Degradation of Polyethylene Glycol in a Localized Reaction Zone during Glow Discharge Electrolysis

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Gel permeation chromatographic studies of poly(ethylene glycol) degraded in 0.002 M NaCl solution by glow discharge electrolysis suggest that cleavage of the polymer chain takes place only in a localized zone of the reaction system.

Glow discharge electrolysis (G.D.E.) is a type of chemical change due to the glow discharge between a conducting solution containing a substrate and an electrode in contact with the solution. According to Hickling's assumption,[1] the mechanism of G.D.E. can be explained as follows: when the discharge is applied to an aqueous solution, gaseous H_2O^+ ions generated in the discharge zone permeate the liquid phase forming a thin disc-like area, called the primary reaction zone, in the surface of the liquid, and in this localized zone various active species such as OH radicals, hydrated electrons, and/or H radicals, H_2O_2, and H_2 arise from the decomposition of water molecules and diffuse into the body of the solution to bring about G.D.E.-promoted reactions. We have demonstrated that the OH and H radicals play an important role in G.D.E.-promoted reactions of organic compounds.[2]

We now report evidence for a localized reaction zone in which the G.D.E.-promoted degradation of poly(ethylene glycol) (PEG) takes place preferentially.

The substrate solution (45.5 mM in terms of monomer units) was prepared by dissolving PEG in 0.002 M NaCl solution. The two average molecular weights for PEG were determined according to the previous method:[3,4] the weight-average molecular weight (M_w) was 101 000, and the number-average molecular weight (M_n) was 3150. G.D.E. was carried out on 50 ml of the sample solution at 30 ± 2 °C with saturation by argon and with constant stirring, using a single straight tube cell[2] (S-cell) equipped with a platinum wire as the anode (discharge side) and a coil of platinum wire as the cathode. The applied electric current was 80 ± 10 mA at 750 V.

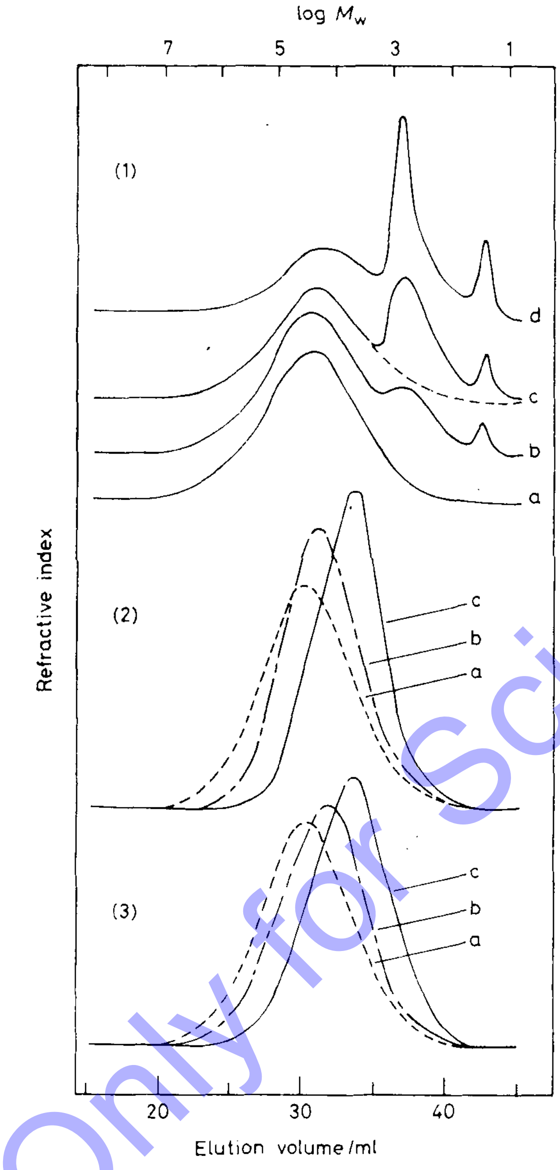

Figure 1. Changes in g.p.c. curve of PEG with G.D.E.-promoted degradation (1) as a function of the reaction time: a, 0 min; b, 10 min; c, 20 min; d, 40 min, photodegradation (2) with H_2O_2/u.v. light as a function of the reaction time: a, 0 min; b, 10 min; c, 20 min, and Fenton's degradation (3) as a function of the amount of the equimolar mixture of H_2O_2 and $TiCl_3$: a, 0 mM; b, 0.15 mM; c, 0.25 mM. Dashed line in curve 1(c) denotes the g.p.c. data for the sample polymer which was obtained by dialysing the degradation product against distilled water in a cellophane tube with permeability for oligomers with molecular weight below 3000, and then lyophilizing the dialysed solution. Fenton's degradation was allowed to continue until H_2O_2 in the system was decomposed completely.

