Cryoscopy of γ-Irradiated Poly(ethylene oxide)

R. P. Kusy* and D. T. Turner

Dental Research Center, University of North Carolina,
Chapel Hill, North Carolina 27514. *Received November 23, 1976*

ABSTRACT: Poly(ethylene oxides) were exposed in vacuum both to γ rays and to high-energy electrons. The depression of the melting point was measured by differential thermal analysis. The depression was found to be 0.15 K/Mrad, independent of sample geometry, molecular weight, heat treatment, dose, and dose rate. From the equation, $T^{-1} - T_0^{-1} = -R\Delta H_u^{-1} \ln X$, it was estimated that 27 repeat units (–O–CH$_2$–CH$_2$–) were excluded from the crystalline lattice per energy deposition of 100 eV. This value exceeds the number of units chemically changed, mainly by cross-linking and fracture, by a factor of 2. It is suggested that the discrepancy is due mainly to each cross-link excluding more than two units in the cryoscopic estimate.

Exposure of a polymer to high-energy radiation causes chemical changes, such as fracture and cross-linking, in a fraction of the repeat units. In a crystalline polymer there is an accompanying depression of the melting temperature and the question has been raised as to whether this observation can be correlated with the total chemical change. As a first approach, two simple working hypotheses have been made: The first is that any kind of chemical change to a repeat unit removes one crystallizing unit from the equilibrium between crystal and melt. On this basis a fracture and a cross-link are counted as removing one and two units, respectively. The second working hypothesis is that melting can be analyzed by reference to the equilibrium between a one-component crystal (unchanged repeat units only) and a two-component melt (unchanged repeat units plus all species of chemically changed units).

The above hypotheses may appear too simplistic but, nevertheless, a consistent and relatively simple pattern has been recognized. The ratio of the cryoscopic to chemical estimates for radiation damage (Table I) ranges from only about one to two for polyoxymethylene,[1] polytetrafluoroethylene,[2] poly(ethylene terephthalate),[3] polyethylene,[3] and poly(hexamethylene adipamide).[3] The ratio is much greater than two for the following polymers: *trans*-1,4-polyisoprene,[3] isotactic poly(methyl methacrylate),[4,5] and polypropylene.[3] This latter discrepancy is attributed to neglect of a contribution to the chemical estimates from changes in stereochemistry. Qualitatively, such changes are known to result from irradiation but they cannot be taken into account until quantitative analyses have been achieved.

The present objective is to extend the comparison of cryoscopic and chemical estimates of radiation damage to include poly(ethylene oxide) (PEO(/ This polymer was chosen because reliable estimates of chemical change have been reported and also because of the absence of complications involving stereochemistry.

Experimental Section

The commercially available powders studied are listed in ascending molecular weight (Table II). The repeat unit for PEO is (–O–CH$_2$–CH$_2$–); the end groups are mainly hydroxyl groups. The lower molecular weight polymers are linear and monodisperse, while the higher molecular weight polymers are polydisperse ($\overline{M}_w/\overline{M}_n > 20$).[17]

Sheets were made by melting the powders at 80 °C (Grade 4000) or 110 °C (WSRN 750 and WSRN Coag) for >5 h followed by slow cooling at about 5 °C/h. Using this procedure large spherulites formed in the polymer of lowest molecular weight. In contrast the higher molecular weight specimens did not flow sufficiently to form a film but, instead, formed coherent mats. Several specimens were given a variety of other heat treatments before and/or after irradiation. As these treatments had no significant influence on estimates of $G(-\text{units})$, the details are limited to figure captions.

Specimens were outgassed for 4–48 h and sealed under vacuum (5×10^{-5} to 5×10^{-7} Torr). Most specimens were exposed to γ rays from a Cs-137 source at a dose rate ($\dot{D}$) of 0.85 Mrad/h with an ambient temperature ca. 30 °C. The other specimens were exposed to 9.7 MeV electrons from a linear accelerator at an average dose rate of 1.8×10^3 Mrad/h. The dose was built up in 5 Mrad increments with water cooling at 14 °C.

