditions. The polybutadiene was treated with a 27.5 wt% aq. solution of hydrogen peroxide, catalytic quantities of acetic acid, and an immobilised lipase isolated from *Candida antarctica* (Novozym 435), in $CH_2Cl_2$ at room temperature.‡ The reaction proceeded rapidly over 24 h. Little further epoxidation and no opening of the epoxide rings (absence of OH absorptions in the infrared spectra) occurred over an additional 72 h. Reactions carried out in the absence of enzyme showed no evidence of epoxidation. The molecular weight of the polymer, determined by GPC, did not alter significantly during the epoxidation procedure, indicating the absence of chain scission and coupling reactions. The degree of epoxidation was readily calculated from the $^1$H NMR spectrum and the elemental analysis of the polymer. The results from both techniques were in close agreement. It was found that 29% of the double bonds had been oxidised over 24 h. The $^1$H NMR spectra also allowed the relative numbers of 1,4-*cis*, 1,4-*trans* and 1,2-vinyl double bonds to be calculated. The signals arising from the phenyl end group were vital to this procedure. It was apparent that the reaction was highly selective, and under all conditions studied the 1,4-*cis* and 1,4-*trans* double bonds of the backbone were epoxidised whilst the 1,2-vinyl groups remained untouched. Thus the epoxidation of 29% of all the double bonds in the polymer after 24 h corresponds to 52% of the backbone double bonds being epoxidised.

Some selective preference for epoxidation of the double bonds of the backbone (1,4-*cis* > 1,4-*trans* ⩾ 1,2-vinyl) has been observed in previous attempts to epoxidise polybutadiene.[2–4] In these systems the vinyl groups began to react before all of the backbone double bonds had reacted and some of the backbone double bonds remained unreacted. Small amounts of ring opened products were also observed in the epoxidation of polybutadiene with a 1 : 2 mixture of acetic acid and 60 wt% hydrogen peroxide.[2] The mild conditions of the enzymatic epoxidation procedure allowed the selective epoxidation of the backbone double bonds without opening the epoxide rings. Only one approach, using a molybdenum catalyst, has shown both high selectivity and complete conversion.[5] With this catalyst the backbone double bonds were completely epoxidised within 3 h at room temperature and there was no further change in the next 70 h. No epoxidation of the 1,2-vinyl groups was observed.

The conditions of the reaction were varied in the hope that the selective epoxidation of all the backbone double bonds would be achieved. It has been reported that for monomeric systems the dropwise addition of the hydrogen peroxide over the course of the reaction gives better yields of epoxides than the addition of the oxidant in one portion at the beginning of the reaction.[6] We found that the percentage of epoxidised double bonds was reduced from 29 to 18% using this procedure. Changing the solvent from $CH_2Cl_2$ to toluene, while using the same dropwise addition procedure, increased the percentage of epoxidation from 18 to 30%. In contrast, using hexane gave only 2% epoxidation. The poor yield of epoxide obtained with hexane as solvent was surprising as hexane had been reported to be amongst the best solvents for the epoxidation of monomeric systems with this enzyme.[6] It is known that the enzyme is deactivated during the course of the reaction.[6] It was anticipated that increasing the amount of enzyme would increase the reaction rate, and more double bonds would be epoxidised in the time taken for the enzyme to become inactive. In fact, doubling the amount of enzyme had no effect and the yield of epoxide was virtually unchanged.

