Some Effects of Ionizing Radiation on a Polyhydroxyether

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Synopsis

The behavior of the polyhydroxyether derived from bisphenol A and epichlorohydrin on exposure to electron irradiation (0–500 Mrads) in vacuum has been investigated. The polymer underwent chain scission, $G = 0.20$ (scission per 100 e.v.), with no evidence of crosslinking. Degradation was accompanied by the loss of H_2 together with smaller quantities of CO, CO_2, and CH_4. Spectroscopic studies are reported, and a mechanism of degradation is proposed. The tensile yield stress and fracture energy of molded specimens were also examined, and changes in these properties as functions of radiation dose and molecular weight are discussed.

INTRODUCTION

We have previously described[1,2] some of the effects of ionizing radiation on the mechanical properties of the polycarbonate derived from bisphenol A and have postulated[3] a mechanism of the degradation process. For this reason it was of interest to compare its behavior with that of the structurally related polyhydroxyether formed by condensation of bisphenol A and epichlorohydrin.[4] Accordingly, the present paper describes the changes in tensile strength and fracture energy and discusses some of the chemical changes observed when the polymer is irradiated with 4 M.e.v. electrons.

EXPERIMENTAL

Preparation of Specimens

Granules of phenoxy resin [Bakelite PRDA 8060, bisphenol A poly-(hydroxyether)], predried at 60°C. at 12 mm. for 7 days, were placed in glass ampules equipped with break-seals. The ampules were degassed (60°C. at 10^{-6} mm.) for 72 hr. and sealed. After irradiation the gas content of the ampules was analyzed, and the polymer was used for viscosity and spectroscopic measurements.

Injection-molded dumbbells of a type previously described[1] were used for tensile measurements. They were stored in a desiccator over P_2O_5 after molding, both before and after irradiation.

Irradiation

Ampules, cooled externally by a water spray, were exposed to a linear accelerator beam (4 M.e.v.) at a dose rate of 5 Mrads/min. The dumbbells were irradiated in an evacuated container[1] (10^{-3} mm.) at a dose rate of 1 Mrad/min.

Test Methods

Specimens were tested approximately 2 wk. after irradiation; during the storage period the dumbbells were kept in a desiccator over P_2O_5, and the ampules were not opened.

Viscosity. The intrinsic viscosity of specimens was determined in tetrahydrofuran at 25°C.; molecular weights were calculated from the relationship derived by Myers and Dagon:[5]

$$[\eta] = 1.48 \times 10^{-4} M_w^{0.765}$$

Tensile Measurements. Tensile yield strength (or breaking strength in the absence of yield) and fracture energy were measured at 21°C. with equipment described previously.[1] The results quoted represent the average of not less than four replicates. Tensile strength was determined at a crosshead speed of 0.00167 in./sec. and fracture energy at an impact velocity of 320 in./sec., corresponding to a maximum straining rate of 32,000 %/sec. Fracture energy measurements were made on (a) unstressed specimens, and (b) specimens prestressed to the tensile yield strength and allowed to recover for 24 hr. (all specimens were then within 0.2% of their original length).

Gas Analysis. Gas analyses were carried out with an A.E.I. M.S.2H mass spectrometer.

Spectroscopy. Films cast from tetrahydrofuran were examined with a Perkin-Elmer 337 infrared spectrometer, and tetrahydrofuran solutions were examined with a Perkin-Elmer 137 ultraviolet spectrometer.

RESULTS AND DISCUSSION

Molecular Weight

The polymer was completely soluble in tetrahydrofuran before and after irradiation in vacuum up to the maximum dose employed (500 Mrads). The absence of gel formation and increased ease of solution after irradiation indicated that chain scission was the dominant feature of the degradation. This was substantiated by an examination of the change in molecular weight with increasing radiation dose, the results of which are presented in Figure 1. The initial nonlinearity of this plot is due to the nonrandom distribution of molecular weight in the early stages of degradation. At radiation doses above 75 Mrads the linear plot indicates a most probable distribution of molecular weights resulting from random chain scission and the relationship[1,6,7]

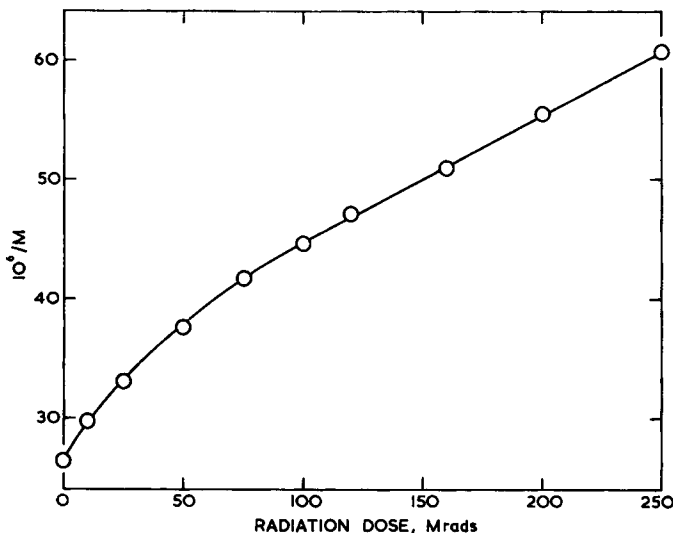$$10^6/M_w = 10^6/M_{w_0} + 10^6(2NE_d)^{-1}R$$

