Epoxidation of Bacterial Polyesters with Unsaturated Side Chains. I. Production and Epoxidation of Polyesters from 10-Undecenoic Acid

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ABSTRACT: Poly(3-hydroxyoctanoate-*co*-3-hydroxy-10-undecenoate)s (PHOUs) with controlled amounts of unsaturated side chains were produced by *Pseudomonas oleovorans* from various mixtures of 10-undecenoic acid and octanoic acid. Epoxidation of the unsaturated side chains in PHOU, by reacting the polymer with *m*-chloroperbenzoic acid (MCPBA) in homogeneous solution, was readily carried out. After complete epoxidation, changes in the molecular weights and thermal transitions of the PHOUs were investigated by gel permeation chromatography (GPC) and differential scanning calorimetry (DSC), respectively, and the thermal stabilities of the initial and epoxidized polymers were measured by thermogravimetric analysis (TGA). The acidic conditions used for the epoxidation reaction did not result in a significant decrease in molecular weight of the PHOUs. The epoxidized PHOUs were completely soluble, indicating that cross-linking did not occur, but transformation of the vinyl groups in PHOU into epoxide groups caused a decrease in the melting temperature and the enthalpy of melting. In contrast, the glass transition temperatures increased in a linear manner with epoxide group content in the product polymer, and the thermal degradation behavior of the epoxidized polymer was considerably different from that of the initial polymer.

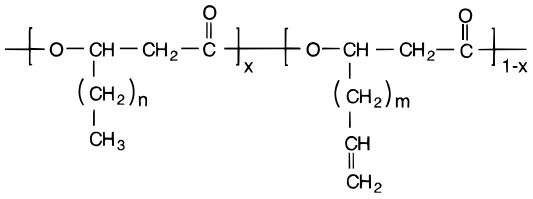
Introduction

A wide variety of microorganisms produce poly(3-hydroxyalkanoates) (PHAs) as intracellular energy and carbon storage materials. Of the microorganisms capable of producing PHAs, *Alcaligenes eutrophus* and *Pseudomonas oleovorans* have been investigated most extensively.[1−3,5,6,8] *A. eutropus* produces PHAs with short chain alkyl substituents whether grown on short or long chain carbon sources. *P. oleovorans*, on the other hand, can only produce PHAs when grown on carbon sources with at least six carbons, and the PHAs so produced contain relatively long pendant alkyl groups (side chains). The differences in the side chain lengths of these two types of PHAs result in different material behavior, from thermoplastic to elastomeric behavior.

In addition to producing PHAs with long alkyl groups, *P. oleovorans* can also utilize many functionalized organic substrates to produce PHAs with functional groups in the side chain. In this manner the production of PHAs with various functional groups such as olefin,[1−4] halogen (chloride,[5] fluoride,[6,7] and bromide[8]), and cyano[8] groups has been achieved. The presence of functional groups in the PHAs provides sites for chemical modification and can affect the physical properties of polymers such as their hydrophobicity and solubility.

A particularly useful type of functional PHA is one containing unsaturated groups in the side chain, and these polymers can be produced in a high yield with broad compositional ranges. PHAs containing repeating units with terminal unsaturated substituents (vinyl groups) were first reported for the growth of *P. oleovorans* with 1-alkenes.[1] The PHAs so obtained also contained significant amounts (40−60 mol %) of saturated repeating units, which were presumably produced by hydrogenation within the cell of the 1-alkene, the sole carbon source. PHAs with unsaturated units have also been produced from 3-hydroxyalkenoic acids,[2] and the fraction of the unsaturated repeating units in these PHAs was higher than those in the PHAs produced from alkenes, but significant amounts (20−35 mol %) of saturated repeating units were still found in the polymers. In contrast, 10-undecenoic acid can be used as a substate to produce PHAs with only unsaturated repeating units in good yields.[3]

Poly(3-hydroxyoctanoate-*co*-3-hydroxy-10-undecenoate), PHOU, which is produced when *P. oleovorans* is fed a mixture of sodium octanoate and 10-undecenoic acid,[3,9,10] has unsaturated units containing a reactive vinyl group located at the terminus of the pendant chain as shown in the following structure:[3]



in which $n = 2$ or 4, $m = 4$ or 6, and $x = 0−1$.

