Radiation Chemistry of Polymers Studied by Depression of Melting Temperature

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

Department of Metallurgical Engineering, Drexel University, Philadelphia, Pennsylvania 19104. *Received December 10, 1970*

ABSTRACT: The depression of the melting temperature from ^{60}Co γ irradiation of various polymers has been measured by differential scanning calorimetry. In the case of nylon-66 and poly(ethylene terephthalate), use of Flory's equation provided an estimate of the loss of crystalline units which was within a factor of 2 of values adduced from the literature for chemically changed units. A similar agreement was adduced from literature values for a number of polyethylene samples. Moreover, in this case a measure of agreement for a variety of samples and irradiation conditions suggests that the depression of the melting temperature has the advantage of being relatively insensitive to the detailed nature of the chemical change. In similar studies of gutta-percha and polypropylene, the loss of crystalline units appeared greater than the number of units chemically changed. In the case of gutta-percha it is suggested that this is due to mobility in the low-melting crystal which allows cross-links, formed by irradiation, to assume their preferred stereochemistry with the result that adjacent isoprene units are unable to fit in the crystal lattice. In the case of polypropylene it is suggested that the discrepancy is due to failure to take into account changes in tacticity.

Progress in the radiation chemistry of polymers has been hindered because of a lack of convenient analytical techniques and in particular of ones which may be used to study changes in the solid state. The objective of the present work is to evaluate information concerning depression of the melting temperature resulting from γ irradiation of polymers, using differential scanning calorimetry (dsc) which has the advantage of being rapid and of requiring only a small mass of sample. Similar advantages are obtained by use of differential thermal analysis, and this method has been suggested as a means of monitoring radiation damage in organic compounds.[1] Previous studies of depression of the melting point resulting from irradiation of polymers have been confined to polyethylene[2,3] and natural rubber[4] and have been limited in scope because of adoption of very slow heating rates. In general, these earlier studies were pursued with different objectives from those prompting the present work, but it should be noted that Dole and Howard used a melting equation, derived by Flory, to estimate the number of units of polyethylene excluded from the crystal lattice by irradiation. Moreover, they pointed to an order of magnitude agreement with an estimate of chemically damaged units as judged by the yield of hydrogen gas.

Experimental Section

Samples of polymer were degassed and sealed under vacuum in ampoules which were exposed to ^{60}Co γ rays at a dose rate of 3 Mrad/hr at an ambient temperature of about 40°. Several days after irradiation the ampoules were opened and samples of about 5 mg rapidly transferred to a nitrogen atmosphere in the dsc unit of a Du Pont thermal analyzer (Model 900). The temperature was raised at 20°/min to just above the melting range, whereupon the sample was quenched and a second run made under similar conditions. In many cases this procedure was repeated to check that a reproducible value was obtained for the endothermic peak, this being recorded as a "melting point." The high rates of heating used resulted in an overestimate of the melting point by several degrees in the case of well-defined samples. For example, benzoic acid gave values of 124 and 126° at heating rates of 10 and 20°/min, respectively, as compared to the literature, equilibrium, value of 121°. However, this lack of absolute precision is relatively unimportant in estimates of depression of the melting point (*cf.* ref 5). Samples not immediately examined, as described above, were stored under vacuum.

Analysis of Data

Following previous workers,[2] Flory's equation[6] is used to relate the mole fraction of crystalline units after irradiation, X, to values of the melting point before ($X = 1$) and after irradiation, T_0 and T, respectively. R is the gas constant, taken approximately as 2 cal/mol deg, and ΔH is the enthalpy of fusion in calories per mole of crystalline units which is to be specified subsequently for each polymer in turn (eq 1).

