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Degradation of Poly(Acrylamide) in Aqueous Solution by Glow Discharge Electrolysis

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Summary

The glow discharge electrolysis was carried out to an aqueous solution containing poly(acrylamide). The analytical results of the degradation products showed that the degradation takes place stepwise caused by the cleavages of the main and also the side chains of the polymer.

Introduction

When an electric discharge is applied to a conducting solution, unique chemical reactions can be brought about in the liquid phase. The process is called glow discharge electrolysis (GDE), which has been studied by Hickling (1964) and Hickling and Ingram (1964). Recently Harada et al. applied GDE to organic compounds and reported on the formation and degradation of various bio-organic compounds by GDE (HARADA and IWASAKI 1974 and 1975; HARADA and TERASAWA 1978 and 1980). The GDE was also reviewed by Hudson (1979) as a method for water treatment. However, no study on the degradation of a water-soluble polymer by GDE has been made, although attention has been paid to the degradation of poly(ethylene glycol) (SUZUKI 1976), poly(acrylamide) (PAAm) (SUZUKI et al. 1978) and poly(vinyl alcohol) (NIKI et al. 1979) by ozone oxidation and of poly(vinyl alcohol) (NIKI et al. 1978) by photooxidation. Thus, it is now of interest to investigate the degradation of water-soluble polymers by GDE.

Materials and Methods

PAAm was commercially obtained from Wako Pure Chemical Industries Ltd. The polymer was fractionated and purified in the same manner as described in the literature (BAYSAL et al. 1963). The weight-average molecular weight (1.0×10^6) was estimated by the following equation (SORENSON et al. 1961);

$$[\eta] = 3.73 \times 10^{-4} Mw^{0.66} \qquad (1)$$

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where [η] represents the intrinsic viscosity in 1 M $NaNO_3$ at 30 °C. The viscometric measurements were carried out by using an Ubbelohde viscometer having a flow time of 304.5 sec for water at 25 °C.

PAAm (0.1 g) was dissolved in 50 ml of 1.7 x 10^{-3}M NaCl and the sample solution was subjected to GDE. An electrolytic cell used here was the same type as described by Hickling and Newns (1961). The anode was a platinum wire and the cathode was a coil of platinum wire. They were arranged so that the cathode was completely immersed in the solution and the anode was fixed so as to contact with the liquid surface. The electric current was supplied by a Tokyo Kagaku potentiostat (model PS-1515) and the voltage was held an 700 ±10 V. The current varied from 60 mA to 120 mA as the GDE proceeded. The cell was immersed in an ice bath and the solution was stirred with a magnetic stirrer, so that the temperature of the sample was kept at 30±4 °C during the reaction.

The molecular weight of the cleaved polymer was estimated in the same manner as described above on the assumption that eq. (1) is applicable to the degradation products. The molecular weight distribution was determined by gel permeation chromatography (GPC) with a Hitachi liquid chromatograph (model 633A) equipped with OH pack B-804 and B-806 columns. The other instruments used for the analyses of the degradation products were: total carbon content (TOC) by a Beckman TOC Analyzer (model 915-B); total nitrogen content (TNC) by a Shimazu TN-TOC Analyzer (model GCT-12N); UV spectrum by a Hitachi Spectrophotometer (model 200-20); IR spectrum by a Hitachi Infrared Spectrophotometer (model 260-30); pH titration by a Hirama Automatic Recording Titrator; amino acid analysis by a Yanagimoto Amino Acid Analyzer (model LC-5S).

Results and Discussion

When the voltage was carefully and quickly raised to 700 V in order to avoid the electrode reactions of the sample, the anode glowed in violet, indicating the establishment of the glow discharge. Figure 1 shows the results of the viscometric measurements. The observed value of [η] decreases by application of GDE, indicating that the PAAm is degraded by GDE-promotive reaction.