PHOUs containing unsaturated units have potential for a wide range of applications including biodegradable elastomers, hydrogels, and adhesives. To achieve specific physical properties, the unsaturated units can be converted into other functional groups, such as epoxy, carboxylic acid, and hydroxyl groups, and all of these PHAs can be cross-linked to improve their mechanical properties, especially their elastomeric properties.[9,10]

As a route to chemical modification, epoxidation of PHOUs is of great interest because the epoxide function

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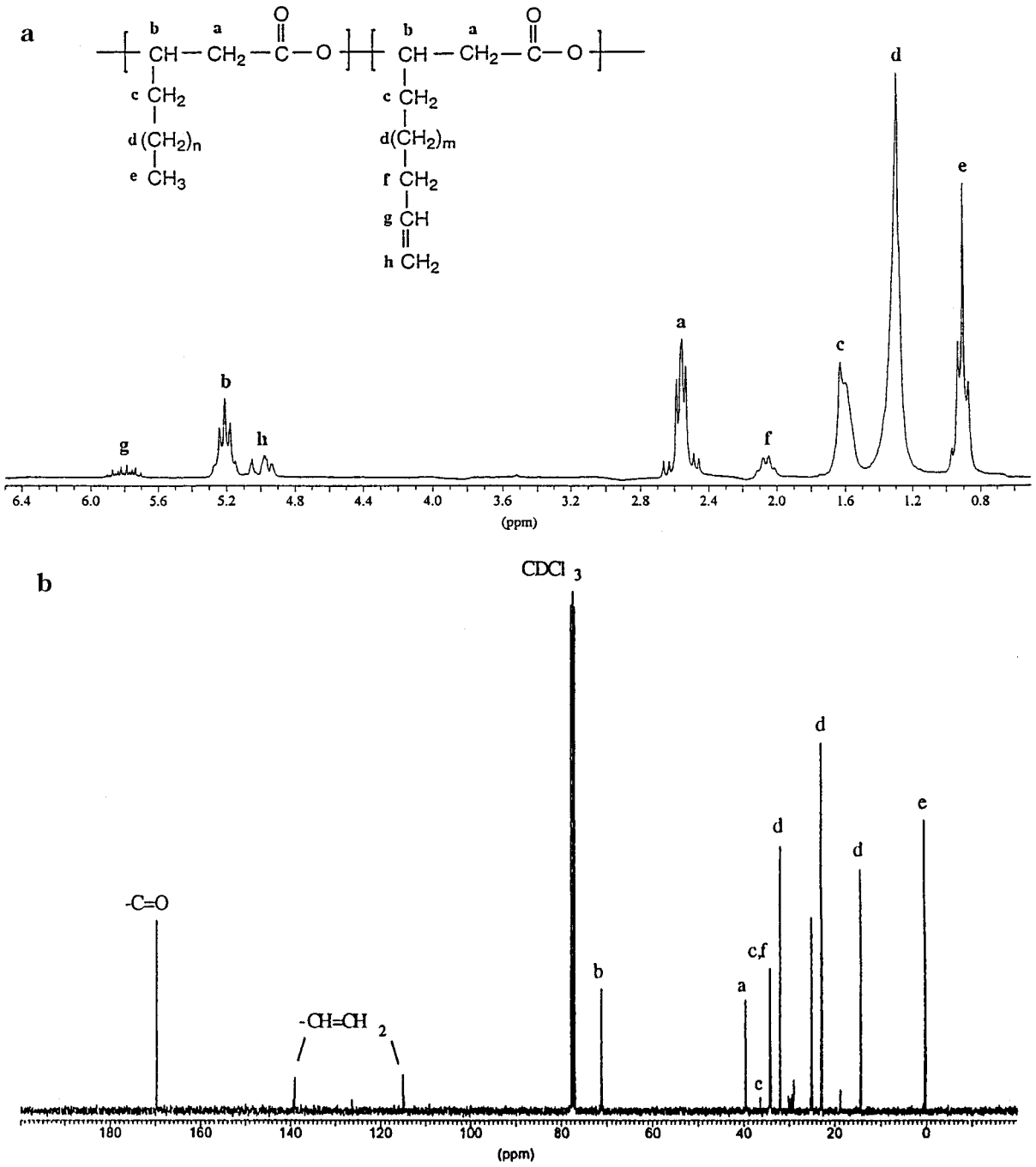


Figure 1. (a) ^{1}H and (b) ^{13}C NMR spectra of PHOU (78/22).

is highly reactive under mild conditions with a variety of reagents. The epoxide groups can participate in a wide variety of reactions without polymer degradation, especially controlled cross-linking reactions and reactions with many types of reagents to prepare derivatives with particular properties such as ionic or hydrogen-bonding groups. In the present study, PHOUs with controlled amounts of units having unsaturated side chains were produced from various mixtures of 10-undecenoic acid and sodium octanoate. The pendant unsaturated groups were completely transformed into epoxide groups using *m*-chloroperbenzoic acid (MCPBA), and the changes in the physical properties after epoxidation were evaluated for a series of copolymers, poly(3-hydroxyoctanoate-*co*-3-hydroxy-10-epoxyundecenoate)s, (PHOEs).