A G value for the number of crystalline units excluded from the crystal per energy deposition of 100 eV, $G(-$ units), is calculated from eq 2. M is the molecular weight of the "crystalline unit," N is Avogadro's number taken approximately as 6×10^{23}, and D is the dose in Mrad with 6×10^{19} as a factor to convert this energy deposition to units of electron volts per gram.

$$\frac{1}{T} - \frac{1}{T_0} = \frac{-R}{\Delta H} \ln X \tag{1}$$

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

Equation 2 is rather insensitive to the choice of "crystalline unit" but for the sake of being definite the latter will be taken as the portion of a polymer molecule accomodated in the unit cell along the c axis, *e.g.*, $-OCOC_6H_4COOCH_2CH_2-$ in the case of poly(ethylene terephthalate), etc. (see ref 7).

The choice of chemical data to provide values of G (units chemically changed), for comparison with $G(-$ units), involves a subjective element at present because analytical data may be incomplete or in dispute.[8] The type of reasoning involved may be exemplified in the case of polyethylene where the stoichiometry relative to hydrogen evolution is reported as[9]

(1) C. B. Murphy and J. A. Hill, *Nucleonics*, **18**,78 (1960).
(2) M. Dole and W. H. Howard, *J. Phys. Chem.*, **61**, 137 (1957).
(3) L. Mandelkern, D. E. Roberts, J. C. Halpin, and F. P. Price, *J. Amer. Chem. Soc.*, **82**, 46 (1960).
(4) D. E. Roberts and L. Mandelkern, *ibid.*, **82**, 1091 (1960).
(5) B. Kee, "Newer Methods of Polymer Characterization," Polymer Reviews, Vol. 6, Interscience, New York, N. Y., 1964, Chapter 9.
(6) P. J. Flory, *J. Chem. Phys.*, **15**, 684 (1947); **17**, 223 (1949).
(7) C. W. Bunn, "Chemical Crystallography," 2nd ed, Clarendon Press, Oxford, 1961.
(8) D. T. Turner, *J. Polym. Sci., Part D*, in press.
(9) H. Y. Kang, O. Saitô, and M. Dole, *J. Amer. Chem. Soc.*, **89**, 1980 (1967).

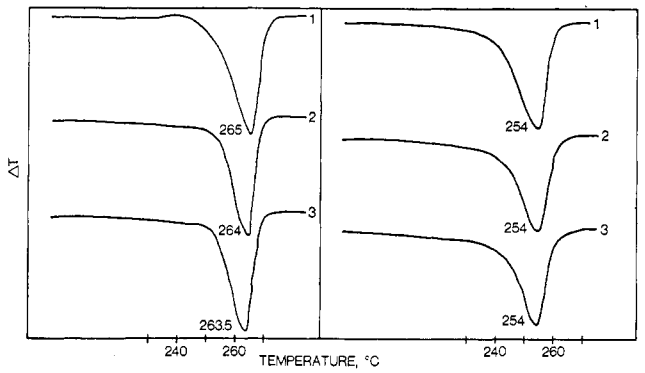

Figure 1. Thermograms for nylon: left set, 0 Mrad; right set, 76.5 Mrad. Consecutive runs numbered 1, 2, and 3.

$$G(H_2) \simeq G(\text{cross-links}) + G(\text{double bonds}) + 2G(\text{conjugated diene})$$
$$3.7 \qquad 1.0 \qquad 2.4 \qquad 0.5$$

On this basis the following approximation may be suggested

$$G(\text{units chemically changed}) \cong 2G(\text{cross-links}) + G(\text{double bonds}) + 2G(\text{conjugated diene}) \cong 4.9$$

In addition, there are probably other changes involving direct fracture of the carbon–carbon chain and other changes in unsaturation, but in a first approach these are judged to be minor and are neglected.

Similar summation procedures will be attempted subsequently for gutta-percha and PET but in these cases the units are more complex and analysis is correspondingly more difficult. For example, the *trans*-1,4-isoprene unit in gutta-percha is expected to be involved in further reactions involving double bonds, such as isomerization and addition.

In most other polymers analysis of products is too incomplete to proceed on the above basis. However, in some cases it may be judged that a considerable fraction of the chemically changed units have free radical precursors, in which case reference may be made to G(polymer free radicals); this procedure will be followed in the case of nylon-66.