After irradiation, specimens were stored under vacuum until they were scanned in a differential thermal analyzer (Du Pont 990 DTA) under dry nitrogen at a heating rate ($\dot{R}$) of 20 °C/min (exception, Figure 4). Immediately after completion of melting, specimens were quenched with liquid nitrogen to subambient temperatures before making further runs. Rigorous exclusion of oxygen, both during and after irradiation, was necessary in order to get reproducible results. The great influence of oxygen or radiation-induced changes in melting was reported previously ($G(-\text{units}) = 110$, cf. ref 18).

Results

Melting temperatures, recorded as endothermic peaks (T_m), are shown for the various weight average molecular weights ($\overline{M}_w$) (Figure 1). The wide range of values observed at a given molecular weight (ca. 6 °C) is due, in part, to the different sample geometries, i.e., as received powder vs. cast sheet. Nevertheless for a particular geometry the melting point scatter could be reduced by limiting measurements to rigorously outgassed specimens. This procedure was followed in obtaining the results subsequently reported.

The definition of a precise value of T_m by a DTA scan is sometimes difficult. The definition achieved in the present work (±1 °C) is documented by a display of thermograms for initial and irradiated specimens (Figure 2). The specimens of low molecular weight often gave thermograms with shoulders and subsidiary peaks (Figure 2a). In such cases the major endotherm was taken as T_m. This procedure became unsatisfactory for doses >100 Mrad because two peaks of comparable intensity were observed. Simpler one-peak thermograms were noted for higher molecular weight specimens (Figures 2b and 2c) even for doses >200 Mrad. As in previous work, greatest reliance is placed on values of T_m obtained in first runs, since complications due to reorganization of crystallites are minimized when the endothermic peak is approached rapidly. Although the second and third runs give lower values of T_m for high molecular weight PEO, these values are reported because they reinforce the conclusions on radiation-induced depression of T_m (Figure 2).

Plots of T_m vs. radiation dose are shown in Figure 3 for powders and sheets exposed at both low and high dose rates. Results for the low molecular weight specimen are scattered. A least-squares line is drawn for all data, including results of second and third runs, giving a depression of T_m of 0.158 K/Mrad (Figure 3a). For the higher molecular weight specimens, the data are less scattered and a distinction is made between the first and subsequent runs (Figures 3b and 3c; cf. upper and lower plots). In the first runs the linear regression analyses for all data shown in Figure 3b and for "●" data

Table I
Comparison of G Values from Cryoscopic vs. Chemical Techniques

Polymer	G(−units) from cryoscopy (A)	G(−units) from chemical analysis (B)	(A)/(B)	Ref
Polyoxymethylene	20	24	0.83	1, 6
Polytetrafluoroethylene	3.3	3.0	1.1	2, 7
Poly(ethylene terephthalate)	0.6	0.45	1.3	3, 8, 9
Polyethylene	7.0	4.9	1.4	3, 10
Poly(hexamethylene adipamide)	9.0	5.8	1.5	3, 11
trans-1,4-Polyisoprene	68	18	3.8	3, 12–14
Isotactic poly(methyl methacrylate)	12	1.7	7.1	4, 5, 15
Polypropylene	47	2.8	17	3, 16

Table II
Summary of PEO Polymers Studied

Designation	$\overline{M}_w$	Manufacturer
Grade 1500	1.5×10^3	Polysciences
Grade 4000	3.4×10^3	Polysciences
WSRN 750	3×10^5	Union Carbide
WSRN 3000	6×10^5	Union Carbide
WSRN Coag	$>5 \times 10^6$	Union Carbide

shown in Figure 3c provide the preferred experimental estimate for the depression of the melting point of 0.150 K/Mrad. Note that this value is insensitive to sample geometry and dose rate (cf. other data of Figure 3c).