Experimental Section

Reagents. Chloroform for the epoxidation reaction was washed with water to remove the ethanol preservative, dried in magnesium sulfate and stored in the dark. *m*-Chloroperbenzoic acid (MCPBA) was purified by washing the powder in a pH 7.4 phosphate buffer solution, filtering, and drying under vacuum for 2 days at 20 °C. All other chemicals were used as received without further purification.

PHOU Biosynthesis. PHOU production was carried out as described in our previous reports.[3,11] A New Brunswick microfermenter using a 12 L glass fermentation tank was used. The total concentration of the carbon sources in the growth medium was 20 mM. Cells were harvested when growth reached the stationary growth phase, generally in 24−48 h depending on the substrate composition. Sodium octanoate and undecenoic acid with mole ratios of 100/0, 95/5, 90/10, 85/15, 75/25, 50/50, and 0/100 were used. The PHOUs were isolated from lyophilized cells by extraction with hot chloro-

form in a Soxhlet extractor. The crude polymer was dissolved in chloroform, reprecipitated by addition of the solution to cooled methanol with rapid stirring, filtered, dried and stored in a sealed sample bottle at 4 °C.

Epoxidation of PHOU. A 1.3 equiv sample (based on olefin groups in PHOU) of purified MCPBA was added to a 20 mL vial containing 0.5 g of PHOU dissolved in 10 mL of purified chloroform. Reactions were carried out with constant, gentle stirring at 20 °C for specified times, and the solution was slowly poured into 100 mL of cooled methanol. The precipitated polymer was washed with methanol twice, dried in vacuo at 20 °C, and stored in a sealed sample bottle at 4 °C. Epoxidation yields (%) were determined by ^{1}H NMR using the ratio of the resonance peak area of the oxirane (2.9 ppm) and olefinic (4.9 ppm) hydrogens.

Polymer Characterization. All molecular weights were measured by gel permeation chromatography in THF using a solvent delivery system with a WYATT/OPTILAB 903 differential refractometer detector and three Polymer Labs PL 5 μm gel mixed columns. A 1 mL/min THF flow rate was used. Molecular weights reported are based on polystyrene standards.

^{1}H NMR and ^{13}C NMR spectra were obtained with either a Bruker AC-200 or a Bruker DPX-300 NMR spectrometer. Chloroform-*d* solutions of the polymer of 10 mg/mL were used for ^{1}H NMR, and the spectra were run using an angle of 90°, a pulse width of 4.3 μs, and a delay time of 5 s, with the peaks referenced to tetramethylsilane. The polymer concentrations for ^{13}C NMR were 30 mg/mL, and the spectra were run using a pulse angle of 90°, a pulse width of 6.3μs, and a delay time of 5s. The peaks were referenced to chloroform.

Differential scanning calorimetry, DSC, was conducted using a TA Instruments 2910. The temperature scale of the instrument was calibrated with mercury and indium. Samples were tested from −80 to 100 °C in a nitrogen atmosphere at a heating rate of 10 °C/min. The glass transition temperature (T_g) reported was taken at the inflection point, and the melting temperature (T_m) reported was the peak temperature. DSC thermograms used were for the first heating cycle because the first and second cycles gave identical results. Thermogravimetric analysis, TGA, was conducted using a TA Instruments 2950. TGA was conducted in a nitrogen atmosphere from 50 to 600 °C at a heating rate of 20 °C/min, and both maximum and onset degradation temperatures are reported.