The degradation of PAAm can also be confirmed by GPC (Figure 2). The results of GPC show that the peak (or peaks) in the chromatogram is (or are) shifted to a low molecular weight range by application of GDE. Furthermore, the chromatogram of the degradation product shows plural peaks and the number of peaks increases with the reaction time. These results are in contrast to those for the ozonized PAAm and poly(ethylene glycol):

the degradation products with ozone showed a broad pattern having one peak (SUZUKI 1976; SUZUKI et al. 1978). Although the GPC method in the present study is different from those of Suzuki et al., the facts mentioned above could be attributed to the difference between the two degradation mechanisms by GDE and ozone. In other words, the different fragments of degradation products appear stepwise in the process of GDE, while the polymer chain is cleaved randomly with ozone.

In the present stage of the studies on GDE to aqueous solution, it is generally believed that the OH radicals which arise from the breakup of a water molecule with the bombardment of gaseous ions, plays an important role in the initial process of the GDE-promotive

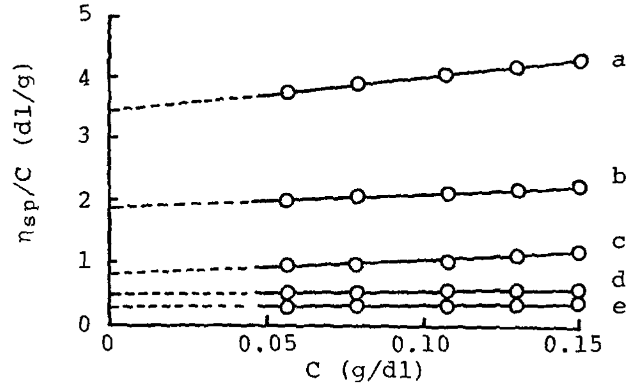

Fig. 1. Plots of reduced viscosity (η_{sp}/C) *vs.* concentration (C) for original PAAm and the degradation products with GDE at different times (min): a,0; b,5; c,10; d,15; e,20.

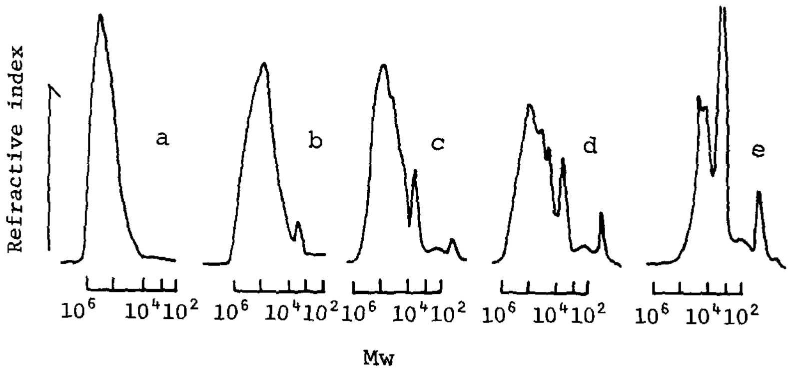

Fig. 2. Change in GPC pattern of PAAm with GDE at different times (min): a,0; b,10; c,20; d,60; e,180.

reaction. This chemical process could be considered to be analogous to the effect of ionizing radiation, such as α-, γ- and x-rays. The chemical reaction of the OH radicals in water can be classified as four different types; addition, hydrogen subtraction, electron transfer and radical interaction (DORFMAN AND ADAMS 1973). Thus, the GDE-promotive degradation could be explained on the basis of these reactions concerning the OH radicals.

In order to obtain information on the reaction mechanism, the degradation products were investigated by different analytical methods. These results are summarized in Table 1. From the TOC data, it is found that the carbon of PAAm is released by application of GDE; 8.2% at 20 min and 41.6% at 180 min. In the GDE-promotive reactions, the attack of the OH radicals to methine and methylene groups in PAAm presumably yields aldehyde, ketone and carboxylic groups caused by the addition and hydrogen subtraction reactions. Thus, the release of carbon by GDE could be interpreted by the assumption that the methine and methylene groups in PAAm are oxidized to carbon dioxide through carboxylic acid (and/or carboxyl group). This assumption can be confirmed by the facts that the acid and/or acidic group arise in the course of GDE and the amount of total acids (Ma) increases with the reaction time (see Table 1).