Results

Nylon-66. A sample of Zytel 101 powder, of particle size 50–200 μ, was donated by E. I. du Pont de Nemours. First, second, and third runs for an unirradiated control and for the sample given the maximum dose of 76.5 Mrad are shown in Figure 1. The observed melting temperature of *ca.* 265°, for the unirradiated sample, is consistent with values reported in the literature.[10] The depression of the melting temperature appears to be relatively insensitive to the run number when results are viewed over the range of doses studied (Figure 2). A straight line drawn through data obtained of the first runs indicates a depression of the melting point in 0.09°/Mrad. Taking M = 226 g and ΔH = 11,200 cal/226 g[11] gives $G(-$ units$) = 9$.

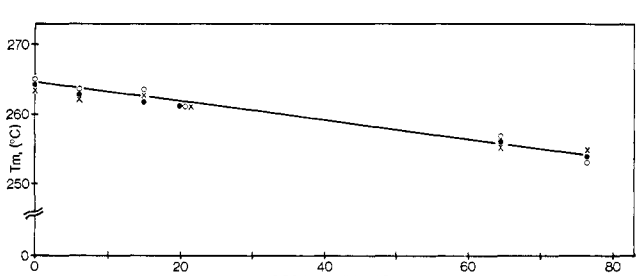

Figure 2. Depression of melting point of nylon on irradiation: run 1, ○; run 2, ●; run 3, ×.

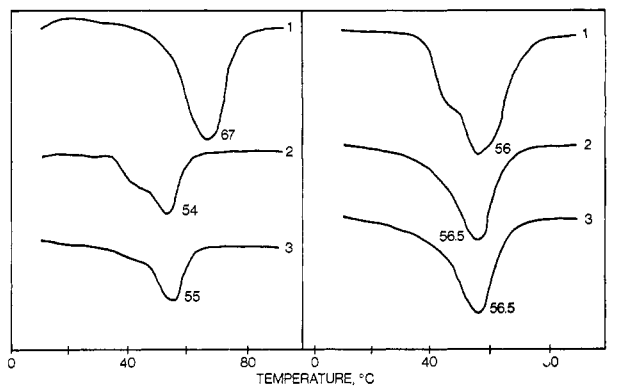

Figure 3. Thermograms for gutta-percha: left set, α form; right set, β form.

Various types of chemical damage have been reported in nylon-66 as a result of irradiation, including formation of cross-links and fractures,[12] but a quantitative total for product analysis still seems uncertain. Nevertheless, if estimates of free radical formation are taken as indicative of permanent damage to the unit, then the agreement between the two methods is close, *cf.* G(free radicals) = 5.8.[13]

Gutta-percha. A sample of Pahang gutta-percha (obtained from Dr. M. R. Porter of The Natural Rubber Producers' Research Association) was purified by recrystallization from petroleum ether in the dark under nitrogen. The sample melted near 65° and could be recrystallized at slow rates to give a similarly high melting form. A form with a lower melting point near 54° was obtained by quenching the melt, at 100°, in liquid nitrogen. Following Bunn, these forms are designated as α and β stereoisomers, respectively. The β form is known to be the less stable but to be indefinitely

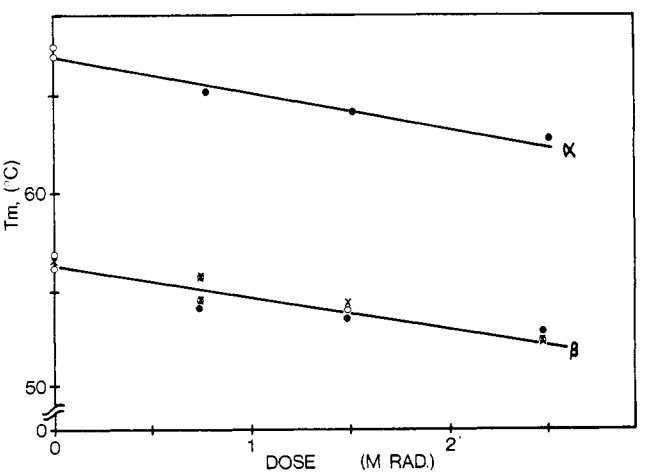

Figure 4. Depression of melting point of gutta-percha on irradiation (runs 2 and 3 for the α form overlap runs 1–3 for the β form and have been omitted for clarity).