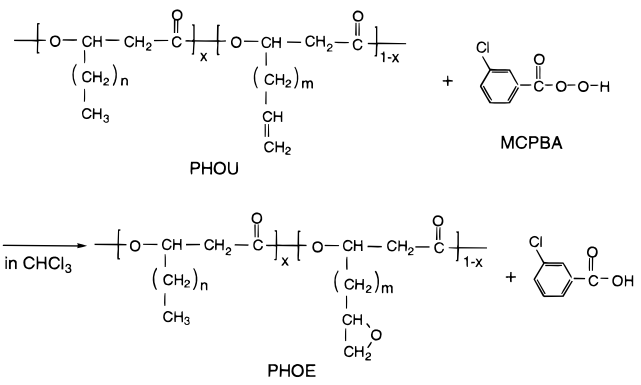
Results and Discussion

Production of PHOU. The bacterial production of the PHOU samples with controlled olefinic contents was carried out on a series of mixtures of the two carbon sources: sodium octanoate and undecenoic acid. The PHOU yields from the mixed carbon sources were in the range 21−25% of the cell dry weight, and when 10-undecenoic acid was used as a sole carbon source, the amount of polymer isolated from the cells was in the range 17−20%. PHOU samples with eight different compositions were produced in this manner, as follows: 95/5, 91/9, 86/14, 78/22, 73/27, 66/34, 50/50, and 6/94 for the molar percentage of saturated O units and unsaturated U units, respectively. However, in all cases, the initial polymers and consequently the epoxidized polymers, too, contained small amounts of units with two carbon atoms fewer; that is, they contained hexanoate ($n = 2$) and nonenoate ($m = 4$) units. Figure 1a shows a typical ^{1}H NMR spectrum of a PHOU copolymer with an U units content of 22 mol %, as determined from the ratio of the integration of peak h to peak e. The ^{13}C NMR spectrum of this polymer is shown in Figure 1b. In this spectrum the carbon signals for the vinyl groups of the unsaturated units in PHOU occurred at 117.5 ppm for CH and 139.5 ppm for CH_2.

The total mole fraction of unsaturated repeating units in the PHOUs was essentially identical to the mole fraction of the alkenoic acid in the substrate mixture, as previously reported.[3] Fermentations were run two to five times for each carbon source mixture, and PHOU samples with precisely controlled amounts of unsaturated repeating units were readily obtained by adjusting the composition of the two carbon substrates, OA and UA.

Table 1 contains data from the characterization of the different olefin-containing PHOUs. The glass transition temperature (T_g) decreased steadily as the unsaturated group content in the copolymer increased, as expected because of the greater length of the pendant groups in the U units compared to the O units. The melting temperature (T_m) and heat of fusion (ΔH_m) also steadily decreased as the amount of U units in the copolymer increased up to approximately 35 mol %, as expected for such a copolymer. Above 50 mol %, a melting peak could no longer be seen in the thermogram. In contrast to these results, neither the thermal decomposition temperature, as measured by thermogravimetric analysis, nor the molecular weight was affected significantly by the inclusion of olefinic repeating units in the PHAs.

Epoxidation of PHOU. In a previous study *m*-chloroperbenzoic acid (MCPBA) was found to be a very effective reagent for epoxidation of the unsaturated units in PHOU copolymers.[12] Although a variety of other peracids have been used to perform the epoxidation reaction on unsaturated polymers,[13−15] MCPBA was used in the present study because of its availability, reactivity and stability. The epoxidation reaction of PHOUs by MCPBA is shown in the following equation:



For the epoxidation of unsaturated, high molecular weight polymers, it is essential to establish the reaction conditions so that there are no side reactions which can cause either cross-linking or degradation. To obtain the completely epoxidized products (an epoxidation yield of 100%) from PHOU, the polymer samples were reacted in purified chloroform using 1.3 equiv of MCPBA, based on the content of unsaturated units in the polymers, at 20 °C for various times. Table 2 contains the epoxidation results for a series of PHOU samples with different unsaturated unit contents. With the conditions used, the desired 100% epoxidation yields were achieved within 12 to 168 h, depending on the amount of unsaturated groups in the PHOU, as determined by ^{1}H- and ^{13}C NMR analysis.

Figure 2a shows the 300 MHz ^{1}H NMR spectrum of the epoxidized polymer, PHOE (78/22), which was obtained from PHOU (78/22) after the epoxidation reaction at 20 °C for 30 h. Besides the complete disappearance of the two peaks at 4.88 and 5.70 ppm, which are in the spectrum of PHOU (Figure 1) and are

Table 1. Characterization of PHOU Samples

PHAs[a]	unsaturated group content[b] (mol %)	M_n ($\times 10^{-3}$)	M_w (10^{-3})	M_w/M_n	T_g (°C)	T_m (°C)	ΔH_m (J/g)	T_{max}[c] (°C)
PHO		83	207	2.5	−33	62	24	291
PHOU (95/5)	5	145	326	2.2	−35	59	20	303
PHOU (91/9)	9	108	238	2.2	−36	58	17	
PHOU (86/14)	14	90	223	2.5	−35	58	17	
PHOU (78/22)	22	109	248	2.3	−38	56	16	302
PHOU (66/34)	34	117	251	2.1	−40	54	11	303
PHOU (50/50)	50	126	272	2.2	−42		0	301
PHOU (6/94)	94	102	246	2.4	−50		0	306

[a] Numbers in brackets are the molar ratios of O/U units. [b] Determined from ^{1}H NMR. [c] Maximum decomposition temperature on TGA thermogram under N_2.

