Table I
Solvent Effect on the Relative Intensity of the Exciplex[a]

Additive (vol) %)	$(F_e/F_m)_{\text{dioxane}}/(F_e/F_m)_{\text{dioxane+add.}}$ 2	3	Ratio[b]
Ethanol (3.4)	2.60	2.34	1.11
Lauryl alcohol (14.0)	2.03	2.34	0.87
Water (0.6)	2.66	2.34	1.14
n-Dodecane (15.0)	0.92	0.97	0.95

[a] [Fluorescer] = 1×10^{-3} M, 20.0 ± 0.5 °C. [b] $[(F_e/F_m)_{\text{dioxane}}/(F_e/F_m)_{\text{dioxane+add.}}$ for 2]/$[(F_e/F_m)_{\text{dioxane}}/(F_eF_m)_{\text{dioxane+add.}}$ for 3].

are considered. In the preceding paper,[3] we compared solvent effects on exciplex formation in monomeric and polymeric systems and interpreted the results as due to specific solvation of polymer chain resulting in changes in the composition of a micro solvent sphere around polymer molecules. In addition to the problem of specific solvation, a comparison of **2** and **3** should take into account hydrophobic interaction as a function of solvent composition. Since the magnitude of hydrophobic interactions between long polymethylene chains increases gradually with an increasing number of methylene units up to 15–16,[10] the contribution of hydrophobic interactions in exciplex formation is certainly more important in **3** than in **2**. From the viewpoint of both solvent polarity and hydrophobic interactions, the effect of solvent in reducing F_e/F_m should be in the order water ≫ ethyl alcohol > lauryl alcohol. This order agrees well with the experimental results. To achieve an arbitrary standard of solvent effects, the concentrations of additives were chosen so that F_e/F_m of **3** was constant at 0.04, and the relative effectiveness of these three protic solvents was compared for **2** and **3**. A 15 vol % was chosen for *n*-dodecane which is nonpolar and affords slight enhancement of F_e/F_m. The results are tabulated in Table I.

It is interesting to compare the relative effectiveness of solvents on exciplex intensity of **2** and **3** as given by the ratio of solvent effect on **2** to that on **3** (the rightmost column of Table I). Very polar solvents (water and ethanol) influence **2** more than **3** whereas lauryl alcohol has a stronger influence on **3** than on **2**. Apparently, the hydrophobic environment resulting from pendant ω-carbazolyldecyl groups would be a barrier separating water or ethanol from **3**. On the other hand, approach of lauryl alcohol to **3** seems to be facilitated by hydrophobic interactions between long polymethylene chains. The role of lauryl alcohol is disruption of the hydrophobic sphere around the polymer chain and/or to bring about a polar environment at the site of exciplex formation. Both effects would reduce the intensity of exciplex emission, particularly of **3**. When *n*-dodecene is added, the F_e/F_m value increases slightly. The interaction of *n*-dodecane, a nonpolar higher alkane, with **3** should be preferred to that with **2**, while the enhancing effect of *n*-dodecane on F_e/F_m is slightly weaker for **3** than for **2**. Disorganization of hydrophobic interactions between pendant decamethylene chains would in part offset the positive effect on *n*-dodecane on F_e/F_m caused by the reduction in polarity around the exciplex.

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Cryoscopy of Polyethylene Oxide Irradiated in Air

R. P. KUSY* and D. T. TURNER

Dental Research Center, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27514. *Received May 17, 1976*

It has been shown that the depression of the melting point caused by irradiation can be used to provide a convenient estimate of overall chemical changes in some crystalline polymers.[1–4] In order to formulate rules which will allow a more informed interpretation of such results, it is desirable to extend studies to all those polymers for which independent analyses of total chemical changes are known. Detailed analytical results of this kind are available for poly(ethylene oxide) (PEO) irradiated in vacuum,[5] and an investigation is in progress on corresponding cryoscopic changes.[6] A sidelight of this work stems from King's report that the radiolysis of PEO is remarkably sensitive to the presence of oxygen in air, giving *G* values of several hundred for scission of the macromolecules.[7] The limited objective of the present note is to report experiments designed to investigate whether or not a similar sensitivity can be detected by cryoscopy.

The sample studied was Polyox WSRN-750 (Union Carbide Corp.), a PEO having a weight average molecular weight of ca. 3×10^5 ($[\eta] = 253$ g^{-1} ml using an aqueous solution at 30 °C where $K = 12.5 \times 10^{-5}$ g^{-1} dl and $a = 0.78$[8]). The polymer was obtained in powdered form with a particle size such that 98% passed through a No. 20 USBS sieve.[9] Dry powder was exposed to γ rays from a Cs^{137} source at a dose rate of 0.85 Mrad/h and at an ambient temperature of 30 °C. To avoid depletion of oxygen at the particulate surfaces, the powder (ca. 100 mg) was spread over ca. 200 mm². Differential thermal analysis (DTA) scans were made on thoroughly mixed samples (10–20 mg) under nitrogen at a heating rate of 20 °C/min in a Dupont Model 990 apparatus. Irradiated samples were examined ¼–½ h after removal from the source to minimize contributions from relatively slow postirradiation reactions. Ten hours after a dose of 20 Mrad, the melting point of each run increased ca. 4 °C over its initial postirradiation value. A similar increase was observed over the same period after a dose of 35 Mrad. Further smaller postirradiation effects (<1 °C) occurred over the interval from 10 to 100 h.

