γ Radiolysis of Cellulose Acetate

S. M. ALI and P. G. CLAY, *Department of Chemical Engineering and Chemical Technology, Imperial College, London S.W.7, England*

Synopsis

The major degradative process in γ-irradiated cellulose acetate is chain scission. For the dry powder the G_s value (number of scissions per 100 eV of energy absorbed) was found to be 7.1. The water-swollen material was found to degrade at the higher rate of $G_s = 9.45$. Additions of ethanol and methanol to the water brought about reductions in G_s, whereas dissolved nitrous oxide produced an increase in G_s. The useful life of cellulose acetate reverse osmosis membranes exposed to γ radiation was estimated by observations of the water permeation rate during irradiation. Membrane breakdown occurred at 15 Mrad in pure water, but the dose to breakdown was extended to 83 Mrad in the presence of 4% methanol.

INTRODUCTION

Cellulose acetate reverse osmosis membranes are widely used in water treatment and in the processing of aqueous solutions more generally. The use of such membranes in radiation environments, e.g., in radioactive waste processing, may be contemplated, and in these circumstances the radiation stability of cellulose acetate could prove to be a limiting factor.

The radiation chemistry of cellulose acetate has not been widely studied, and most recent work has been concerned with the identification and measurement of radical species by electron spin resonance techniques.[1,2] Earlier work on the effect of irradiation upon mechanical properties gives widely different estimates of cellulose acetate stability. Thus, Chapiro[3] found that the polymer became brittle at about 20 Mrad whereas Sisman and Bopp[4] estimated that a 50% reduction in tensile strength would require a dose of 200 Mrad.

The effectiveness of cellulose acetate reverse osmosis membranes would be reduced either by significant loss of acetate groups or by radiation-induced chain scission leading to the loss of mechanical strength. In this paper we report measurements of molecular weight changes and changes in the water permeability characteristics brought about by γ irradiation. Preliminary work showed that the rate of loss of acetate groups was at least an order of magnitude lower than the rate of chain scission, and this aspect of cellulose acetate radiolysis has not been considered further.

EXPERIMENTAL

Eastman-Kodak 398-10 cellulose acetate (degree of substitution 2.5) was used in all the experiments reported here.

Irradiations were carried out using a ^{60}Co γ-ray source delivering a dose of 3.3×10^{16} eV/g sec^1 as measured by Fricke dosimetry. Dry cellulose acetate was obtained by air drying the powder at 80°C followed by storage over P_2O_5. Wet samples were prepared by slurrying the powder in water (cellulose acetate:water

Journal of Applied Polymer Science, Vol. 23, 2893-2897 (1979)
0021-8995/79/0023-2893$01.00

ratio 1:2). Saturation with N_2 or N_2O was achieved by bubbling the gas through the slurry immediately prior to and during radiolysis. Other solutes were added to the water prior to slurrying.

After irradiation samples were dried and stored as before. Viscosity-average molecular weights were measured in a.r. grade acetone at 25 ± 0.1°C using an Ubbelohde viscometer. The Mark–Howink–Sakurade constants used were $K = 2.8 \times 10^{-4}$ and $\alpha = 0.78$. Acetic acid and acetaldehyde in aqueous solution were determined by gas chromatography. A flame ionization detector and a crosslinked polystyrene column (145–190°C) were used.

Water flux measurements were the only indicator of membrane performance used in this study. The membranes were of the Loeb 7 type and were supplied by the United Kingdom Atomic Energy Authority Research Establishment, Harwell. The water flux measurements were made using an unstirred Gelman stainless-steel pressure vessel about 5 cm in diameter and a capacity of 200 ml. Distilled water was used as feed. The membranes were mounted on a perforated steel disk and the pressure applied using a gas cylinder and conventional cylinder head reducing valves. The measurements were usually made at 180–200 psi.

The water flux was measured during radiolysis by allowing the drops of permeate to fall onto electrodes connected to a chart recorder upon which each drop was registered as a "spike." The drop volume was measured and the water flux over any period conveniently estimated from the frequency of occurrence of the "spikes."

RESULTS AND DISCUSSION

G Values for chain scission (G_s) under different conditions are shown in Table I. These values were obtained from plots (Fig. 1) of the reciprocal of the viscosity-average molecular weight ($\overline{M}_v$) versus dose (D) according to

$$\frac{1}{\overline{M}_v} = \frac{1}{\overline{M}_{v,o}} + \frac{G_s - 4G_x}{200N_A} D$$

where $\overline{M}_{v,o}$ is the original molecular weight, N_A is Avogadro's number, and G_x is the G value for crosslinking. Samples of irradiated cellulose acetate in tetrahydrofuran were examined by gel permeation chromatography, which showed the absence of material of molecular weight higher than $M_{v,o}$, indicating that G_x was close to zero.

