Cryoscopy of γ-Irradiated Polyoxymethylene

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ABSTRACT: γ irradiation of polyoxymethylene results in sensitization to thermal depolymerization. Notwithstanding, at doses <100 Mrad a uniform depression of the melting point was measured of 0.115 to 0.160°C/Mrad. Substitution of these values in the Clapeyron–Clausius equation gives a value for crystalline units destroyed by irradiation of $G(-\text{units}) = 17$ to 23. This cryoscopic estimate is in agreement with estimates reported previously of units undergoing chemicalchange (24 ± 1) as a result of electron irradiation.

In some cases the chemical changes caused by high-energy irradiation of a polymer can be calculated from cryoscopic data.[1,2] The validity of this approach has been evaluated by comparison with quantitative chemical analyses. For the case of polyoxymethylene (POM) suitable analytical data have been reported by Fischer and Langbein.[3] Moreover, preliminary calculations using cryoscopic data reported by Jaffe and Wunderlich,[4] in a study of the "Effect of X-Rays on Extended Chain Crystals of Polyoxymethylene," indicate agreement between the two methods. Therefore, a more detailed investigation was made.

Experimental Section

Pellets of poly(oxymethylene diacetate), $CH_3COO(CH_2O)_nCOCH_3$, were obtained from E. I. du Pont de Nemours. This polymer is reported[5] to be 70% crystalline and to melt at 175 to 180°. The number average molecular weight is about 4×10^4.

The polymer pellets were cut with a razor blade into pieces (0.25 mg). Samples (25 mg) were placed in differential thermal analysis tubes and sealed in ampules (5 cm^3) under vacuum. Ampules were irradiated at an ambient temperature of 30° in a Cs-137 γ-ray source at a dose rate of 0.9 Mrad/hr.

Three days after irradiation the ampules were opened and the DTA tubes were transferred rapidly to a Du Pont 990 thermal analyzer under nitrogen. Unless stated otherwise, the samples were scanned in a DTA mode at 20°C/min. Differential scanning calorimetry measurements (DSC) were made by standard techniques.[2]

Results and Discussion

Thermal Analyses. A DTA scan of POM exhibits an endothermic peak at 175 ± 1° in agreement with values reported previously for the melting transition.[5] At higher temperatures other endothermic changes are observed which are due to thermal decomposition (Figure 1, 0 Mrad). As a result of irradiation these decompositions occur at lower temperatures and superpose on the melting endotherm, as exemplified after doses up to 13.2 Mrad (Figure 1). This marked sensitivity is due to the formation of end groups[3] which are less stable than the acetyl capped ends initially present. These less stable groups initiate thermal depolymerization at lower temperatures by a chain reaction ("unzipping").

After doses >20 Mrad two endothermic peaks are observed, as exemplified after a dose of 100 Mrad in Figure 2. After the DTA run, heating causes further thermal degradation of the specimen but the peaks remain, only shifting by a few degrees. Such phenomena are commonly observed in DTA scans of other crystalline polymers in cases which do not involve the complication of a concurrent chemical reaction and therefore, it is believed that both peaks are caused by melting. For present purposes, it is not mandatory to elucidate the crystalline morphologies responsible for the occurrence of the peaks. It is sufficient to note that both peaks were monitored, as in Figure 3, and gave similar values for the depression of the melting point (Figure 4).

DSC scans gave the following overall values for the endotheric processes monitored near the melting points: 0 Mrad, 37.7 cal/g; 6.6 Mrad, 45.4 cal/g; 19.8 Mrad, 40.7 cal/g; 100 Mrad, 203 cal/g. In the case of the unirradiated polymer (0 Mrad) the measurement provides a value for the enthalpy of fusion. Accepting a previous report[5] that the polymer is 70% crystalline, the enthalpy of fusion for the crystalline regions is calculated to be 53.7 cal/g which is in agreement with values reported in the literature of 58.7,[5] 53.3,[6] and 53.4[7] cal/g. In the case of the sample given the highest dose (100 Mrad) it is clear that contributions to the enthalpy changes from thermal decomposition predominate. Therefore, the DSC technique is invalid for monitoring changes in crystallinity even at low doses.

Comparison of Results of Chemical Analysis and Cryoscopy. Detailed product analysis for polyoxymethylene diacetate (Delrin 500), following irradiation with 1 MeV electrons under vacuum, has been reported by Fischer and Langbein.[3] Dole judges that thanks to their excellent work "we probably are more certain of the actual chemistry of irradiation effects in polyoxymethylene than in any other polymer."[8] Yields of the following groups were shown to increase linearly with dose up to at least 100 Mrad: OCH_3, OCHO, OH, and $-CH_2CH_2-$. G values for these and other chemical changes are quoted in Table I.