The results of other experiments can be summarized as unsuccessful attempts to find conditions under which the depression of the melting point departed significantly from the value of 0.15 K/Mrad cited above. One of the variables examined was the heating rate used during the DTA scan. As expected, the faster the heating rate the higher the value recorded for T_m. This effect is illustrated with results obtained with the specimen of highest molecular weight (Figure 4). Despite this dependence the *depression* of the melting point is independent of heating rate, in the range 1 to 50 °C/min, as shown by the constancy of slopes of data obtained in the first runs (Figure 4; top). A similar trend was confirmed, for doses >20 Mrad, from results obtained in second and third runs (Figure 4; bottom). A variety of pre- and/or post-irradiation heat treatments significantly affected the initial value of T_m. However, the *depression* of the melting temperature per unit dose was little affected. These treatments were chosen to test various ideas which seemed important at the time but now serve only to document the general viewpoint that the depression of the melting point is insensitive to a wide range of experimental conditions (cf. Figure 5 with Figure 3c).

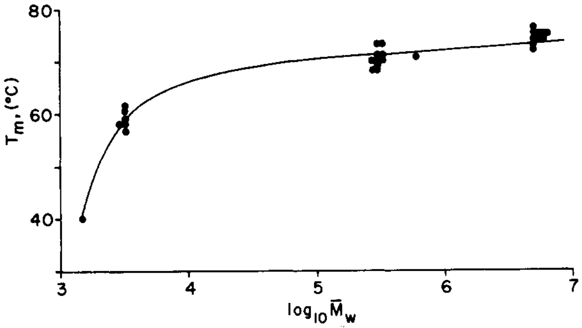

Figure 1. Influence of weight average molecular weight on the melting point of PEO ($\dot{R}$ = 20 °C/min, run No. 1).

Discussion

G Values from Chemical Analysis.[19] The radiation chemistry of PEO has been elucidated by the work of Fischer, Hellwege, Johnsen, and Langbein. Poly(ethylene oxides), $HO(-CH_2-CH_2-O-)_nH$, of molecular weights 2000, 4000, and 20 000 were irradiated in vacuum with 1 MeV electrons at a dose rate of 10 Mrad/min at 14 °C. Successful material bal-

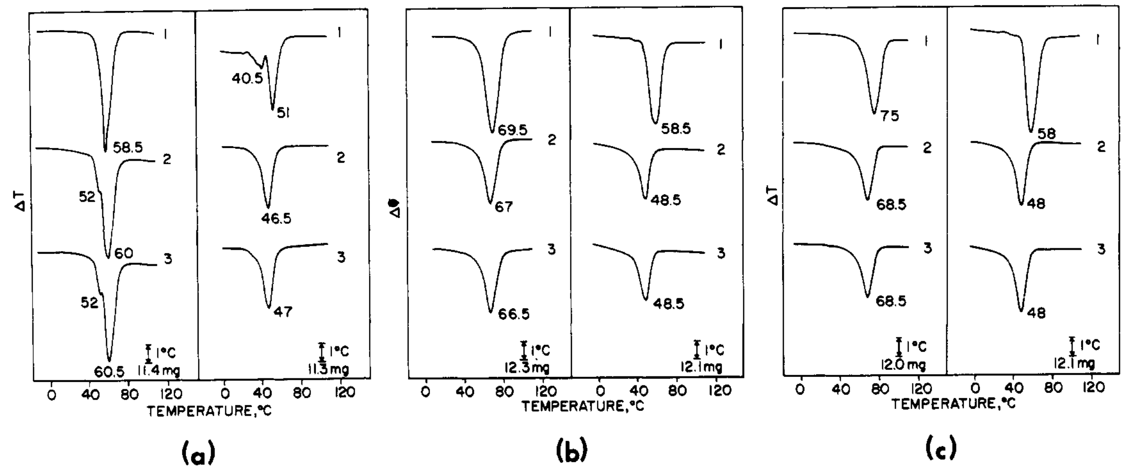

Figure 2. Thermograms of PEO: (a) Grade 4000; (b) WSRN 750; and (c) WSRN Coag. Left and right half of each frame represents melting data for three successive runs at 0 and 100 Mrad, respectively ($\dot{R}$ = 20 °C/min; sheet or mats; $\dot{D}$ = 0.85 Mrad/h).

