Epoxidaion of Unsaturated Poly(3-hydroxyalkanoate)s with *m*-Chloroperbenzoic Acid

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INTRODUCTION

The production of unsaturated poly(3-hydroxyalkanoate)s, PHAs, by *Pseudomonas oleovorans* has been studied extensively in this laboratory[1-3], and recently a procedure has been developed for the quantitative conversion of the unsaturated groups to epoxide groups[4]. The PHA used for the epoxidation reaction was poly(3-hydroxyoctanoate-*co*-3-hydroxyundec-10-enoate), PHOU, which contained controlled amounts of olefinic side chains, and these could be completly epoxidized with *m*-chloroperbenzoic acid (MCPBA) under mild reaction condition without molecular weight loss.

The epoxidation of unsaturated polymers is an important reaction because epoxide groups can be used as reactive intermediates for further reactions such as crosslinking, the attachment of bioactive substance, and the introduction of ionizable groups. Epoxidation reactions have been applied to natural rubber and other unsaturated elastomers, and many types of peracids, such as performic acid, peracetic acid and *m*-chloroperbenzoic acid (MCPBA), have been used for these reactions

and for the epoxidation of low molecular weight unsaturated compounds. For polymers it is particularly important that the reaction occur in a homogeneous phase without side reactions, especially chain scission and crosslinking.

In the present study, PHOUs with controlled amounts of unsaturated units were produced from various mixtures of 10-undecenoic acid and sodium octanoate, and the double bonds in the pendant substituent groups were converted into epoxide groups (Figure 1). The rate of epoxidation was followed by the use of NMR spectroscopy, and changes in the physical properties, especially the glass transition temperature (T_g), of the partially epoxidized PHOU samples were investigated.

EXPERIMENTAL

Chloroform and MCPBA for the epoxidation were purified as described in the previous report[5]. Purity of MCPBA checked by iodometric titration was >98%. Other chemicals were used as received without further purification. PHOU sample was produced by *P. oleovorans* as previously described[5].

To a 20mL vial containing 0.5g PHOU dissolved in 10mL purified chloroform was added 1.3eq parts(based on olefin groups in PHOU) of purified MCPBA with constant gentle stirring at 20°C. After completion of the reaction, the solution was slowly poured into 100mL cool methanol. The precepitates formed was washed with cool methanol twice and then dried in vacuo at 20°C. For the kinetic studies of the epoxidation, aliquots of the reaction solution were removed periodically from tightly stopped bottles, and epoxidation yields(%) were determined with ^{1}H-NMR using the ratio of the resonance peak area of oxirane(2.8 ppm) and olefinic(4.9 ppm) hydrogens.

RESULTS AND DISCUSSION

The epoxidation yield as a function of reaction time obtained for the entire series of PHOUs is shown in Figure 2. An epoxidation yield of 100% was attained after reaction times varing from 12 hours to 30 hours depending on the initial PHOU composition. The rate constant, k, obtained was in the range of $1.1 \sim 1.3 \times 10^{-3} Lmole^{-1} sec^{-1}$. The constancy of rate constants k within experimental error, irrespective of the PHOU unsaturated unit content, indicates that the epoxidation of PHOUs proceeded without any significant amount of side reactions.

The glass transition temperatures, T_g, increased with increasing epoxidation as shown in Figure 3. The increase in T_g as a results of epoxidation may be caused by the presence of the polar epoxide group, which can form intramolecular interactions. Figure 4 shows the plot of the T_g increment(°C) as function of the epoxide content for each of the PHOU samples. A single linear plot of the T_g increment was obtained for all of the four different PHOU samples even though the samples varied greatly in compositions.

REFERENCES

1. K. Frizche, R. W. Lenz, and R. C. Fuller, *Int. J. Biol. Macromol.*, **12**, 85(1990)
2. Y. B. Kim, R. W. Lenz, and R. C. Fuller, *J. Polym. Sci.: Part A: Polym. Chem.*, **33**, 1367(1995)
3. H. W. Ulmer, R. A. Gross, M. Posada, P. Weisbach, R. C. Fuller, and R. W. Lenz, *Macromolecules*, **27**, 1675(1994)
4. M. A. Leboucher-Durand, M. M. Bear, A. Le Gall, V. Langlois, P. Gurin, S. Goodwin, and R. W. Lenz, submitted to *J. Reactive Functional Polymers.*
5. W. H. Park, R. W. Lenz, and S. Goodwin, *Macromolecules*, in press.

