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SELECTIVE THERMAL OXIDATION OF OLIGOOXYETHYLENE RESINS DERIVED FROM CHLOROMETHYLATED CROSS-LINKED POLYSTYRENE

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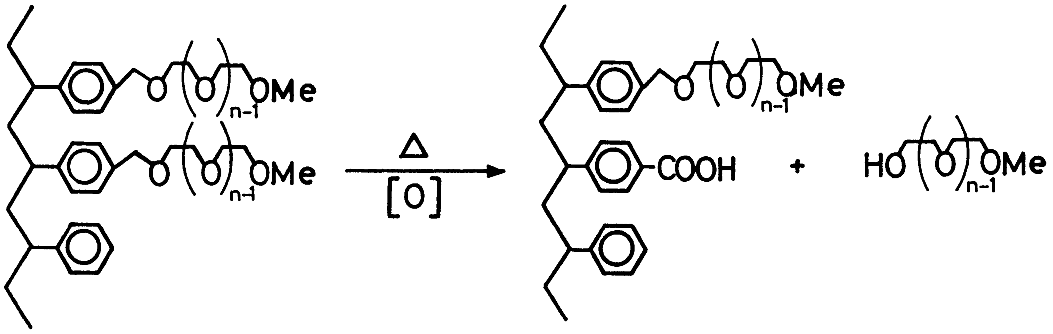
Solid-state oligooxyethylene resins derived from chloromethylated cross-linked polystyrene are oxidized thermally but selectively at the benzyl carbons bound to oligooxyethylenes, giving the resins with oligooxyethylene chains and carboxylic groups (0.1-2.5 mequiv COOH/g-resin).

Some oligooxyethylene(POE) derivatives insolubilized on chloromethylated cross-linked polystyrene have drawn much attention because of their excellent phase transfer catalysis[1,2] and good functions as nonionic ion exchange resins.[3,4] Such insoluble polyethers have been considered to be chemically stable compared with insoluble quaternary ammonium salts which are susceptible to dequaternization. We have found that the POE resins are subject to the selective thermal oxidation at high temperature in solid state, leading to the formation of new resins with both POE and carboxylic groups as shown below.



A,BEOnMe (n=3~7)

POE resins(AEOMe, BEOnMe, n=3-7)[5] prepared by the same method as in the preceding papers,[2] were readily oxidized by allowing them to stand in a drying oven at 80°C for 24 h. The oxidized POE resins dried after washing with methanol showed the characteristic IR absorptions at 1720 and 1685 cm^{-1} attributed to carbonyl groups, which are identical with those observed in poly(vinylbenzoic acid).[6] Assignment of the broad absorption in the region 3500-3350 cm^{-1} was ambiguous because of the absorption of water onto the POE chain. Moreover, the oxidized POE resins showed ion exchange with alkali in aqueous ethanol, and the exchange capacity determined under reflux was 0.1 to 2.5 mequiv/g-resin, depending on the oxidation conditions and the POE chain length of the starting POE resins. The completely neutralized resins showed the intense absorptions at 1590-1600, and 1540-1550 cm^{-1} attributed to carboxylate groups.[7] The carboxylic groups in the resin have been further characterized by treatment of the oxidized resins with thionyl chloride and then with hydroxylamine in the presence of sodium hydroxide. A deep coloration of the resulting resin on treatment with ferric chloride solution, suggested that the carboxylic groups was converted into hydroxamic groups.

To confirm the selective oxidation at the benzyl carbon bound to the POE chain, the fragments liberated in the oxidation of the resins(A,BEOnMe, n=3-7) were examined by glpc and the main fragments were shown to be the starting oligooxyethylene glycol monomethyl ether(EOnMe), which was probably formed via initially-formed hemiacetal.[8] The liquid products also showed weak IR absorption in the region 1720-1750 cm^{-1}, indicating the presence of a small quantity of some oxidized products.