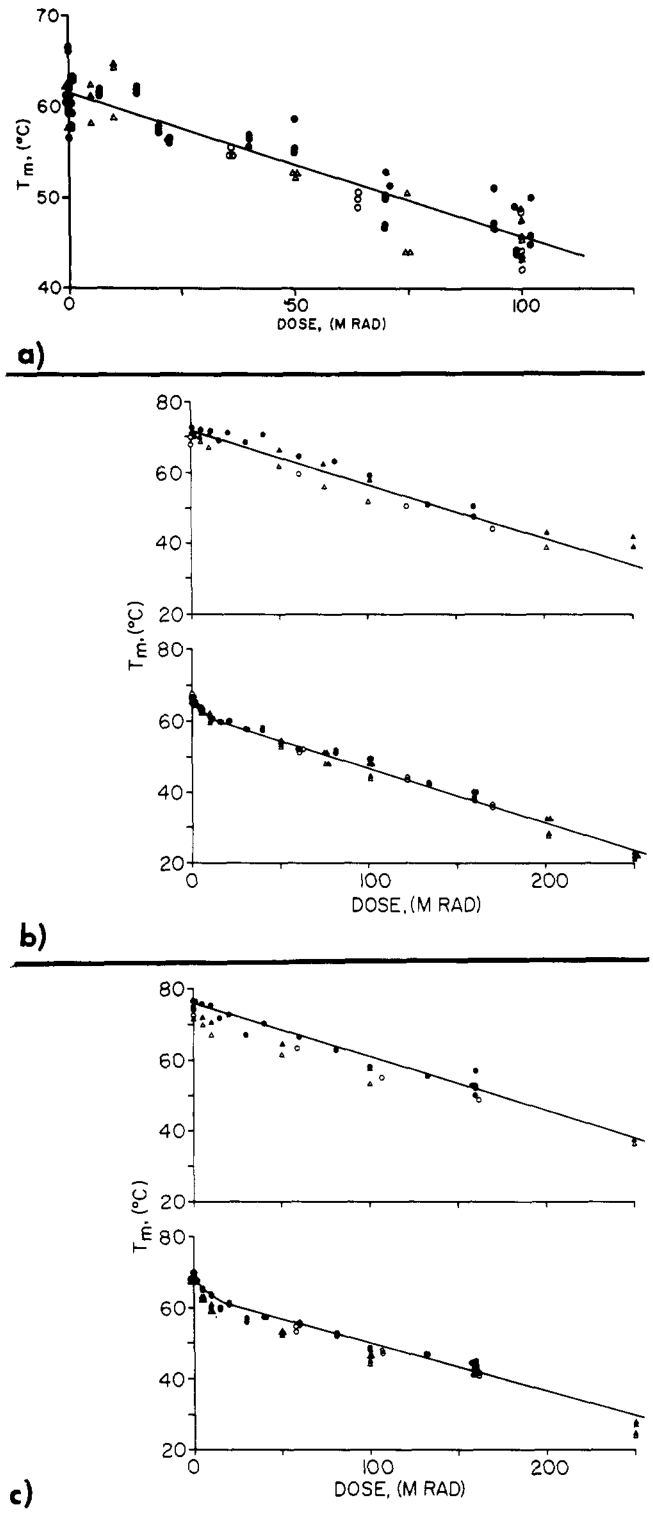

Figure 3. Influence of dose on T_m of PEO with variation of molecular weight: (a) Grade 4000; (b) WSRN 750; and (c) WSRN Coag. (●) sheet, $\dot{D}$ = 0.85 Mrad/h; (▲) sheet, $\dot{D}$ = 1.8 × 10^3 Mrad/h; (○) powder, $\dot{D}$ = 0.85 Mrad/h; (△) powder, $\dot{D}$ = 1.8 × 10^3 Mrad/h. For Grade 4000 runs 1, 2, and 3 are not distinguished. Top halves of frames (b) and (c) show melting point data for run 1, while bottom halves of frames (b) and (c) show melting point data for runs 2 and 3.