Fig. 1. Reciprocal molecular weight of polyhydroxyether versus radiation dose.

can be applied, where M_{w_0} is the initial weight-average molecular weight, R is the radiation dose (Mrads), E_d is the total energy absorbed per chain scission produced, and N is Avogadro's number. From this equation E_d was calculated to be 510 e.v., which gives a value for G (scissions per 100 e.v.) of 0.20.

Tensile Properties

The tensile yield strength (brittle strength in the absence of yield) and fracture energy results are shown in Figures 2 and 3 as functions of radiation dose. A molecular weight scale is also included in these figures, based on the results described in the preceding section.

Figure 2 shows that specimens exhibit ductile failure with no change in tensile yield strength (determined at 0.00167 in./sec.) down to a molecular weight of 24,000. Thereafter a transition occurs, accompanied by a rapid loss in strength. The increased scatter of results observed in the transition region is due to the occurrence of brittle failures. This pattern of behavior is comparable to that previously established for polycarbonate,[1,2] which suggests that even at molecular weights below 15,000 the polyhydroxyether still possesses a finite, low strength.

Figure 3 shows comparative fracture energy results obtained at 320 in./sec. from unstressed specimens and specimens previously prestressed to their tensile yield stress and allowed to recover for 24 hr. prior to test. The toughness of unstressed specimens is retained up to doses of 30 Mrads, but thereafter the material becomes brittle with rapid loss in impact strength. By contrast, the impact strength of prestressed specimens decreases rapidly with radiation dose, and brittle failures occur at a dose of 10 Mrads. It is probable that this difference in behavior is attributable either to the introduction of critical flaws or to a change in the time de-
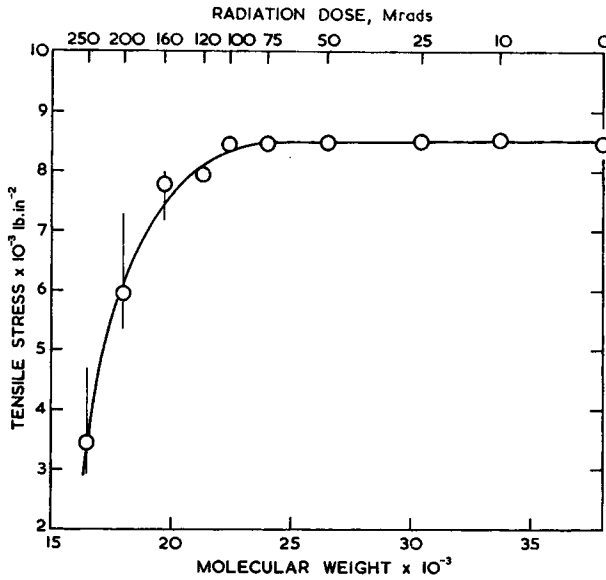
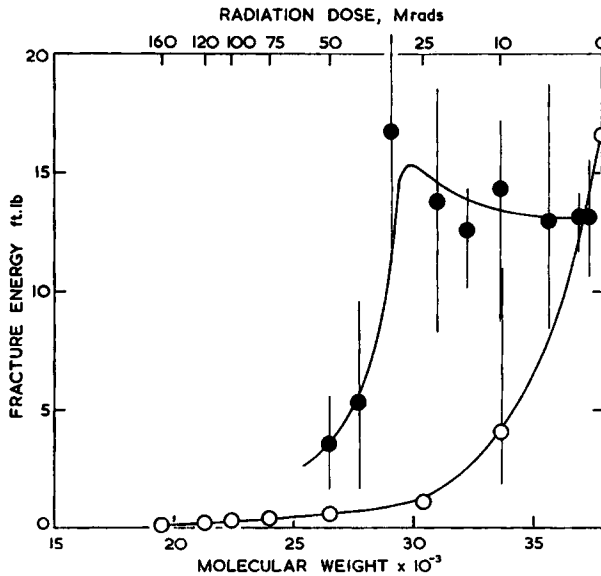Fig. 2. Tensile stress of polyhydroxyether dumbbells versus molecular weight.

Fig. 3. Fracture energy of polyhydroxyether dumbbells versus molecular weight: (●) unstressed specimens; (○) specimens prestressed to maximum tensile yield stress. Scatter limits indicated.

pendence of the specimens caused by prestressing.   Further work on the effect of prestressing on strength properties is currently in progress.

