Epoxidation of Polyolefin by Peroxy Acid Generated *in situ*[1)]

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Synopsis. The epoxidation of a new type polyolefin copolymer, poly(ethylene-co-1,9-decadiene) (PED) was carried out with performic acid produced *in situ* from formic acid and 35% hydrogen peroxide. The reaction was performed at room temperature or at 50°C with conversion of vinyl group in the polymer chain and high selectivity to epoxide.

Epoxidation of polymer showed a contradiction in the reaction process, because of the high temperature needed for dissolving polymer and the low temperature needed for the selectivity of epoxidation;[2)] one problem is non-productive destruction of oxidizing agents and decomposition of epoxide[2a)] and the other problem is an impossibility in the separation of polymer products and catalyst, when a catalyst is used in order to allow the reaction at a low temperature.[2b)] In the preceding paper,[3)] we reported that peroxy acid such as *m*-chloroperbenzoic acid was effective for the epoxidation of polyolefin copolymer at room temperature in heterogeneous conditions. The reaction with peroxy acid proceeds without catalyst and this process shows no contamination of impurity. The work-up of the reaction mixture is also easy. Thus, we envisioned *in situ* generation of peroxy acid from carboxylic acid under heterogeneous conditions. This paper presents the epoxidation of poly(ethylene-co-1,9-decadiene) (PED) by an application of *in situ* generation of peroxy acid with commercially available 35% hydrogen peroxide without catalyst.

Results and Discussion

The Reaction Conditions of the Epoxidation. In the presence of various carboxylic acids, PED was epoxidized with 35% hydrogen peroxide. No epoxidation proceeded without carboxylic acid. The results are summarized in Table 1. Formic acid showed high activity even at room temperature. Acetic acid, heptanoic anhydride and phthalic anhydride required relatively a high reaction temperature (50—60°C). The infrared spectra of the products obtained at room temperature, 50 and 60°C were the same as the starting material except the 1260, 847, and 837 cm^{-1} band assigned to epoxy group. On the other hand, the product obtained at 80°C showed O-H stretching band in the region 3400—3470 cm^{-1} and a very weak absorption of epoxy group was observed. The reaction at 70—80°C was not effective for epoxidation, because of non-productive reaction of hydrogen peroxide and/or performic acid and decomposition of oxirane group. The vinyl group in PED was converted directly to oxirane with a peroxy acid generated *in situ*, when the reaction temperature was below 60°C. The conditions for this reaction follow the general method described in the previous report.[3)] The epoxidized PED obtained in this manner was converted to the film in order to determine the content of the epoxy and the vinyl groups by FT-IR spectrum; this method has already been described.[3)]

The Relation Between Formic Acid and Hydrogen Peroxide. The reactivity of the epoxidation of PED depends on the quantity of formic acid and hydrogen peroxide. The results are shown in Table 2. Molar content of formic acid equivalent to or higher than that of hydrogen peroxide gave the better results, when the content of hydrogen peroxide was the same (Table 2).

The Effect of the Reaction Temperature. The reaction rate was faster at 50°C. After that, the yield of epoxide decreased gradually. The acid-promoted decomposition of epoxide occured after 3 d at 50°C and after 5 d at room temperature, for it was preceived from the IR spectrum that the absorption band of hydroxyl group appeared with the disappearance of that of epoxide (Figs. 1 and 2).

The Relation between Reactivity and Solvent. Table 3 shows the relation between the reaction and

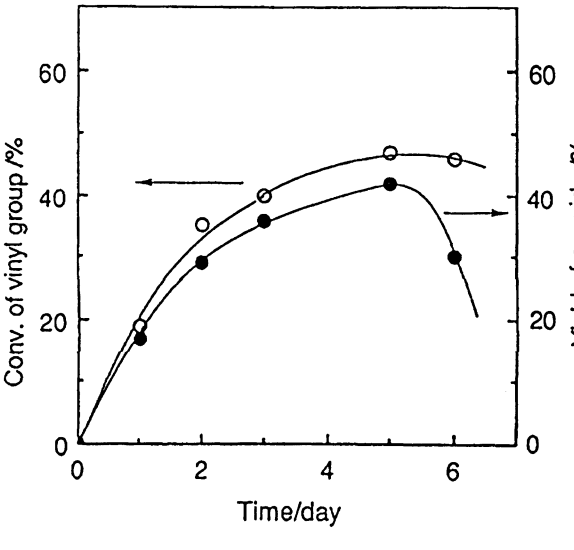

Fig. 1. Epoxidation of PED at R.T.

Table 1. Epoxidation of PED with H_2O_2–Carboxylic Acid System

No	Carboxylic acid / mmol		Temp/°C	Time/d	Conversion[b]/%	Yield of epoxide/%
1	Formic acid	10	R.T.	3	40	36
2	Formic acid	10	50	2	62	54
3	Acetic acid	10	R.T.	3	5	4
4	Acetic acid	10	50	2	67	61
5	Heptanoic anhydride	10	R.T.	3	8	1
6	Heptanoic anhydride	10	50	2	91	29
7	Phthalic anhydride	1	R.T.	3	13	8
8	Phthalic anhydride	1	50	2	52	41

a) Reaction conditions: PED 0.14g, H_2O_2 10 mmol, toluene 5 ml. b) Conversion of vinyl group (reactivity).