ances were established for cross-link (c) and fracture (F) reactions as follows:

$$G(H_2) = G(c) + G(R_1CH{=}CHR_2)$$
$$(4.7 \pm 0.3) \simeq (3.3 \pm 0.2) + (0.90 \pm 0.04)$$

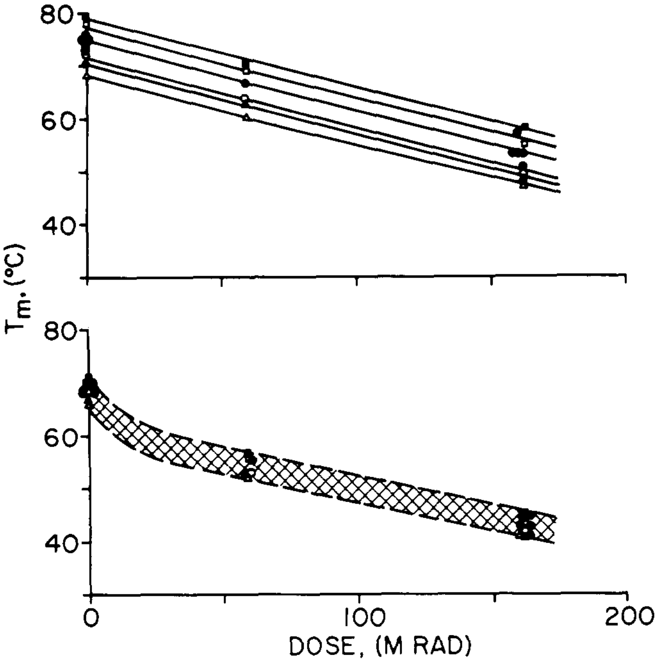

Figure 4. Influence of dose on T_m of WSRN Coag as a function of heating rate: (■) $\dot{R}$ = 50 °C/min; (□) $\dot{R}$ = 35 °C/min; (●) $\dot{R}$ = 20 °C/min; (○) $\dot{R}$ = 10 °C/min; (▲) $\dot{R}$ = 5 °C/min; (△) $\dot{R}$ = 1 °C/min. (Upper frame, run 1; lower frame, runs 2 and 3; sheet; $\dot{D}$ = 0.85 Mrad/h.)