Effects of Radiation on the Polymer Structure

Degradation was accompanied by chain scission ($G = 0.20$), and no evidence of crosslinking was obtained, although the possibility of chain branching cannot be eliminated.

When irradiated in vacuum with doses of up to 500 Mrads the polymer progressively darkened to amber-brown; on exposure to air this color faded slightly, suggesting the destruction of long-lived radicals by oxygen, as observed in polycarbonate.   The permanent color was associated with an absorption maximum at 323 mμ, the intensity (E, at 1% and 1 cm.) of which was linearly related to radiation dose (R in megarads) by $E = 0.0034R$.   The infrared spectra of unirradiated and irradiated (500 Mrads) specimens were identical except for the appearance of weak carbonyl absorption at 1722 cm.$^{-1}$.

Mass spectroscopic analysis showed that the gas evolved from irradiated polymer (0 to 250 Mrads) consisted of hydrogen and carbon monoxide together with traces of carbon dioxide and methane.   Figure 4 shows that the yields of the components were linearly proportional to the radiation dose (methane cannot be conveniently illustrated on the scale adopted); the calculated G values are given in Table I.

These results are comparable to those obtained by radiolysis of simple alcohols which yield carbonyl compounds together with hydrogen, as
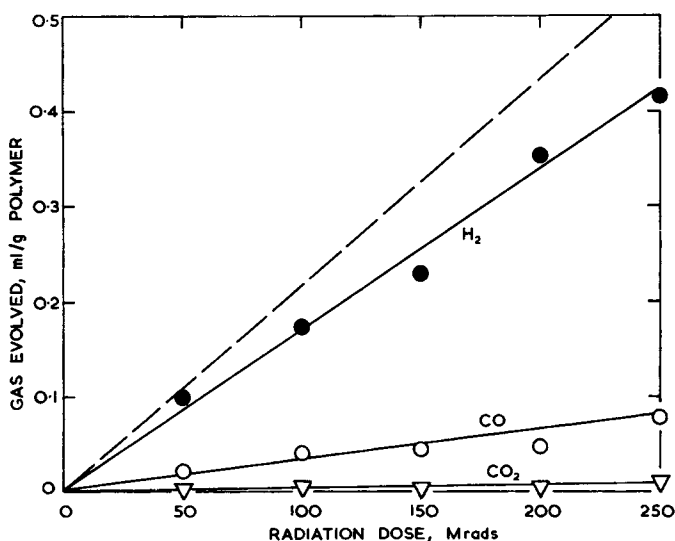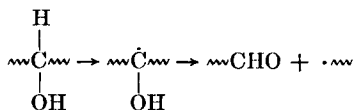

Fig. 4. Gas evolution from polyhydroxyether versus radiation dose; (●) H_2; (O) CO;
($\triangle$) CO_2; (− −) total gas.

TABLE I
Evolution of Gas from Irradiated Polymer

Gas	G (molecules of gas per 100 e.v.)
Total	0.0833
H_2	0.0677
CO	0.0133
CO_2	0.0016
CH_4	0.0008

principal gaseous product, accompanied by carbon monoxide and hydrocarbons.[8,9] Studies of deuterated alcohols[7] have shown that the hydrogen is derived mainly from the hydrogen atoms attached and α to the carbinol group.   Thus it is probable that the principal mode of degradation of the polymer is loss of hydrogen atoms, leaving radicals, which subsequently rearrange with concomitant chain scission, such as in

$$\overset{\displaystyle H}{\underset{\displaystyle OH}{\text{ⱴⱴⱴC}ⱴⱴⱴ}} \rightarrow \underset{\displaystyle OH}{\text{ⱴⱴⱴ}\dot{C}\text{ⱴⱴⱴ}} \rightarrow \text{ⱴⱴⱴCHO} + \cdot\text{ⱴⱴⱴ}$$

On this basis, neglecting other contributory reactions, G (scission) would be not less than 0.125.

The carbon monoxide and carbon dioxide apparently arise from further degradation of radicals derived from the carbinol group.   The traces of methane can be ascribed to scission of isopropylidene groups, forming methyl groups, which subsequently abstract hydrogen from the polymer, as observed in the radiolysis of polycarbonate.[3]

It is apparent that polyhydroxyether and polycarbonate are relatively stable to radiation and that this can be attributed to their predominantly aromatic character, since in both cases degradation occurs principally at the group linking the bisphenol A residues.   It is noteworthy that although the carbonate group is more severely degraded than the hydroxyether group, as shown by gas evolution ($G = 0.57$ and 0.083, respectively), the extent of chain scission in polycarbonate ($G = 0.09$) is reduced by radical recombination to a value lower than that observed in polyhydroxyether ($G = 0.20$).[1,3]

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