(10) B. Ke and A. W. Sisko, *J. Polym. Sci.*, **50**, 87 (1961).
(11) I. Kirshenbaum, *ibid.*, *Part A*, **3**, 1869 (1965).
(12) J. Zimmerman, *ibid.*, **46**, 151 (1960).
(13) J. Zimmerman, *J. Appl. Polym. Sci.*, **2**, 181(1959).

metastable at room temperature.[14] Samples were irradiated under conditions similar to those reported for nylon-66.

Dsc curves for the α and β forms are shown in Figure 3. It will be seen that after a first run the α form changes to the β form on quenching, as judged by reference to melting temperature. The low-temperature shoulder (run 1) was a common, but not invariable, feature in dsc curves of the β form and is not understood. Exposure of both α and β forms to γ rays for doses up to 2.5 Mrad resulted in a depression of the melting point of 1.6°/Mrad (Figure 4). This is considerably greater than the value observed in the case of nylon-66 and leads to a correspondingly higher value for the β form of $G(-$ units$) \cong 68$, when $M = 68$ g, $\Delta H = 3040$ cal/68 g.[15]

A more extensive study of the β form up to a dose at which crystallinity had almost completely disappeared, as judged by the area of the endothermic peak, showed a good fit to first-order kinetics, *i.e.*, to eq 3, in which C_0 is the initial concentration of units in the crystalline regions and C is the concentration accomodated after a dose of D Mrad. The rate constant, k, may be determined from eq 4 obtained by combining eq 1 and 3, noting that $C/C_0 \equiv X$, *i.e.*

$$C = C_0 e^{-kD} \tag{3}$$

$$\frac{\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) = kD \tag{4}$$

Then, by reference to a plot of data according to eq 4 (Figure 5), $k = 5.4 \times 10^{-3}$ Mrad^{-1} and $G(-$ units$) \cong 50$. It should be noted that this value, which is in agreement for the first runs obtained from data at low doses, applies for disappearance of almost all the crystallinity only for runs subsequent to run 1. A similar study was made of the α form, but the results did not fit any simple pattern and are withheld.

Only a limited amount of radiation chemical data are available for purified gutta-percha, *viz.*, G(cross-links) = 1.3 and G(fractures) = 0.15.[16] However, further data may be adduced from studies of a *trans*-1,4-polyisoprene obtained from Balata, *viz.*, G(trans → cis) = 10.[17] Finally an allowance should be made for the saturation of double bonds, predominantly due to cyclization. A value has not been determined for a solid *trans*-1,4-polyisoprene, but reference to values for squalene, a liquid hexaisoprene, for which $G(-$ double bonds$) = 4.6$[18] and a number of *cis*-1,4-polyisoprenes for which $G(-$ double bonds$) = 6.7$[17] suggests a value not in excess of $G(-$ double bonds$) = 7$. Thus the sum total of radiation chemical damage may be summarized as $G(-$ isoprene units$) \simeq 18$, which appears to be significantly lower than the corresponding value estimated from depression of the melting temperature.

Polypropylene. A sample of a 15-denier polypropylene fiber (donated by Dr. F. B. Marcotte, Celanese) was irradiated and handled under conditions similar to those described for nylon-66. Examples of dsc scans for the unirradiated control and the sample given the maximum dose (76.5 Mrad) are shown in Figure 6. In a first run a double peak was generally, but not always, observed, but this was eventually reduced to a single peak by recycling, usually by run 2. Previously a double peak had been observed in dta studies of oriented fibers of nylon-66 and the lower temperature peak attributed to the disorientation of crystallites.[10] Consistently, in the present work the higher peak is taken as the melting temperature. It is always the more pronounced and gives a value of 165° for the unirradiated control, which is closer to literature values, *cf.* 169° for a dta study of an isotactic polymer.[19] A straight line drawn through the results obtained in first runs (Figure 7) gives $G(-$ units$) = 47$ using a value of $\Delta H = 7800$ cal/126 g.[20]