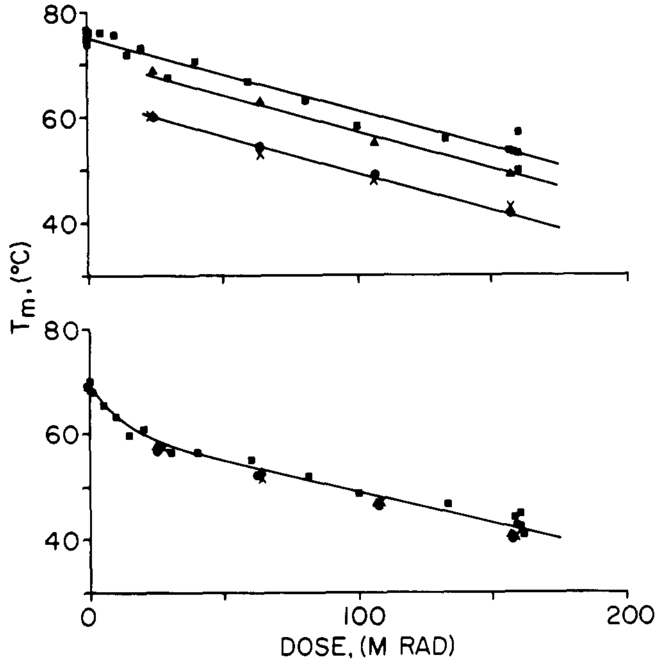

Figure 5. Influence of dose on T_m of WSRN Coag as a function of heat treatment: (■) no heat treatment; (▲) heated 1000 min at 66 °C, then irradiated; (X) irradiated, then heated 1000 min at 66 °C; (●) heated 1000 min at 66 °C, irradiated, and then heated 1000 min at 66 °C. Note that all specimens were quenched in $N_{2(l)}$ after each heat treatment step. (Upper frame, run 1; lower frame, runs 2 and 3; sheet; $\dot{D}$ = 0.85 Mrad/h; $\dot{R}$ = 20 °C/min.)

$$G(F) = G(\text{-OH}) + G(C{=}O)$$
$$(3.9 \pm 0.2) \simeq (3.6 \pm 0.1) + (0.4 \pm 0.03)$$

These balances refer to G values for hydrogen gas, olefin groups, and hydroxyl and carbonyl end groups. In addition, gaseous products other than hydrogen were measured but these were negligible (total G value <0.18).

On the basis of the above data a G value can be estimated for all reacted units:

$$\begin{aligned} G(\text{chemically reacted units}) &= 2G(\mathrm{H_2}) + G(\mathrm{F}) \\ &= 2 \times 4.7 + 3.9 \\ &\simeq 13 \end{aligned}$$

The chemical analyses indicated that the G value of 13 remains approximately constant for doses up to several hundred Mrad (i.e., in the same range in which constant values were subsequently established for the depression of the melting point).

***G* Values by Cryoscopy.** Following the procedure used in previous papers in this series[1-5,18] a value for units excluded from the crystalline lattice per 100 eV energy deposition, $G(-\text{units})$, is calculated from eq 1 and 2. T_0 and T are respectively the melting points (K) before and after a dose of D Mrad (1 Mrad = 6×10^{19} eV/g). X is the mole fraction of repeat units, taken as $\text{-O-CH}_2\text{CH}_2\text{-}$ (M = 44 g/mol). A corresponding value of the enthalpy of fusion, ΔH_u = 1980 cal/mol, was derived by Mandelkern from results obtained in studies on the influence of diluents on depression of the melting point.[20] Other values obtained on polymers covering a wide range of molecular weights are similar, ranging from 1750 to 2800 cal/mol.[21,22] The other factors in eq 1 and 2 are the gas constant, R = 2 cal/(mol K), and Avogadro's number, $N = 6 \times 10^{23}$.

$$\frac{1}{T} - \frac{1}{T_0} = \frac{-R}{\Delta H_u} \ln X \qquad (1)$$

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

$$G(-\text{units}) \simeq \frac{\Delta H_\mathrm{u}}{R} \frac{(T_0 - T)}{T T_0} \frac{N}{M} \frac{10^2}{6 \times 10^{19} D} \qquad (3)$$

By re-arrangement of eq 1 and 2 using the approximation $-\ln X = (1 - X)$, the depression of the melting point per unit dose $(T_0 - T)/D$ is revealed as the important experimental factor (eq 3). This factor is approximately constant despite unusually wide variations in experimental conditions ($(T_0 - T)/D$ = 0.150 K/Mrad). The corresponding G value, from eq 1 and 2, is $G(-\text{units})$ = 27.