Table 2. Epoxidation Results for the Reaction of PHOU Samples with *m*-chloroperbenzoic Acid (MCPBA)

PHAs[a]	MCPBA (equiv)	reaction time for 100% yield (h)	M_n ($\times 10^{-3}$)	M_w ($\times 10^{-3}$)	M_w/M_n	T_g (°C)	T_m (°C)	ΔH_m (J/g)
PHOE (95/5)	1.3	168	184	312	1.7	−34	54	13
PHOE (91/9)	1.3	96	97	240	2.5	−33	51	8
PHOE (86/14)	1.3	72	112	248	2.2	−32	47	5
PHOE (78/22)	1.3	30	142	305	2.1	−34	45	4
PHOE (66/34)	1.3	24	101	246	2.4	−32	41	2
PHOE (50/50)	1.3	20	142	192	1.4	−30		
PHOE (6/94)	1.3	12	93[b]	234[b]	2.5[b]	−28		

[a] Numbers in brackets are O/U molar ratios of initial PHOU; see Table 1. [b] For PHOE (6/94) with epoxidation yield of only 80%.

assigned to the unsaturated groups, it can be seen that three new signals at 2.89, 2.74, and 2.46 ppm are present, and these are assigned to the oxirane (epoxy) groups. Similarly, in the ^{13}C NMR spectrum in Figure 2b, two new peaks assigned to oxirane carbon signals are seen at 47 and 52 ppm, and the carbon signals at 115 and 139 ppm for the unsaturated groups in PHOU are absent.

Possible changes in molecular weight after epoxidation were investigated with the results listed in Table 2. A comparison of the data in Table 2 and Table 1 confirms that the molecular weights of the completely epoxidized polymers were close to those of the corresponding PHOU samples. It can be concluded, therefore, that the acidic conditions used for the epoxidation reactions did not cause a substantial reduction in the molecular weight of the PHOEs produced. Furthermore, the complete solubilities of the PHOEs in organic solvents, including chloroform, THF, methylene chloride, and acetone, as well as the essentially constant molecular weights of the samples, showed that crosslinking reactions did not occur to any measurable extent for all of the samples except PHOE (6/94). In the case of PHOE (6/94), the solution of this polymer in chloroform appeared clear at above 90% conversion of the epoxidation reactions, but the solution could not be filtered for GPC measurement because of the presence of microgel particles, although no characteristic signal, that could be attributed to a side reaction product, was detected in the NMR spectrum.

Thermal Transitions of PHOE. DSC analyses were made approximately 2 weeks after epoxidation to allow sufficient time for the polymers to crystallize. As shown in Tables 1 and 2, the T_g values of the PHOE samples increased substantially compared to those of the corresponding PHOU samples. Similarly, epoxidation was also reported to increase T_g for natural rubber.[13,15] The increase in T_g for both types of polymers may be attributed to the polar epoxide groups, which can form intramolecular interactions, but the incremental increase in T_g was lower for PHOE than that reported for epoxidized natural rubber. In PHOE the epoxide groups are placed at the terminal position of the pendant side chains, and this type of modification would not affect backbone mobility as much as in natural rubber in which the epoxide groups are placed on the backbone of the polymer chain.

The effect of epoxidation on T_g was analyzed with the Fox equation[16]

$$1/T_g = w_1/T_{g1} + w_2/T_{g2}$$

in which w_1 and w_2 are the weight fractions of O and either U or E units in the PHOU and PHOE samples, T_g is the glass transition temperature of either PHOU or PHOE, T_{g1} is for the homopolymer PHO, and T_{g2} is for either the PHU or PHE homopolymer. It should be noted, however, that PHO and PHU are not true homopolymers because their repeating units contain approximately 8% of C_6 units and only 92% of C_8 units in the structure shown above. As seen in Figure 3, the variation of T_g for both the PHOU and PHOE copolymers followed this equation very closely. The T_g values for PHU and PHE, as extrapolated from the plot in Figure 3, are −50 and −28 °C, respectively, and the former value is in agreement with the value reported by Kim et al.[3]

As shown by the data in Tables 1 and 2 and in Figure 4, the melting temperatures (T_m) and heats of fusion (ΔH_m) of the PHOE copolymers decreased to a much greater extent than for the PHOU copolymers with increased degree of substitution. This result is unexpected because neither the E units nor the U units should cocrystallize with the O units, so both should have identical effects on reducing the ability of the O units in PHOU or PHOE to crystallize and in lowering T_m. Indeed, when the T_m data were analyzed by the Flory equation, which relates the melting point of copolymers to their composition (assuming that the epoxidation reactions occurred to yield essentially random, derived copolymers[18]) and to the heat of fusion of the crystalline homopolymer, much different results were obtained for the value of ΔH_m of the O segments for the two series of copolymers.