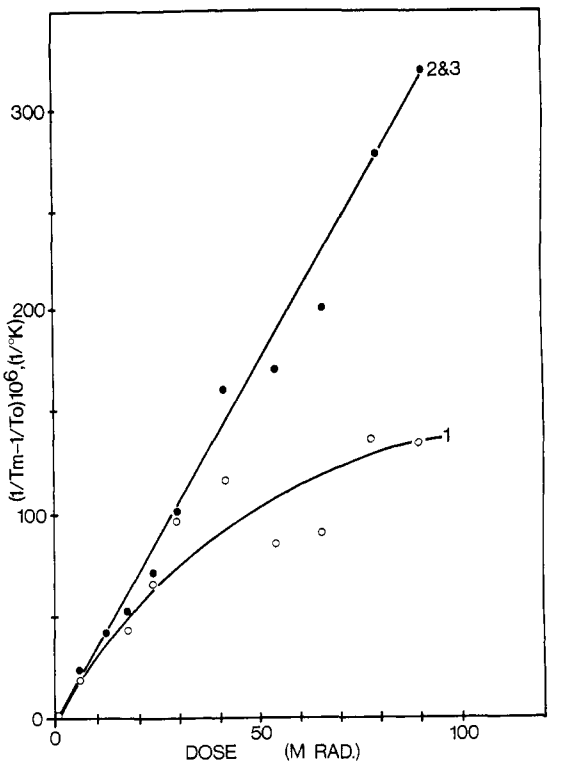

Figure 5. Test of conformity of gutta-percha data to eq 4 (in text). (Data for runs 2 and 3 were coincident.)

A measure of the radiation chemical damage of isotactic polypropylene is provided by reference to gas formation, *viz.*, $G(H_2 + CH_4) = 2.7 + 0.08 \simeq 2.8$; by this criterion, a similar amount of damage would occur in an atactic sample.[21] Part of this damage can be accounted for through the formation of cross-links and fractures. The yield of fractures can be increased due to post-irradiation reactions of free radicals

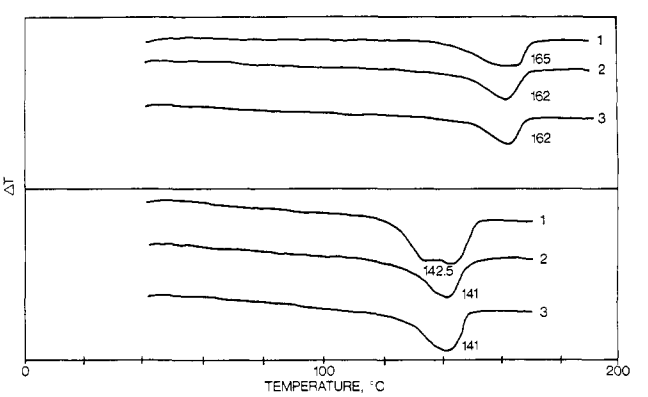

Figure 6. Thermograms for polypropylene: upper set, 0 Mrad; lower set, 76.5 Mrad.

(14) C. W. Bunn, *Proc. Roy. Soc., Ser. A*, **180**, 40 (1942).
(15) L. Mandelkern, *Rubber. Chem. Technol.*, **32**, 1392 (1959).
(16) D. T. Turner, *Polym. Lett.*, **4**, 717 (1966).
(17) M. A. Golub and J. Danon, *Can. J. Chem.*, **43**, 2772 (1965).
(18) M. A. Golub and J. Danon, *ibid.*, **42**, 1577 (1964).
(19) B. Ke, *J. Polym. Sci.*, **42**, 15 (1960).
(20) F. Danusso, G. Moraglio, and E. Flores, *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Natur., Rend.*, **25**, 520 (1958).
(21) W. Schnabel and M. Dole, *J. Phys. Chem.*, **67**, 295 (1963).