Table 2. Epoxidation of PED with H_2O_2–Formic Acid System

No	HCOOH/mmol	H_2O_2/mmol	Temp/°C	Time/d	Conversion[b]/%	Yield of epoxide/%
1	10	10	50	2	62	54
2	10	5x2[c]	50	2	76	71
3	10	5x2[c]	60	2	79	76
4	1	10	50	2	33	24
5	10	10	R.T.	5	47	42
6	20	10	R.T.	5	57	55
7	50	10	R.T.	3	61	53

a) Reaction conditions: PED 0.14g, toluene 5 ml. b) Conversion of vinyl group (reactivity). c) Two 5 mmol portions of 35% H_2O_2 were added at 24 h intervals.

Table 3. Epoxidation of PED in Various Solvents[a]

No	Solvent (5 ml)	Dielectric constant (20°C)	Conversion[b]/%	Yield of epoxide/%
1	Toluene	2.24	62	54
2	Chlorobenzene	5.65	63	51
3	1,2-Dichloroethane	10.45	69	55
4	Hexane	1.89	0	0

a) Reaction conditions: PED 0.14 g, HCOOH 10 mmol, H_2O_2 10 mmol, temp 50°C, time 48 h. b) Conversion of vinyl group (reactivity).

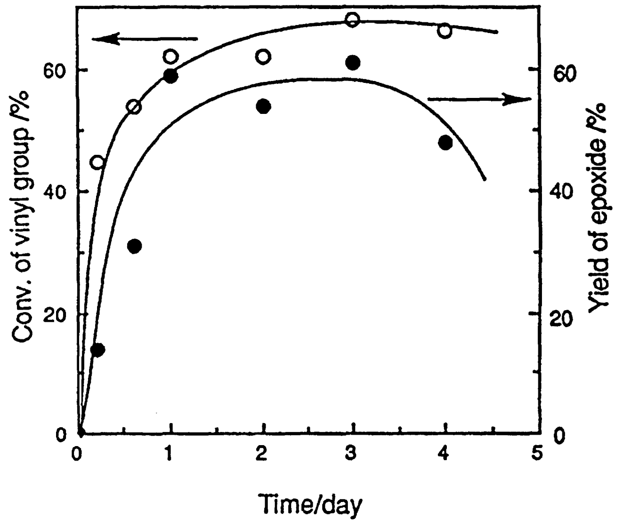

Fig. 2. Epoxidation of PED at 50°C.

solvent for the epoxidation of PED. Hexane did not dissolve PED and the reaction did not occur at all. On the other hand, the epoxidation of PED was observed in 1,2-dichloroethane which did not dissolve PED. Toluene and chlorobenzene, which dissolve slightly and swell PED, could promote the epoxidation in satisfactory yields. Generally speaking, as for the solvent effect of epoxidation with peroxy acid, Asahara and coworkers[4] reported that the stronger the intermolecular hydrogen bond became, the more active the peroxy acid was for the epoxidation. Hanzlik[5] said that the low basicity and high polarity of the solvent were effective for epoxidation. Our case, as shown in Table 3, did not agree with the report described by them. The affinities of the solvents were effective for the epoxidation of PED. This difference comes from the complexity of macromolecular chains.

The Other Characteristic of the Reaction System. The dependence on the molecular weight of PED has also investigated for the epoxidation. As for the number average molecular weight of PED (Mn: 4700, 9300, and 33000), yield of epoxide did not show significant difference. This system was applicable to a macroscale experiments: Two hundred fifty times of the substrate (PED) could be treated in a similar manner to that mentioned above.[3)]

Experimental

Materials. Hydrogen peroxide (35% aqueous solution) and formic acid (90 or 99% aqueous solution) were obtained from Wako Pure Chemical Industries. Poly(ethylene-co-1,9-decadiene) (PED) was synthesized by the method already reported.[3)] Other chemicals were of reagent-grade and were used as received.

Analytical Procedure for PED. The contents of vinyl group in PED were analyzed using FT-IR already reported.[3)]

General Procedure for the Epoxidation of PED. At an arbitrary temperature, 35% hydrogen peroxide (10 mmol) was added dropwise to a solution of carboxylic acid (10 mmol) and PED (0.14 g vinyl group content 0.09 mmol equiv) in toluene (5 ml) with stirring. After stirring for a given time, the reaction mixture was washed in a separatory funnel twice with saturated sodium carbonate solution (25 ml), followed by repeated washing with distilled water. The organic phase was poured into methanol (50 ml). The precipitate was separated, washed with methanol and ether, and dried overnight under reduced pressure.

References

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