It has been established that the role of the enzyme in this system is to catalyse the synthesis of peracid, the actual species which attacks the double bond.[6] The enzyme plays no part in the actual epoxidation step. The generation of peracid *in situ* removes the need for handling these potentially hazardous compounds. Medium chain alkanoic acids ($C_8$ to $C_{16}$) were used with this enzyme in previous epoxidation reactions of monomeric systems.[6] With polymeric systems we found that very stable emulsions were formed, making the work up procedure extremely difficult. The use of acetic acid, instead of medium chain alkanoic acids, allowed the reaction to proceed efficiently and greatly simplified the work up procedure. Confirmation that the enzyme plays no part in the epoxidation of alkene by peracetic acid was obtained by epoxidising the polymer in $CH_2Cl_2$ with a 32% solution of peracetic acid in acetic acid with and without enzyme present. In both cases, over 96 h polybutadiene was completely epoxidised and the majority of the epoxide rings opened and esterified [$\nu_{max}$ (thin film) 1736 $cm^{-1}$]. There was no evidence of residual acid being retained by the polymer. Interestingly, the epoxide groups of polyepoxide polymers derived from polybutadiene have been reported to be relatively inert to ring opening reactions with carboxylic acids, requiring forcing conditions.[7]

**Table 1** Enzymatic epoxidation of polybutadiene

| Run | *t*/h | Solvent | Hydrogen peroxide addition[a] | Enzyme/ wt% | Yield of epoxide (%)[b] | Yield of 1,4-*cis* and 1,4-*trans* epoxide (%)[b] |
|---|---|---|---|---|---|---|
| 1 | 2 | $CH_2Cl_2$ | A | 10 | ~0 | ~0 |
| 2 | 6 | $CH_2Cl_2$ | A | 10 | 12 | 21 |
| 3 | 24 | $CH_2Cl_2$ | A | 10 | 29 | 52 |
| 4 | 96 | $CH_2Cl_2$ | A | 10 | 31 | 57 |
| 5 | 24 | $CH_2Cl_2$ | B | 10 | 18 | 33 |
| 6 | 24 | Hexane | B | 10 | 2 | 4 |
| 7 | 24 | Toluene | B | 10 | 30 | 55 |
| 8 | 24 | $CH_2Cl_2$ | B | 20 | 21 | 39 |

[a] A: Oxidant added in one portion at the start of the reaction. B: Oxidant added dropwise over the course of the reaction. [b] Determined *via* $^1$H NMR spectroscopy.

Further investigation of this intriguing approach to polymer modification and its potential for modifying polymers for speciality materials applications, such as biomaterials, and polymer degradation are currently underway.

We thank the EPSRC for a studentship (to N. O.) and Novo Nordisk for the gift of Novozym 435.

## Footnotes and References

† E-mail: stpourcb@aston.ac.uk

‡ A typical procedure is as follows: Polybutadiene (5.0 g, 92 mmol of double bonds) was dissolved in $CH_2Cl_2$ (100 $cm^3$). AcOH (0.23 $cm^3$, 9 mmol), a 27.5 wt% aq. solution of $H_2O_2$ (17.0 $cm^3$, 0.14 mol) and Novozym 435 (0.5 g) were added and the mixture stirred for 24 h in the dark. The mixture was then filtered, extracted with saturated aq. $NaHCO_3$ and sodium metabisulfite, and dried ($MgSO_4$). The solvent was removed and the polymer dried in a vacuum oven at 55 °C and 1 mmHg.

1 A. W. P. Jarvie, B. K. Samra and A. J. Wiggett, *J. Chem. Res.* (*S*), 1996, 129.
2 D. Zuchowska, *Polymer*, 1980, **21**, 514.
3 R. V. Gemmer and M. A. Golub, *J. Polym. Sci.*, 1978, **16**, 2985.
4 M. Aguiar, S. Cabral de Menzezes and L. Akcelrud, *Macromol. Chem. Phys.*, 1994, **195**, 3937.
5 M. Gahagan, A. Iraqui, D. C. Cupertino, R. K. Mackie and D. J. Cole-Hamilton, *J. Chem. Soc., Chem. Commun.*, 1989, 1689.
6 F. Björkling, S. E. Godtfredsen and O. Kirk, *J. Chem. Soc., Chem. Commun.*, 1990, 1301.
7 A. Iraqui and D. J. Cole-Hamilton, *J. Mater. Chem.*, 1992, **2**, 183.

*Received in Liverpool, UK, 3rd October 1997; 7/07168J*