Comparison of Chemical and Cryoscopic Estimates. The cryoscopic estimate (27) exceeds the chemical estimate (13) by a factor of 2. Although in previous work such a discrepancy was accepted without further analysis, the results obtained for PEO by both chemical and cryoscopic analysis appear sufficiently reliable to justify more detailed consideration. It is suspected that the discrepancy lies mainly in the assumption that the chemical reaction of one repeat unit also reduces the number of crystallizable units by one. This assumption will be examined for the two major chemical changes in which repeat units are fractured or cross-linked.

One approach to the consequences of fracture would be by reference to Flory's analysis of the influence of molecular weight on melting point. For a polymer with a random molecular weight distribution the appropriate relationship is given by eq 4, in which $\overline{X}_n$ is the average number of repeat units per macromolecule.[23] This equation is more directly comparable with an approximate form of eq 1 obtained by substituting $-\ln X = (1 - X) = X_\mathrm{B}$; X_B represents the mole fraction of repeat units chemically changed (eq 5).

$$\frac{1}{T} - \frac{1}{T_0} = \frac{R}{\Delta H_\mathrm{u}} \frac{2}{\overline{X}_n} \qquad (4)$$

$$\frac{1}{T} - \frac{1}{T_0} = \frac{R}{\Delta H_\mathrm{u}} (1 - X) = \frac{R}{\Delta H_\mathrm{u}} X_\mathrm{B} \qquad (5)$$

From a comparison of eq 4 and 5 each macromolecule, and hence each fracture, should be counted as removing two units from the total of crystallizable units. This is in contrast to the first hypothesis which counted each fracture as removing only one unit. In order to judge the importance of this difference in the present work, theoretical values for the depression of the melting point per unit dose were computed for both cases (Table III). Relative to the larger discrepancy with the experimental value, it makes little difference whether a fracture is assumed to remove one or two units.

Table III
Comparison of Experimental and Calculated Values of $(T - T_0)/D$

	Calcd (eq 1 and 2) on basis of $G(-\text{ units}) \equiv$	
Exptl	$2G(\mathrm{H_2}) + G(\mathrm{F}) = 13.3$	$2G(\mathrm{H_2}) + 2G(\mathrm{F}) = 17.2$
0.150 K/Mrad	0.069 K/Mrad	0.090 K/Mrad

With respect to the general reliability of eq 4, satisfactory agreement was observed for experimental data in which the dependence of melting point on molecular weight was tested for a number of polymers.[24] More specifically, in a study of monodisperse samples of PEO, good agreement was reported between experimental data and eq 4, suitably modified for such a molecular weight distribution.[22]

A more serious cause of discrepancy between cryoscopic and chemical analysis is likely to reside in the assumption about the influence of cross-links on the depression of the melting point. There is no theoretical treatment to give direct guidance in this matter but it may be pursued provisionally by treating one cross-link as equivalent to two copolymer units, i.e., two cross-linked units. The influence of randomly distributed copolymer units on the depression of the melting point has been treated by Flory with derivation of eq 1 (mole fraction of copolymer units = $1 - X$).[25] However, it has been pointed out that although eq 1 correctly predicts the functional relationship between T and X it generally underestimates values of ΔH_u by a factor of about 2.[26] An alternative interpretation of this discrepancy is that eq 1 involves approximately correct values of ΔH_u but underestimates the depression of the melting point. For example, cryoscopic data have been reported by Simon and Rutherford for copolymers of ethylene oxide with up to a few mole percent of either styrene oxide or butylene oxide.[27] Their data can be interpreted as indicating that the actual depression of the melting point exceeds that predicted from eq 1, assuming ΔH_u constant, by a factor of about 2. A discrepancy of this kind would account, qualitatively, for the higher values obtained by cryoscopy using eq 1 in the present work. However, as Simon and Rutherford expressed doubt about the randomness of their copolymers, their data will not be used to draw quantitative conclusions.

Conclusions

(1) Irradiation of PEO in vacuum results in a depression of the melting point of 0.15 K/Mrad.