Both infrared and nmr spectroscopy were used to estimate OCH_3 and OCHO groups; the limits reported are remarkably narrow considering that they include results of both methods. Infrared and nmr spectroscopy were used, respectively, to estimate OH and $-CH_2CH_2-$ groups. All the other products were pumped out after irradiation and analyzed by gas chromatography.

Material balances provided evidence that the yield of fractures (F) is given by the equality $G(F) = G(OCH_3) = 11.1 \pm 0.7$. A case was made that the $-CH_2CH_2-$ groups are present as cross-links (X), so that $G(X) = G(-CH_2CH_2-) = 6.5 \pm 0.3$.

The results of Fischer and Langbein can be interpreted as showing that chemically changed units are given by the following equation: $G(F) + 2G(X) = (11.1 \pm 0.7) + 2(6.5 \pm 0.3) = 24.1 \pm 1.0$.

A value for units excluded from the crystal may be calculated from the Clapeyron–Clausius equation. The application in the case of irradiated polymers has been discussed previously.[1,2] A convenient approximation for the case where the mole fraction of unreacted units, X, remains close to unity, so that $\ln X \simeq X - 1$, is given by eq 1 (this can be derived from eq 1 and 2 of ref 1): R is the gas constant, taken approximately as 2 cal/(mol°K), and δH_u is the enthalpy of fusion, taken in the present work as 53.3 cal/g. T is the melting point to which an initial value of T_0 is depressed by a dose of D Mrad.

$$G(-\text{units}) = \frac{\delta H_u 10^6}{R T_0^2} \frac{(T_0 - T)}{(D)} \tag{1}$$

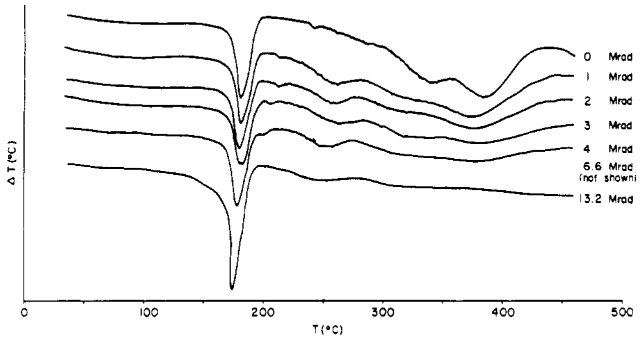

Figure 1. DTA runs over a wide temperature range for low doses.

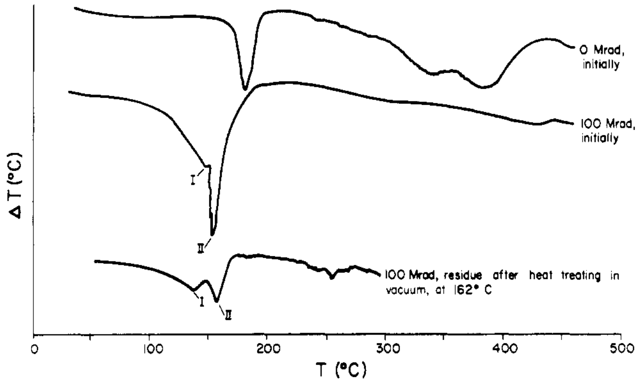

Figure 2. DTA runs over a wide temperature range for a high dose.

Jaffe and Wunderlich[4] irradiated an extended chain polyoxymethylene in air at a dose rate of 0.1 Mrad/min and reported that the melting point was depressed from a value of T_0 = 455.5°K by 18° after 480 min. Substitution of these data in eq 1 gives a value of $G(-\text{units}) = 48$. These melting points were measured at low heating rates, of a few degrees per minute, to avoid superheating. A more extensive body of data was plotted for a heating rate of 20°/min. As shown in Figure 4, this may be interpreted to mean that eventually a constant value is approximated for the decrease in peak temperature per unit dose. Substitution of this value, 0.154°K/Mrad, in eq 1 gives $G(-\text{unit}) \simeq 20$ in agreement with G(units chemically changed) = 24.1 ± 1.0.

The results obtained in the present work for samples irradiated in vacuum follow a similar trend, for both DTA peaks, to those obtained by Jaffe and Wunderlich (Figure 4). The depression of the melting point per unit dose begins to approach a constant value for doses >100 Mrad. The value in the interval 100–150 Mrad (T_0 = 432°K) is 0.160°/Mrad; in the interval 200–300 Mrad the corresponding values are T_0 = 424°K and 0.115°/Mrad. Substitution of these values in eq 1 gives respectively values of $G(-\text{units}) \simeq 23$ and 17. The choice of T_0 is somewhat arbitrary and has only a small influence on the calculated value.