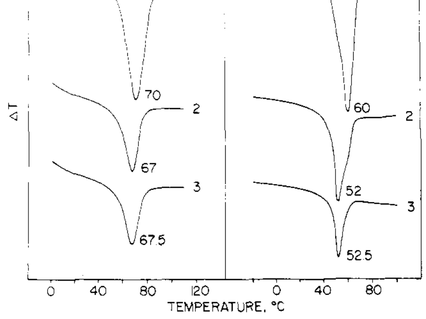

Figure 1. Thermograms for PEO irradiated in air: left set, 0 Mrad; right set, 14.1 Mrad. Consecutive runs numbered 1, 2, and 3.

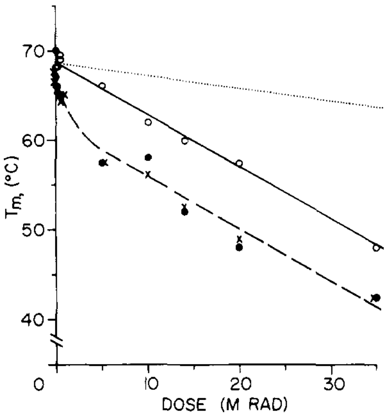

Figure 2. Depression of melting temperature of PEO irradiated in air: run 1, ○; run 2, ●; run 3, ×. The dotted line represents the linear extrapolation of data obtained by irradiation of PEO under vacuum (Table I, run 1).

Table I
Depression of Melting Temperature of PEO Irradiated under Vacuum[a]

Dose, Mrad	T_m, °C		
	Run 1	Run 2	Run 3
0	68.0	66.0	65.5
5	69.0	62.0	62.0
10	67.0	60.0	59.5
50	61.0	53.5	53.0
60	59.5	51.5	50.5
75	56.0	48.0	48.0
100	51.5	43.5	44.0
121	50.5	43.5	44.0
169	44.5	36.0	36.5
200	38.0	27.5	28.0

[a] 10^{-5}–10^{-7} Torr.

Values for the number of repeat units affected per 100 eV dose, G(−units), were calculated from eq 1 in which M is the molecular weight of one unit, N is Avogadro's number, and D is the dose in Mrad (1 Mrad = 6×10^{19} eV/g). The mole fraction of units which survives irradiation without chemical change (X) is calculated from eq 2[10] in which T_0 and T are the melting points before and after irradiation, respectively. R is the gas constant, taken as approximately 2 cal/mol °C. With a choice of $M = 44$, the corresponding value of the heat of fusion per mole of crystalline units, ΔH_u, is 1980 cal.[11] The general use of eq 2 to estimate chemical damage caused by irradiation was discussed previously.[1-4] In the present system in which the scission reaction is believed to predominate, the use of eq 2 implies that one repeat unit is excluded from the crystalline regions per scission.

$$G(-\text{units}) = \frac{(1-X)N}{M}\,\frac{10^2}{6 \times 10^{19}\,\text{D}} \qquad (1)$$

$$(1/T) - (1/T_0) = (-R/\Delta H_u) \ln X \qquad (2)$$

Thermal analysis of the unirradiated powder yielded a single endotherm indicating an average melting temperature of 342 ± 1 °C (Figure 1). Although on occasion a slight shoulder was detected in the scan of irradiated samples, in general the appearance resembled that of the unirradiated sample (cf. Figure 1, left and right). After heating to more than 30 °C above the melting peak, each sample was quenched with liquid nitrogen to subambient temperatures. On rescanning, lower melting temperatures were measured, a result observed previously for other polymers[1-4] (Figures 1 and 2, runs 2 and 3). For reasons discussed in earlier work,[1] however, calculations of G values will be confined to results obtained in run 1.

The straight line drawn through data obtained in run 1 (Figure 2) indicates a depression of the melting point of 0.59 °C/Mrad. Use of this result in eq 1 and 2 with T_0 = 341.5 °C gives a value of G(−units) = 110. This result confirms the large values reported previously by King on the basis of viscosity data, i.e., G(scissions) of 210, 185, and 250 for doses of 0.1, 0.2, and 0.4 Mrad, respectively, and is consistent with the theory of an oxidation chain reaction.[7] The magnitude of the G values can be put in perspective if a comparison is made (Figure 2) between powdered samples irradiated in air (solid line, run 1) and those irradiated under vacuum (dotted line, run 1). The latter result was obtained from the linear extrapolation of data measured; for the most part, at doses ≥50 Mrad (Table I). Such information yields a much smaller value of G(−units) $\simeq$ 30 for samples irradiated with vigorous exclusion of air.[6] This value is about twice as great as the G value for chemically changed units inferred from analytical data[5] and is the subject of a detailed investigation involving geometrical, thermal, dose rate, and molecular weight effects.

A referee has pointed out that it would be preferable to make a direct comparison with our own estimates of G(scissions). In fact we did make measurements of changes in limiting viscosity number of PEO with dose but were unable to derive reliable estimates of number average molecular weight because we did not know the initial molecular weight distribution of the polymer. We do know that the distribution of polymers of this type can be very broad; for example, a value of $\overline{M}_w/\overline{M}_n$ = 22 has been reported.[12] Therefore, any estimate would be subject to considerable error as the distribution approaches a value of two on irradiation as a result of random scission. Under these circumstances, we preferred to rely on King's estimate,[7] since he is an authority on PEO.

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