(2) This value is insensitive to wide variations in molecular weight, sample geometry, heat treatment, dose rate, and dose.

(3) Cryoscopic data indicate that 27 repeat units are excluded from the equilibrium between crystal and melt per 100 eV of absorbed energy.

(4) The cryoscopic estimate exceeds the total of units chemically changed, i.e., 13 units/100 eV, because each cross-link excludes more than two units.

Acknowledgments. We wish to thank Ms. S. Shope and Ms. B. Lytwyn for their assistance with the experimental work and the U.S. Army Natick Development Center and the U.N.C. Physics Department for use of the linear accelerator and Cs-137 source, respectively. This investigation was supported by USPHS Research Grant No. DE 02668 from the National Institute of Dental Research and, in part, by General Research Support Grant No. RR 05333 from the General Research Support Branch of the National Institutes of Health.

References and Notes

(1) R. P. Kusy and D. T. Turner, *Macromolecules,* 8, 235 (1975).
(2) R. P. Kusy and D. T. Turner, *J. Polym. Sci.,* **10,** 1745 (1972).
(3) R. P. Kusy and D. T. Turner, *Macromolecules,* **4,** 337 (1971).
(4) R. P. Kusy and D. T. Turner, *J. Polym. Sci.,* **12,** 2137 (1974).
(5) R. P. Kusy, *J. Polym. Sci.,* **14,** 1527 (1976).
(6) H. Fischer and W. Langbein, *Kolloid Z. Z. Polym.,* **216,** 329 (1967).
(7) R. E. Florin and L. A. Wall, *SPE Trans.,* **3,** 1 (1963).
(8) S. D. Burow, G. F. Pezdirtz, G. F. Sands, and D. T. Turner, *J. Polym. Sci., Part A-4,* **4,** 613 (1966).
(9) D. T. Turner, *Adv. Chem. Ser.,* **No. 66,** 127 (1967).
(10) H. Y. Kang, O. Saitô, and M. Dole, *J. Am. Chem. Soc.,* **89,** 1980 (1967).
(11) J. Zimmerman, *J. Appl. Polym. Sci.,* **2,** 181 (1959).
(12) D. T. Turner, *Polym. Lett.,* **4,** 717 (1966).
(13) M. A. Golub and J. Danon, *Can. J. Chem.,* **43,** 2772 (1965).
(14) M. A. Golub and J. Danon, *Can. J. Chem.,* **42,** 1577 (1964).
(15) M. Dole, "The Radiation Chemistry of Macromolecules", Vol. II, Academic Press, New York, N.Y., 1973, Chapter 6.
(16) W. Schnabel and M. Dole, *J. Phys. Chem.,* **67,** 295 (1963).
(17) H. G. Elias, *Angew. Chem.,* **73,** 209 (1961).
(18) R. P. Kusy and D. T. Turner, *Macromolecules,* **10,** 217 (1977).
(19) H. Fischer, K.-H. Hellwege, U. Johnsen, and W. Langbein, *Makromol. Chem.,* **91,** 107 (1966).
(20) L. Mandelkern, *Chem. Rev.,* **56,** 903 (1956).
(21) D. R. Beech and C. Booth, *J. Polym. Sci., Part B,* **8,** 731 (1970).
(22) W. Braun, K.-H. Hellwege, and W. Knape, *Kolloid Z. Z. Polym.,* **215,** 10 (1967).
(23) P. J. Flory, *J. Chem. Phys.,* **17,** 223 (1949).
(24) L. Mandelkern, "Crystallization of Polymers", McGraw-Hill, New York, N.Y., 1964, Chapter 2.
(25) P. J. Flory, *Trans. Faraday Soc.,* **51,** 848 (1955).
(26) L. Mandelkern, ref 24, Chapter 4, p 90.
(27) F. T. Simon and J. M. Rutherford, Jr., *J. Appl. Phys.,* **35,** 82 (1964).