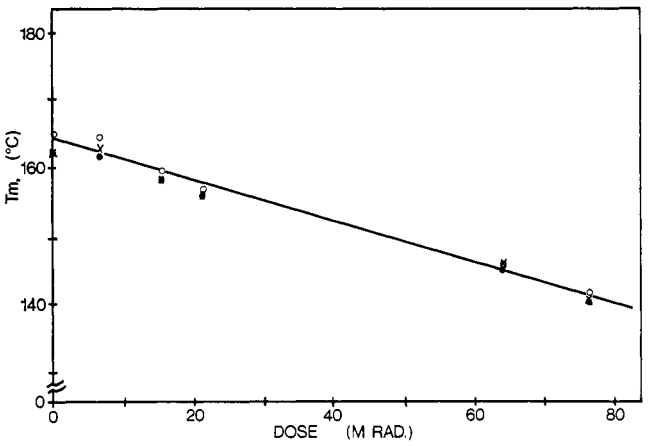

Figure 7. Depression of melting point of polypropylene on irradiation: run 1, ○; run 2, ●; run 3, ×.

with oxygen.[22] However, this effect is pronounced only after low doses, *e.g.*, G(fracture) $\simeq$ 10 after 1 Mrad, and is much too small to account for the large discrepancy with the estimate of $G(-$ units) = 47.

Poly(ethylene terephthalate). Samples of biaxially oriented capacitor grade PET (Mylar film of 25 μ; du Pont) which had been exposed under vacuum to Co-60 γ rays at a dose rate of 1.5 Mrad/hr and stored in air for several years were examined. An additional variable in these experiments was the temperature of irradiation, which ranged from an ambient value of 47 to 175°.[23,24]

Examples of runs for unirradiated controls and for the sample given the maximum dose investigated (1930 Mrad) are shown in Figure 8. The melting temperature of the unirradiated control, 255° in run 1 and 253° in runs 2 and 3, is lower than values reported in the literature, *cf.* 265° for a sample of similar origin examined by dta.[25] Moreover, there is considerable scatter among control samples, many of which had been heated at 100° for times up to 600 hr. As there was no obvious trend due to heating, no distinction is made in the designation of these samples in Figure 9. Moreover, heating the sample up to 175° during irradiation also has little influence on depression of the melting point and, therefore, a straight line has been drawn through all the data

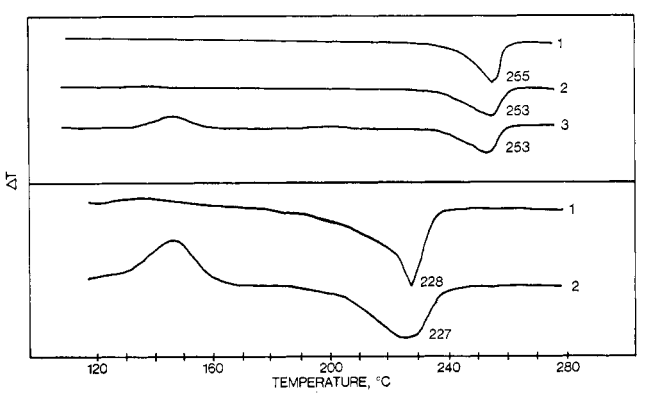

Figure 8. Thermograms for PET: upper set, 0 Mrad; lower set, 1930 Mrad.

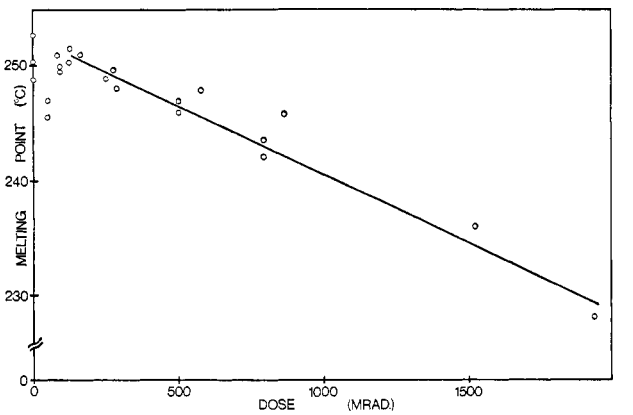

Figure 9. Depression of melting point of PET on irradiation.