A more objective comparison of chemical and cryoscopic data is given in Figure 5. This serves to emphasize that after small doses the cryoscopic method gives a much higher estimate of chemical change. In the work of Jaffe and Wunderlich[4] this could be explained, at least in part, by the superheating effect. However, the polymer studied in the present work is not expected to superheat. Consistently, evidence that it did not was obtained by showing that the DTA scans were independent of heating rate in the range 20–75°C/min. Therefore, the initially high values observed in the present work cannot be attributed to this effect.

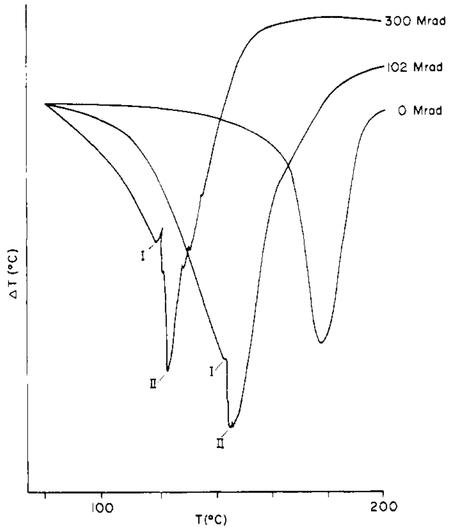

Figure 3. DTA runs specifying peaks selected for monitoring.

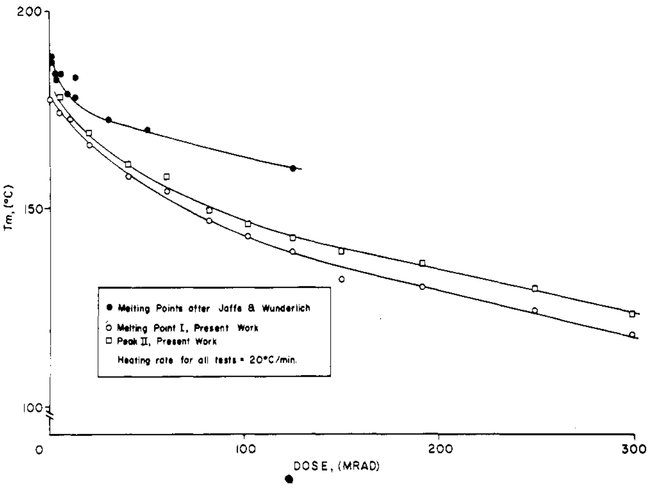

Figure 4. Influence of radiation dose on melting peaks.

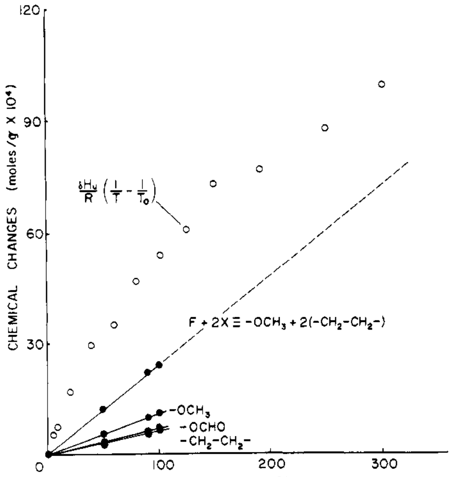

Figure 5. Comparison of changes by chemical analyses (●) with changes calculated from cryoscopic data (○). (Chemical analyses by Fischer and Langbein.)

Influence of Depolymerization. Fischer and Langbein detected monomer in the gas phase to the extent $G(\text{HCHO}) = 4 \pm 1$. However, they report losses of mass of their irradiated samples which indicate more extensive depolymerization. An approximate value may be estimated,

Table I
G Values for Chemical Changes in POM

	Change								
	OCH_3	OCHO	OH	$-CH_2CH_2-$	HCHO	H_2	CH_4	CO	Other
G value	11.1 ± 0.7	6.6 ± 0.3	4.7 ± 0.2	6.5 ± 0.3	4 ± 1	1.7 ± 0.2	0.14 ± 0.02	0.013 ± 0.002	< 0.2

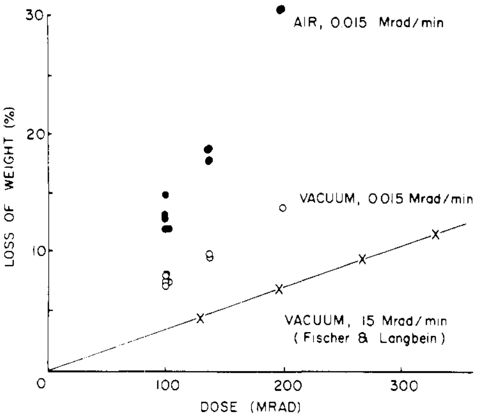

Figure 6. Loss of sample weight immediately after irradiation.