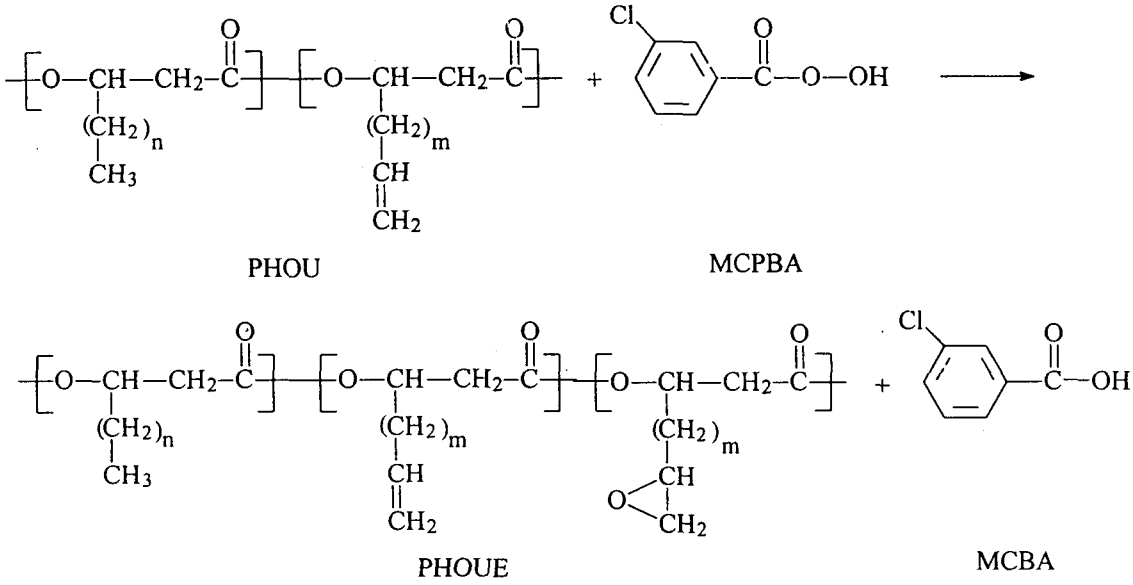

Fig.1. Epoxidation reaction of PHOUs by m-chloroperbenzoic acid

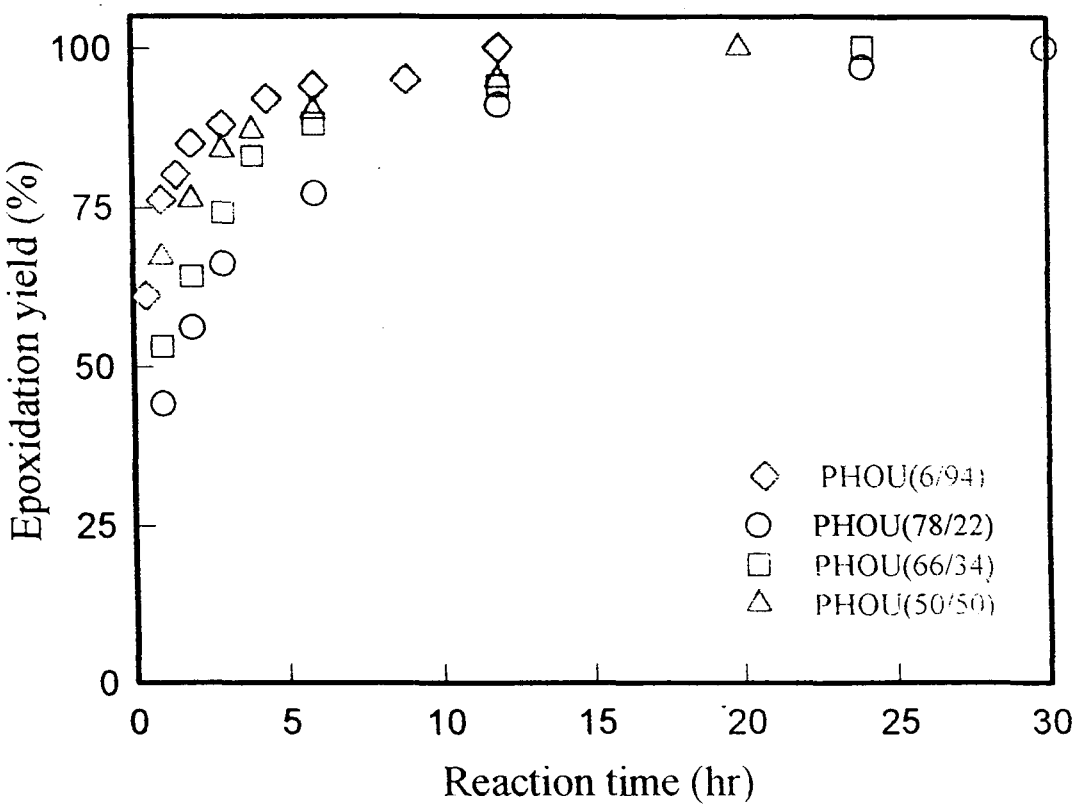

Fig.2 . Epoxidation yield(%) as a function reaction time(t).