for doses >100 Mrad. The slope of 0.013°/Mrad gives $G(-$ units) = 0.6; ΔH = 5400 cal/192 g.[26]

Previous analytical data[23,24] on the same samples resulted in the following G values, averaged over the same dose range: G(carboxyl end groups) = 0.3, $G(CO_2)$ = 0.1, $G(CO)$ = 0.05, $G(H_2)$ = 0.015, $G(CH_4)$ < 0.01. The three major products may be taken to give a measure of $G(-$ units) = 0.45, which is fairly close to the value estimated by depression of the melting point. In the previous analytical work the initial G values, for doses <100 Mrad, for the major products were observed to be higher, *viz.*, G(carboxyl end groups) = 0.8, $G(CO_2)$ = 0.17, and $G(CO)$ = 0.11. On this basis the initial value of $G(-$ units) = 1.1. The data in Figure 9 are too erratic to allow comment on initial changes.

Polyethylene. Although a variety of work has been done providing information about the influence of irradiation on the depression of the melting point of polyethylene, no consistent picture emerges unless attention is focused on initial values at low doses (Table I). The agreement that the melting point is depressed by 0.03–0.04°/Mrad provides values of $G(-$ units) = 6–8 using ΔH = 1842 cal/28 g.[2] It may be supposed that comparison may be made with the value of G(units chemically changed) $\cong$ 4.9. The agreement between the two methods is within a factor of 2.

Table I does not include all the data in the literature. In particular, the judgment has been made that samples which were melted either during or after irradiation should be excluded on the grounds that the large decrease in melting point observed in subsequent experiments was influenced by the cross-link assuming a preferred stereochemistry which resulted in exclusion of neighbors of the cross-linked pair from the crystalline regions.

Discussion

The present results indicate that depression of the melting point may be used as an index of the total chemical change produced in a polymer by exposure to γ radiation. In some cases the correspondence between $G(-$ units), as measured by reference to the Flory equation, and G(units chemically changed) is sufficiently close to consider the plausibility of a one to one relationship. Consider, first, whether use of Flory's equation is appropriate. The equation was derived for the case of a random copolymer comprising predominantly one type of unit, A, along with other units, B. On cooling from the melt, only the A units are accommodated in the crystalline regions, the B units being rejected. The crystalline

(22) D. O. Gehmer, *Makromol. Chem.*, **100**, 186 (1967).
(23) S. D. Burow, G. F. Pezdirtz, G. F. Sands, and D. T. Turner, *J. Polym. Sci., Part A-4*, **4**, 613 (1966).
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(25) B. Ke, *J. Appl. Polym. Sci.*, **6**, 624 (1962).
(26) C. W. Smith and M. Dole, *J. Polym. Sci.*, **20**, 37 (1956).

TABLE I
INFLUENCE OF EXPERIMENTAL CONDITIONS ON DEPRESSION OF MELTING POINT ON IRRADIATION OF POLYETHYLENES

Density of polyethylene	Low	High	Low		High
Form of polyethylene	Bulk granules	Bulk	Bulk	Bulk	Powder (60–80 μ)
Environment during γ irradiation	Vacuum	Vacuum	Air	Vacuum	Vacuum
Post-irradiation treatment	None	Melted in air	None	Annealed in vacuum at 80°	
Depression of mp at low doses, °C/Mrad	0.03	0.01	0.04	0.04	0.04
Depression of mp at high doses	Not studied	Levels off (2 points)	Continues to fall	Levels off	Continues to fall
Ref	2	3	*a*		*b*

[a] E. Keneally, J. Gard, and G. Adler, *J. Polym. Sci., Part A*, **2**, 1463 (1964). [b] A. Malliaris and D. T. Turner, unpublished work.