Fenton's degradation and photodegradation, which can be regarded as homogeneous reactions over the whole system, were also investigated to compare with the G.D.E.-promoted degradation. Fenton's degradation was carried out at 25 ± 1 °C using 50 ml of the substrate solution in the presence of an equimolar amount (0 to 20 mM) of H_2O_2 and $TiCl_3$, while photodegradation was performed at 30 ± 1 °C with 10 ml of the solution in the presence of 1 mM H_2O_2 using a Pyrex glass vessel with a high-pressure 400 W mercury lamp.

When the reaction was complete, the degradation products were examined by gel permeation chromatography (g.p.c.), which was carried out in the same manner as reported previously.[4] Figure 1 shows the changes in the g.p.c. curves of PEG caused by the G.D.E.-promoted degradation, Fenton's degradation, and photodegradation. Both Fenton's degradation and photodegradation lead in all cases to a monotonic shift of the original peak to the low molecular weight side. However, the results of G.D.E. indicate that the two peaks assigned to degradation products appear without shifting the original peak to the low molecular weight side. The peaks at elution volumes *ca.* 37 and 43 ml are due to the oligomeric degradation products ranging in M_w from 1000 to 100 and to the low molecular weight compounds (carboxylic acids and aldehydes), respectively. These low molecular weight species could be separated from other degradation products because of their strong affinities for the gel used for g.p.c. The changes in the g.p.c. curve during G.D.E. are not attributed to a degradation–polymerization equilibrium, since (a) no polymerized products were obtained by G.D.E. of tetraethylene glycol, and (b) the i.r. spectrum of the polymer, which was separated from the reaction mixture using the same method as described in the Figure 1 caption for oligomer separation, was consistent with that of the original polymer.

To make a quantitative comparison of the g.p.c. data, the M_w/M_n ratio, which is an indication of the molecular weight distribution (M.W.D.) of a polymer, was determined from the curves in Figure 1 according to the method of Cazes:[5] 30.1 from curve 1(c) indicated by the dashed line, 11.2 from curve 2(c), 13.6 from curve 3(c), and 32.1 from the curves 1(a), (b), or (c) for the original PEG. It is found that the M.W.D. of the remaining polymer after G.D.E. is similar to that of the original PEG. In contrast to G.D.E., both Fenton's degradation and photodegradation simultaneously bring about a shortening of M.W.D. and a lowering of molecular weight, which could be governed by decreasing the high molecular weight fractions rather than by increasing the low molecular weight fractions.

As described, the most interesting aspect of the G.D.E.-promoted degradation is that the reaction mixture contains polymers with the original M.W.D. in addition to the oligomeric and further degraded products. This is not explicable in terms of the chain cleavage occurring in a random fashion, which is generally characterized by a monotonic M.W.D. change like that observed in Fenton's degradation or photodegradation. Taking into account the fact that Fenton's degradation and photodegradation are homogeneous reactions in which OH radicals may participate, this characteristic of G.D.E. degradation could be related to the heterogeneity of the reaction system. When G.D.E. is applied to the aqueous solution containing PEG, the active species are generated in a localized zone, and their attack leads to the rapid rupture of the bonds in the polymer chain yielding the oligomeric and further degraded products. However, the polymer placed outside such a reaction zone is free from attack by the active species and remains unchanged, since the lifetimes of the active species could be so short as to be unable to diffuse into the whole reaction system. At present we believe that rupture of the bonds is initiated by abstraction of hydrogen from the methylene group with active species such as OH radicals to generate $-O-\dot{C}H-CH_2-$ radicals, which are then oxidized to formyl and carboxy groups. This is because the degradation products contain glycolaldehyde, glyoxal, glycolic acid, and glyoxylic acid, in addition to oxalic and formic acids which are eventually oxidized to gaseous compounds (CO_2 and CO). The reaction of aqueous ethanol under G.D.E. has been described[6] and the yields of products quantitatively related to the initial input of OH radicals.

In conclusion, the present results reveal that the G.D.E.-promoted degradation of PEG occurs preferentially in a localized reaction zone, which may correspond to Hickling's primary reaction zone or its neighbouring region.

The authors are deeply indebted to Dr. K. Fujimori, University of Tsukuba, for his helpful encouragement and discussion.

Received, 13th August 1984; Com. 1170

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