The data for the PHOU copolymers gave a meaninglessly high value of ΔH_m, suggesting that the U units

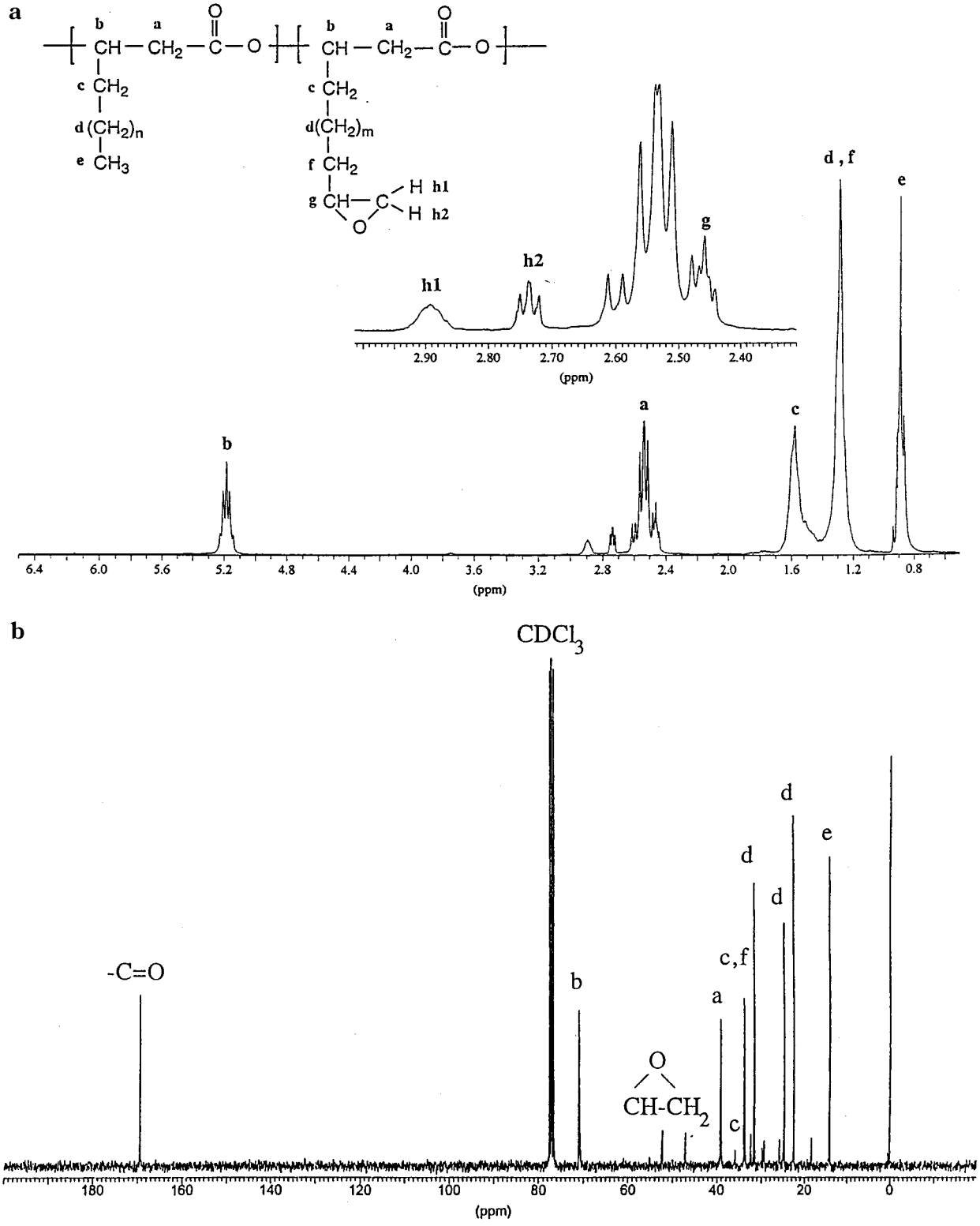


Figure 2. (a) ^{1}H and (b) ^{13}C NMR spectra of epoxidized PHOU (78/22) and PHOE (78/22), with an epoxidation yield of 100%.

may cocrystallize to some extent with the principal O units. In contrast, the value of ΔH_m, which as obtained from the T_m data of the PHOE series, was reasonable: 9.2 kJ/mol. This value is close to that reported for a low molecular weight PHO homopolymer, 5.4 kJ/mol, which was prepared by the chemical polymerization of a lactone monomer.[19] The type of deviation from the Flory equation observed for the PHOU copolymers was also reported by Doi and co-workers for 3-hydroxybutyrate−4-hydroxybutyrate copolymers.[18]