Table 1. Analytical data of original PAAm and degradation products with GDE at different times[a].

Time (min)	TOC [b] (*m* mol)	TNC [b] (*m* mol)	Ma [b] (*m* mol)	$\bar{D}_p$ [c]	S_o [b] (μ mol)
0	4.21	1.38	0	14,507	0
5	4.10	1.34	0.04	5,652	0.16
10	4.13	1.39	0.07	1,915	0.64
15	4.04	1.37	0.11	775	1.72
20	3.87	1.35	0.10	360	3.81
180	2.43	1.35	0.21		

[a] The original sample solution contains 0.1 g of PAAm in 50 ml of 1.7 x 10^{-3}M NaCl.

[b] Represented by moles in 50 ml of sample solution.

[c] Calculated from the results in Fig. 1 by eq.(1).

In order to identify the carbonyl and carboxyl groups in the degradation products, the lyophilized products were subjected to IR and UV analyses. The carbonyl and carboxyl groups are not observed clearly by IR analysis because of the strong absorption band of the amide group of PAAm. However, the UV spectra obtained in the alkaline media show an absorption maximum at 264 - 267 nm. The absorption is strengthened by the addition of bivalent cation such as Ca^{2+} and Mg^{2+}, whereas the absorption maximum is reduced to shoulder by the addition of HCl. Suzuki et al. (1978) reported that the ozonized PAAm shows an absorption maximum at 266 nm in the alkaline medium. From this fact, they assumed that new functional groups (aldehyde or ketone) are produced in the polymer chain and they combined with the amide groups to form a certain ring structure. On the basis of the absorption at 270 nm for the ozonization and photooxidation products of poly(vinyl alcohol), Niki et al. (1978 and 1979) also showed the formation of $-C(=O)-(C=C)_2-$ group in the polymer chain. Thus, the present results could indicate that the degradation of PAAm by GDE is attributable to the oxidation of carbon in the polymer to carbon dioxide through the carbonyl and carboxyl groups.

In order to investigate further the degradation reaction, the total number of statistical chain scissions (So) was evaluated by the results of viscometric measurements. Assuming that the degree of polymerization ($\bar{D}p$) of the degradation products could be estimated by eq.(1), So can be calculated by following equation (NIKI et al. 1979);

$$So = [Mu](1/\bar{D}p,t - 1/\bar{D}p,o) \qquad (2)$$

where [Mu] represents the moles of the monomeric residues of PAAm in the sample solution (50 ml), and $\bar{D}p,o$ and $\bar{D}p,t$ are the $\bar{D}p$ values for original PAAm and the degradation product at a certain reaction time, respectively. The So values calculated are listed in Table 1, together with the values of $\bar{D}p$. It is found that the So value increases with reaction time, but the value is smaller than the moles of the released carbon at the same reaction time (see TOC data). If the carbon is released by the cleavage of the main chain due to the oxidation of the methine and methylene groups in PAAm, the So value ought to be larger than the moles of the released carbon since one mole of the released carbon gives two moles of cleavage points. Although there is an ambiguity in the estimation of So value, the results mentioned above could, at least in a qualitative way, reveal that the cleavage of PAAm chain occurs in the main chain and also in the side chain.

The results of TNC are almost unchanged during GDE (see Table 1). This indicates that no evolution of nitrogen occurs in the process of the degradation reaction. The results of TNC seem to contradict with those of TOC, but this contradiction might be avoided if we assume that the amino radical is produced by the cleavage of the side chain and then combined with the degradation products to form new amino and/or amide compounds. This assumption was supported by the fact that 0.7 - 1.2 μ moles of amino acids such as alanine, aspartic acid, glutamic acid, glycine, lysine, serine, threonine, and unidentified basic amino acids are observed in the sample solution at the reaction time of 180 min. Thus, the difference between the So value and the moles of the released carbon mentioned above could be due to the cleavage of the amide bond in the side chain of PAAm by the OH radicals.

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