Table I shows that the sample slurried with water has a higher G_s value (9.45) than the dried sample (7.1). The difference can be ascribed to the degradation

TABLE I
γ Irradiation of Cellulose Acetate Powder

Radiolysis condition	G_s
Dry	7.1
Immersed in:	
Water	9.45
N_2O-saturated water	11.6
Aqueous $FeSO_4$ (1 mol/l.)	7.6
Aqueous methanol (4%)	3.4
Aqueous ethanol (4%)	3.3

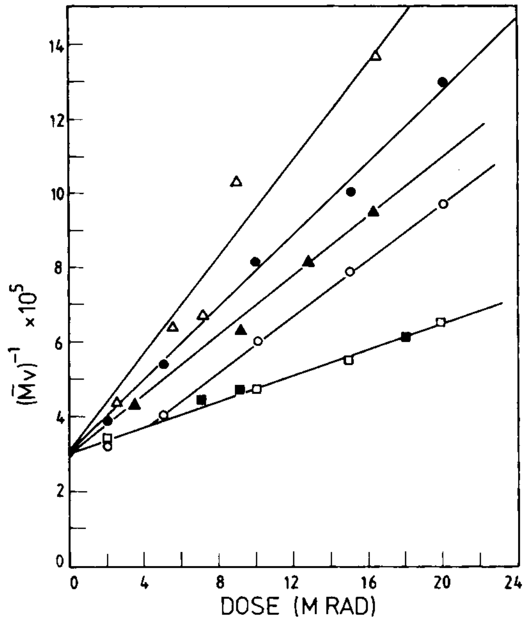

Fig. 1. Plots of $(\overline{M}_v)^{-1}$ vs. dose for dry cellulose acetate (○) and cellulose acetate immersed in water (●); N_2O-saturated water (△); 1 mol/l. $FeSO_4$ solution (▲); 2% aqueous ethanol (□); 2% aqueous methanol (■).

initiated by the attack of water radiolysis products upon cellulose acetate. The rate of degradation was observed to be unaffected by the presence or absence of oxygen, indicating that OH radicals rather than e^- (aq) or H atoms were responsible for the increase.

This hypothesis was further tested by irradiating cellulose acetate samples slurried by solutions containing ferrous ions, ethanol, methanol, or nitrous oxide. In the presence of ferrous ions, which are known to react with OH radicals, G_s was reduced to 7.6, close to the value G_s = 7.1 for the dry cellulose acetate. N_2O on the other hand reacts with hydrated electrons to produce OH radicals by the reaction

$$N_2O + e^- \text{ (aq)} \xrightarrow{H^+} N_2 + OH$$

and an increase in G_s of 2.1 was recorded for this solute. The results of these experiments were thus, qualitatively at least, in agreement with the hypothesis that the increased yields of scission in the water-swollen system were due to OH radical attack.

Methanol and ethanol, which also react with OH radicals, would be expected to behave similarly to ferrous ions, but the table shows that these solutes (~2%) reduced the rate of degradation of the cellulose acetate to values below that recorded for the dry material. Ethanol and methanol do not, then, behave simply as OH-radical scavengers, and some interaction between the irradiated cellulose acetate and the alcohol is indicated. This possibility was tested by irradiating cellulose acetate–4% aqueous ethanol slurries (cellulose acetate:solution ratio 1:2) and measuring the yields of acetic acid and acetaldehyde, a characteristic radiolysis product of ethanol.

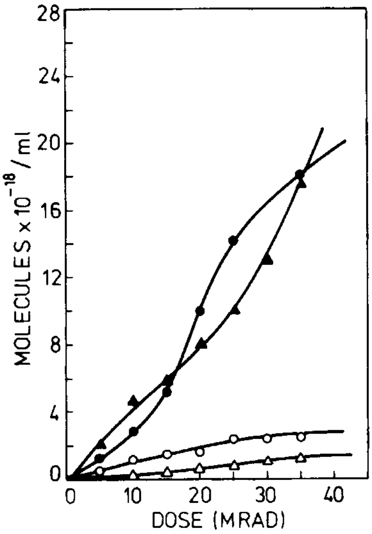

Fig. 2. Effect of cellulose acetate on radiolysis of aqueous ethanol. Yields of acetaldehyde in the presence (●) and absence (○) of cellulose acetate and acetic acid in the presence (▲) and absence (△) of cellulose acetate.