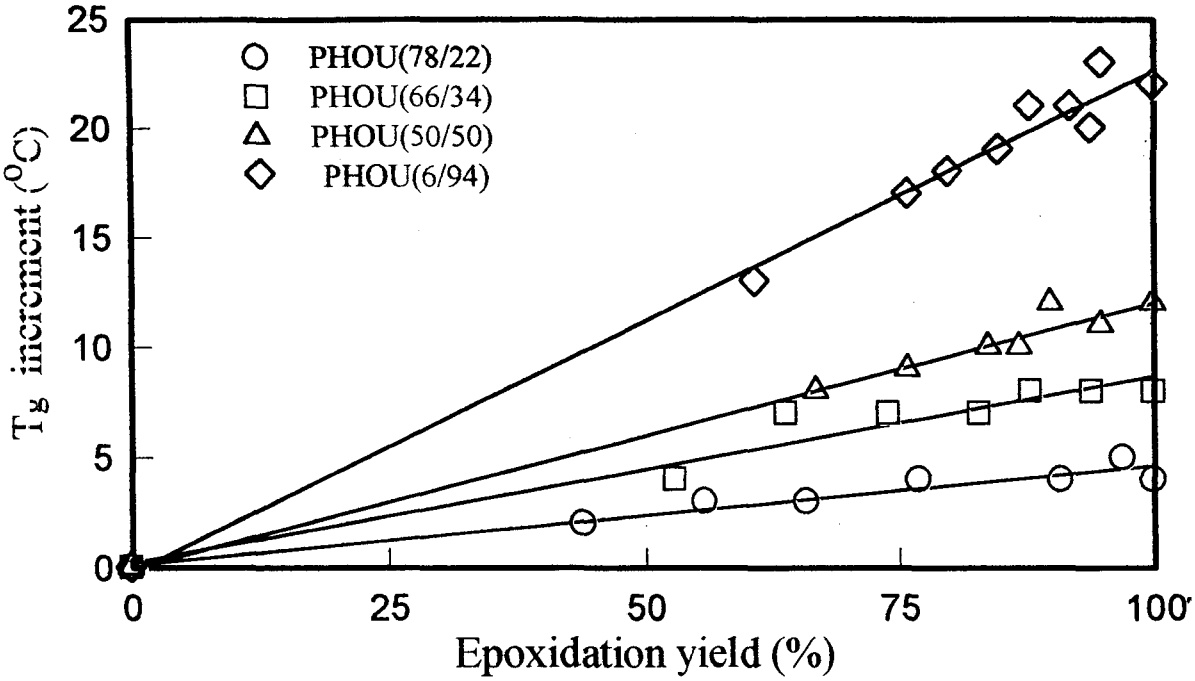

Fig. 3. Incremental changes in Tg for partially epoxidized PHOUs as a function of epoxidation yield(%).

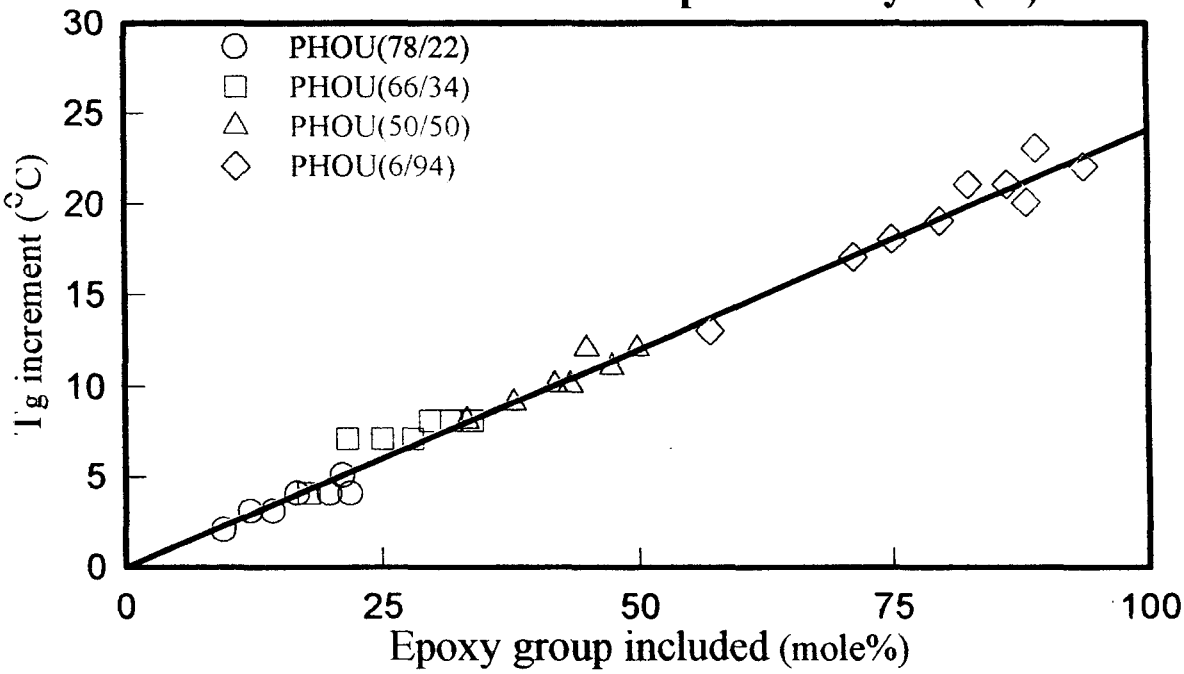

Fig. 4. Incremental changes in T_g for partially epoxidized PHOUs as a function of the absolute epoxide group included(mole%)