To know the extent of random POE chain oxidation,[9] relationship between the degree of oxidation and the decrease in weight were precisely examined in the oxidation of AEO6Me resin. As seen in the Figure, the decrease in weight is linearly dependent in the degree of oxidation and is almost comparable with that calculated from the alkali absorption capacity by assuming the exclusive oxidation at the benzyl carbons, indicating that the oxidation of AEO6Me resin was not much accompanied by the random oxidative fission of the POE chain. Thus, we can conclude that, as a typical example, treatment of AEO6Me resin(2.28

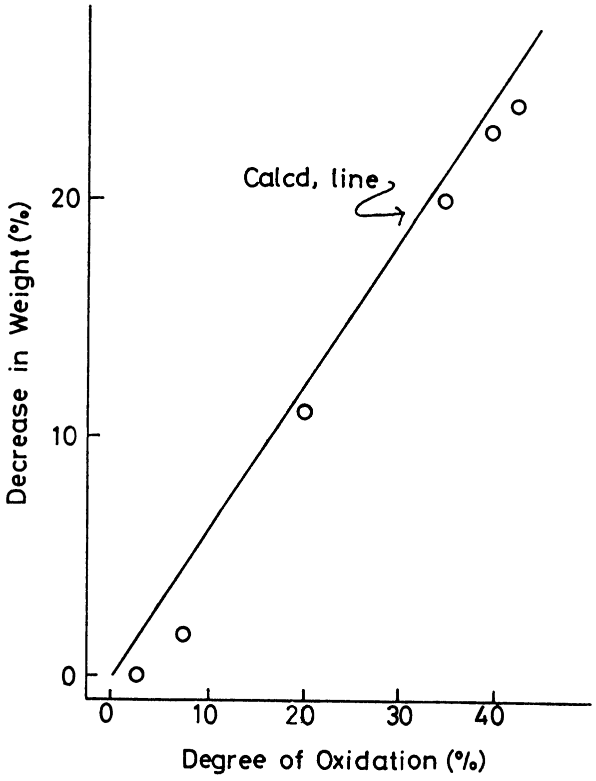


Figure. Plot of the percentage of the decrease in weight as a function of the degree of oxidation in the thermal oxidation of AEO6Me resin at 80°C. The AEO6Me resin which contained 2.28 mequiv-EO6Me, 0.27 mequiv-COOH, and 0.06 mequiv-Cl/g-resin was used (300 mg). The degree of oxidation was determined by the following equation; Degree of oxidation = COOH(mequiv/g-resin)/[EO6Me(mequiv/g-resin) + COOH(mequiv)/g-resin)].

mequiv-EO6Me/g-resin) at 80°C for 24 h in a drying oven, gave an oxidized AEO6Me resin with the functionality of 1.41 mequiv-COOH, 1.75 mequiv-EO6Me/g-resin. Similarly, BEO3Me resin(1.53 mequiv-EO3Me/g-resin) gave an oxidized BEO3Me resin(0.09 mequiv-COOH, 1.50 mequiv-EO3Me/g-resin).

For the resins with longer POE chain, however, there was found a tendency to degrade randomly. The liquid fragments obtained from the oxidized BEO10Me (1.32 mequiv-COOH/g-resin) were examined by glpc and found to be mixtures of degraded products by the random POE chain oxidation.

Finally, it is worthy to note that the POE resins are not readily susceptible to thermal oxidation in the swollen state nor in solvent. On the other hand, in view of the facile and selective thermal oxidation of the dried POE resins, the present finding will contribute to the chemical modification of the cross-linked polystyrene.

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5) Abbreviations are identical with those in ref. 2. A type polystyrene: porous type, surface area, 4.8 m^2/g, average pore diameter, 380 Å, 6.36 mequiv Cl/g-resin, cross-linked by 3% DVB, 80-400 mesh (Mitsubishi Chemical Co. Ltd.) and B type polystyrene: ca. 2.0 mequiv Cl/g-resin, cross-linked by 2% DVB, 200-400 mesh(Kodak).

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