Thermal Stability. The thermal degradation of the PHOE copolymers was also different from that of the PHOU copolymers. Typical thermograms obtained by dynamic thermogravimetric analysis, TGA, are shown in parts a and b of Figure 5 for the PHOU and PHOE copolymers, respectively, containing 6 mol % of O units. The TGA thermal degradation of poly(3-hydroxybutyrate), PHB, proceeds by a one-step process, which is known to involve a random, chain scission reaction of the ester groups to form olefinic and carboxylic acid

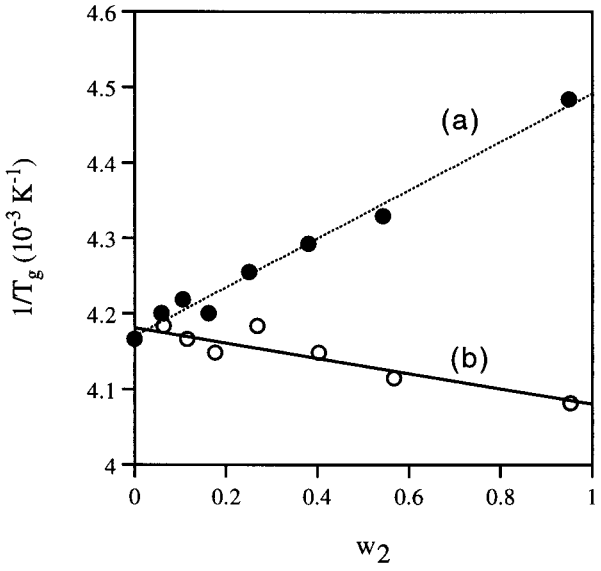


Figure 3. Dependence of T_g on the composition of (a) PHOU and (b) PHOE copolymers; w_2 is the weight fraction of saturated O units.

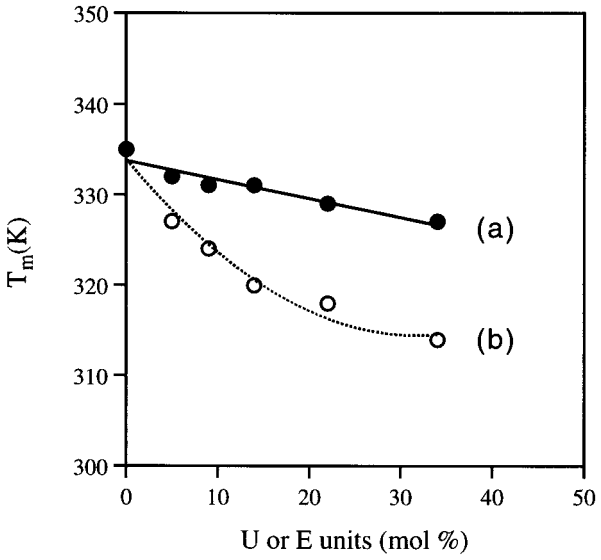


Figure 4. Dependence of T_m on the composition of (a) PHOU and (b) PHOE copolymers.

groups.[19,20] Similarly, the thermal decomposition of PHOU (6/94) occurred in a single step above 270 °C in the TGA thermogram shown in Figure 5a. It is likely, therefore, that the thermal degradation of PHOU follows the same type of reaction pathway as that for PHB. In contrast, the thermal decomposition pattern of PHOE (6/94), in which 100% of the U units were epoxidized, followed a considerably different pattern from that of PHOU (6/94), as seen in Figure 5b.

The TGA onset temperature for the thermal decomposition of PHOE (6/94), as measured by the intersection of the baseline with a tangent to the weight loss curve, had a similar value to that of PHOU (6/94) as shown in Figure 5b. However, the degradation pattern for PHOE contained three separate degradation stages with three different rate peaks in the differential thermogravimetric analysis, DTA, thermogram, which is also shown in Figure 5b. The complex decomposition process for PHOE may result from cross-linking reactions of epoxide groups with terminal carboxyl groups in the melt at the elevated temperatures involved in the decomposition. That is, the carboxylic acid groups formed in the decomposition could react with epoxide groups to form new interchain bonds. In addition, the cross-linking reactions of epoxide groups could also occur by reactions with hydroxyl groups, which form when the epoxide groups react with terminal carboxyl groups.