regions are limited in size and there is a range of melting temperatures corresponding to variations in surface energy contributions. In these circumstances a melting point was defined as the lowest temperature required for the complete disappearance of crystallinity.[6]

The polymers considered in the present work probably range in crystallinity from about 40%, in the case of PET, to up to about 90%, in the case of a high-density polyethylene. The distribution of the crystalline phase is a matter requiring detailed study, and some conjecture, in any particular case, but a common feature is that crystalline order is generally limited in one of the dimensions to a distance of the order 10^2 Å. Energy from the ^{60}Co γ rays may be considered to be deposited, more or less at random, in amounts up to about 100 eV in elements of volume of diameter about 100 Å. Somehow, in a way not understood, the energy becomes sufficiently localized to break chemical bonds[8,27] which in the present polymers involves energies up to about 5 eV. The distribution of these chemical effects between crystalline and noncrystalline phases and along the lengths of the polymer molecules is not known. However, there is conclusive evidence from esr studies that free radicals are formed in both phases.[8] Accordingly, the Flory equation is not strictly applicable to the present case since it does not take into account chemical defects in the crystalline regions. Its present use should be regarded as a provisional measure. Another possible objection to its use in the present work is that the measurements by no means provide equilibrium temperatures relating to the complete disappearance of crystallinity. This objection is generally applicable to rapid scanning techniques such as dsc and dta. There is evidence that results in agreement with another closely related equation of Flory can be obtained in dta studies of diluents which are soluble in the noncrystalline phase of polyethylene.[28] Nevertheless, the possibility of the melting behavior being controlled by kinetic rather than equilibrium factors is not ruled out in the present work. In this connection comment should be made on the preference given to results obtained in run 1. It is considered that comparisons of first runs are more meaningful because they are made on samples of similar morphology. In subsequent runs differences may arise because of variations during crystallization. In most cases major differences are not observed in runs 2 and 3 and this somewhat arbitrary decision is not critical.

The second important quantity considered in the present work is the value designated G(units chemically changed) which may be challenged on the grounds that a successful total product analysis in an irradiated polymer is open to doubt and involves a rather subjective choice of data of the kind indicated at the beginning of this paper. Then again, it may be objected that in comparing this value with G(− units) it does not follow that all types of chemical change should be weighted equally in their influence on depression of the melting point. On the one hand, minor chemical changes might have negligible influence while, on the other, cross-links might produce effects in excess of the two units directly involved. Evidence that cross-links can prevent many adjacent units from crystallizing is well documented in crystallization studies of natural rubber. Evidence that cross-linking would result in a large depression of the melting point may be adduced from experiments in which polyethylene was irradiated in the melt. Samples were then allowed to crystallize and the subsequent melting behavior was shown to result in estimates of loss of crystallizing units, using the Flory equation, which were an order of magnitude greater than those expected from other analytical techniques, *cf.* ref 3. These types of objections do not appear to be serious in PET, nylon-66, and polyethylene, since in all these cases the two types of G value agree within a factor of 2, and coincidence seems an unlikely eventuality in three cases out of five. In these circumstances, it seems permissible to seek an explanation of the two exceptions, in both of which it appears that there is the inequality G(− units) > G(units chemically changed). A reasonable explanation in the case of gutta-percha is that the melting temperature is sufficiently low to allow the cross-links to assume their preferred stereochemistry and by so doing to prevent neighboring isoprene units from crystallizing, or from remaining in the crystal lattice. This same explanation cannot be applied to polypropylene, since this has a melting temperature higher than that of polyethylene. In this case it is suggested that isotactic sequences undergo racemization on irradiation. Previously, racemization of isotactic poly(methyl methacrylate) resulting from electron irradiation has been deduced from nmr studies.[29] In other words, it is suggested, in the case of polypropylene, that G(units chemically changed) = 2.8 is a gross underestimate because it fails to include radiation-induced changes in tacticity.

Acknowledgments. We would like to thank the Division of Isotopes Development, U. S. Atomic Energy Commission, for their support of this work. For the use of the ^{60}Co source we are indebted to Dr. Leo Wall and the National Bureau of Standards.

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