Figure 2 shows that the yields of acetaldehyde were greater in the slurries than in the ethanol solution itself, suggesting that the protective action of the ethanol involves a concomitant oxidation of the ethanol. It is not possible to discuss this protection in detail, but there should presumably be a correlation between the decrease in the number of chain scissions in the presence of ethanol and the increase in the yield of ethanol oxidation products. At 20 Mrad the radiolytic yield of acetaldehyde + acetic acid in 4% aqueous ethanol was increased from 2.2×10^{18} molec/ml to 18.0×10^{18} molec/ml by the addition of cellulose acetate. These experiments were carried out on slurries of 1 g cellulose acetate + 2 ml solution. The total increase of ethanol oxidation products in the system was accordingly 3.17×10^{19} molecules. The associated reduction in the rate of chain scission $\Delta G_s = 7.1 - 3.3 = 3.8$ corresponds to a reduction of 4.7×10^{19} scissions in the 1-g cellulose acetate sample at 20 Mrad. It is possible that ethanol oxidation products other than acetaldehyde and acetic acid would be formed or that intermediates in the ethanol oxidation are lost by reaction with radicals on the cellulose backbone. Under these circumstances the agreement obtained is quite satisfactory and supports the general mechanism proposed.

The service lifetime of cellulose acetate reverse osmosis membranes in radiation fields could be determined by the rate of radiation-induced polymer chain scission. In this context it has been suggested[5-7] that the tensile strength of cellulose acetate would be zero at degrees of polymerization below 50. According to this figure complete loss of strength should occur at 9–10 Mrad and 35 Mrad for membranes of initial molecules weight 35,000 irradiated in the presence of water and 4% aqueous methanol, respectively.

Estimates of the lifetimes of Loeb type 7 membranes were made by measuring the water flux at 200 psi pressure during radiolysis. These results are shown in Figure 3. The early changes in flow rate appear to be due to radiation heating of the membrane (increase) and compaction of the membrane under pressure (subsequent decline). The ultimate marked increases in flow rate occur at the

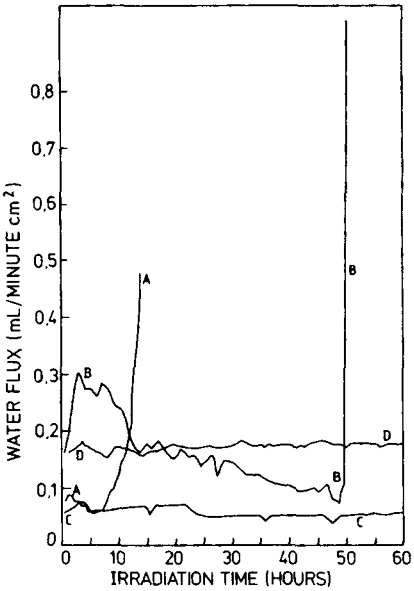

Fig. 3. Changes in water flow rate through cellulose acetate membranes during γ radiolysis: (A) water feed; (B) 4% aqueous methanol feed; (C) and (D) unirradiated controls. Dose rates: (A) 2 Mrad/hr; (B) 1.65 Mrad/hr.

doses at which the degradation of the membranes is such that they begin to tear under the applied pressure.

It would be expected that this breakdown would occur at the 9 to 10-Mrad level, but it can be seen that the membrane irradiated in water survived to 15 Mrad. However, while the support offered by the perforated plate in the apparatus used enabled the membrane to preserve its integrity at these higher doses, they were unable to withstand handling once removed from the apparatus. It seems probable that in membrane geometries and applied pressures more typical of commercial plant the dose for breakdown would correspond more closely to the 9 to 10-Mrad dose indicated by the molecular weight measurements.

The lifetimes of membranes irradiated in the presence of 4% aqueous methanol were considerably greater (~83 Mrad) than those predicted from the molecular weight measurements (35 Mrad). The explanation for this is not clear, but it is likely that effects other than those arising from the radiation chemistry of the system are responsible.

This work was supported by the United Kingdom Atomic Energy Research Establishment, Harwell.

References

1. U. Deffner and H. Paretzke, *Radiat. Res.*, **49,** 272 (1972).
2. P. K. Chidambareswaran, V. Sundaram, and B. B. Singh, *J. Polym. Sci. A-1,* **10,** 2655 (1972).
3. A. Chapiro, *J. Chem. Phys.* **53,** 295, 1956.
4. C. D. Bopp and O. Sisman, *Nucleonics,* **13**(7), 28 (1955).
5. A. M. Sookne and M. J. Harris, *J. Res.*, **34,** 467 (1945).
6. A. M. Sookne and M. J. Harris, *Ind. Eng. Chem.*, **37,** 478 (1945).
7. P. J. Flory, *J. Am. Chem. Soc.*, **67,** 2048 (1945).

Received October 5, 1977
Revised June 18, 1978