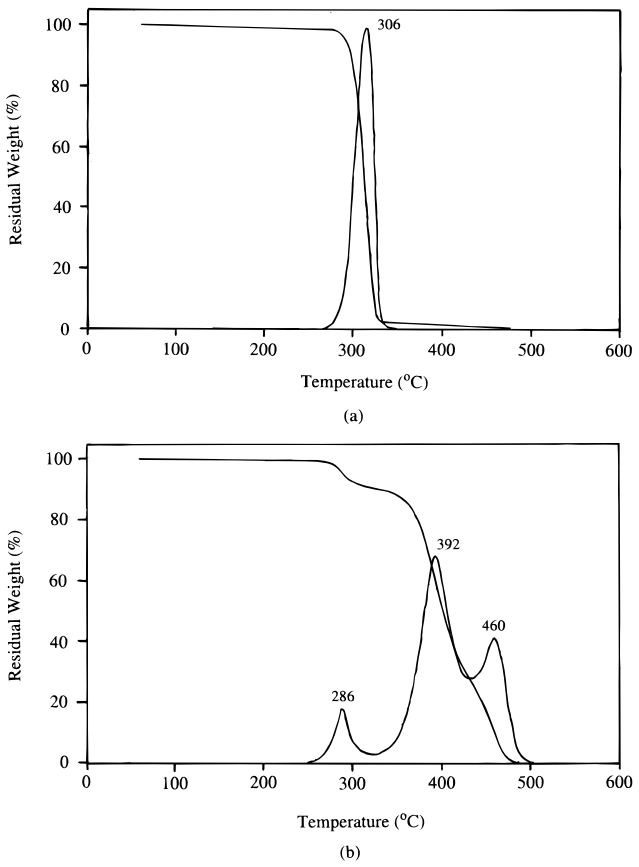


Figure 5. Dynamic TGA and differential TGA thermograms of (a) PHOU (6/94) and (b) PHOE (6/94).

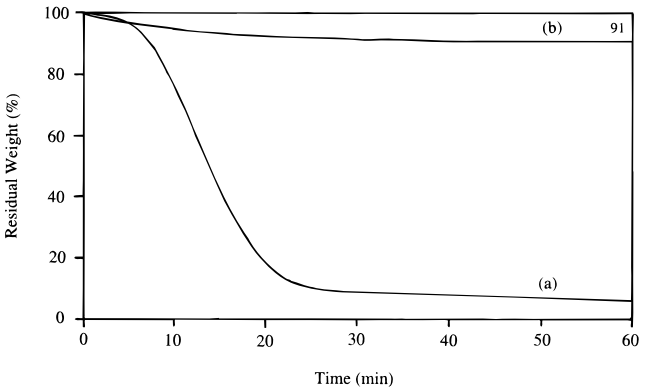


Figure 6. Isothermal TGA thermograms of (a) PHOU(6/94) and (b) PHOE(6/94).

Figure 6 shows isothermal TGA results obtained at 250 °C for both PHOU (6/94) and PHOE (6/94). At that temperature the PHOU sample was almost completely degraded and volatilized within 30 min at 250 °C as shown in Figure 6a, while the residual weight of PHOE remained at approximately 91% after isothermal degradation for 60 min as shown in Figure 6b. The relationship between initial epoxide group content in PHOE and residual weight after isothermal degradation at 250 °C is shown in Figure 7. The residual weight is directly related to the amount of epoxide groups in

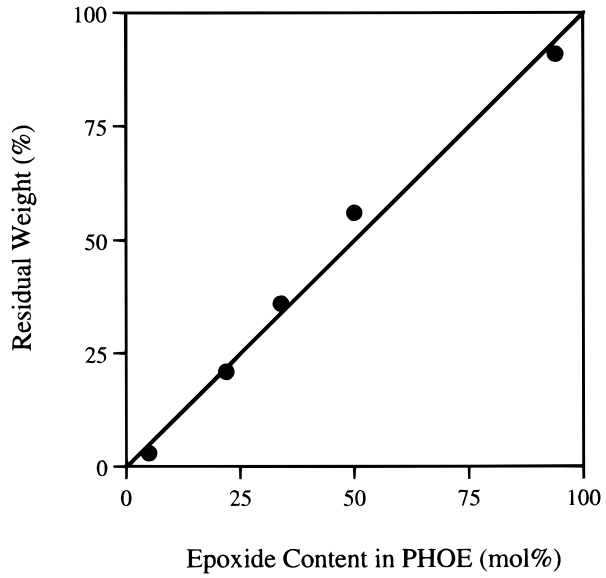


Figure 7. Residual weight as a function of initial epoxide group content (mol %) in PHOE after isothermal degradation at 250 °C for 1 h.

PHOE in a linear manner, indicating that most, if not all, of the epoxide groups may have participated in thermal cross-linking reactions, as described above. The samples of PHOE after the isothermal study at 250 °C were insoluble and were only slightly swellable in chloroform, THF, acetone, methylene chloride.

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