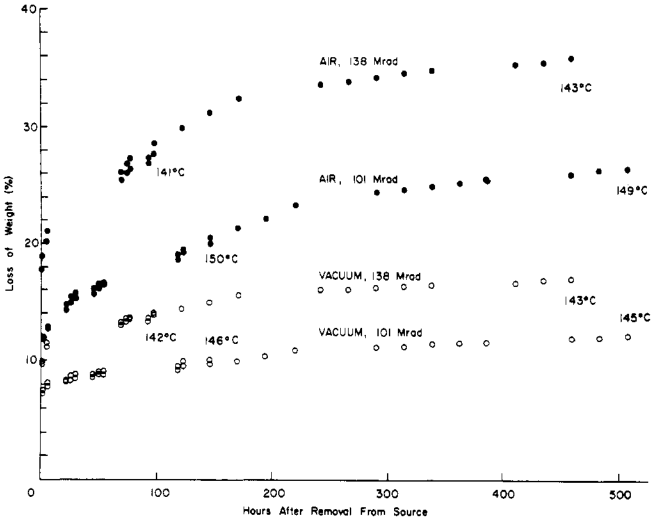

Figure 7. Postirradiation changes in sample weight. (Runs were terminated to check melting peaks, I.)

noting that other volatiles are negligible (Table I), from the loss of mass as $G(\text{HCHO}) \simeq 13$ (Figure 6). In the present work, measurements of loss of mass were limited to doses between 100 and 200 Mrad but the results indicate twofold greater depolymerization (Figure 6). Loss of mass continued after irradiation was completed (Figure 7). This could not be due simply to the loss of absorbed monomer for two reasons. First, the loss does not follow the kinetics of a diffusion-controlled process. Second, although the diffusion coefficient of formaldehyde in polyoxymethylene is not known to allow definitive calculations, experiments have been reported which show that the monomer usually comes to within 10% of its equilibrium uptake in the polymer within 2 hr.[9] Therefore, a continuous loss of monomer over a period as long as 500 hr is not explicable simply in terms of diffusion. A more likely explanation would be a prolonged postirradiation chemical reaction involving the unzipping of unstable end groups. For example, Bevington remarks that the odor of formaldehyde can be detected in polymers with terminal hydroxyl groups even at room temperature.[10] Accepting this explanation, the greater loss of mass observed in the present experiments at the end of irradiation can be attributed, at least in part, to the longer period of irradiation, the dose rate being three orders of magnitude less than that used by Fischer and Langbein. The still greater loss of mass in air, and the greater postirradiation loss, can be attributed to the known sensitivity of the depolymerization of polyoxymethylene to oxidative degradation.[11]

Depolymerization is expected to have only a minor influence on material balances involving fractures and cross-links. Depletion of the polymeric reactant is small, about 10% of the $-CH_2O-$ units having reacted chemically after a dose of 100 Mrad. The monomer is only sparingly soluble in the polymer and is not expected to accumulate and thereby affect the radiation chemistry. Evidence that neither of these complications is important is provided by the linear relationship between chemical yields and dose reported by Fischer and Langbein (see Figure 5).[3]

Depolymerization might be expected to influence cryoscopic data. A small dose results in the formation of sufficient unstable groups to cause thermal degradation of the polymer even at room temperature. During the DTA scan this results in considerable evolution of monomer. Because of this complication, analysis of data is limited to doses >100 Mrad. It is suggested that this procedure is justified because irradiation results in the formation of a sample which has sufficient thermal stability to permit measurement of the melting point.

The influence of irradiation on the thermal stability of poly(oxymethylene dihydrate) has been studied by Torikai.[12] The unirradiated polymer was unstable at 200° because of the reactivity of the CH_2OH end groups. However, after irradiation, heating at 200° revealed the presence of a thermally stable fraction amounting to 0.8 to 0.95 of the total mass. Torikai suggested that this was due to the formation of more stable end groups, giving the order of increasing thermal stabilities as $OH < OCHO < OCH_3$. He also suggested that unzipping might be limited by cross-linking or branching, *i.e.*, by $-CH_2CH_2-$ groups. He gave eq 2 for calculating the stable fraction, S. In eq 2, in which Torikai's notation has been simplified, N_s and N_t refer to the

$$S = [(N_s + 2Q)/(N_t + 2Q)]^2 \qquad (2)$$

number of stable and total end groups, respectively, and Q to the number of branches or cross-links. These refer in Torikai's analysis to unit dose and unit main chain but may be replaced by the G values reported by Fischer and Langbein to give $S = 0.75$ (*i.e.*, where $N_s = G(\text{OCH}_3) + G(\text{OCHO}) = 17.7$, $N_t = G(\text{OCH}_3) + G(\text{OCHO}) + G(\text{OH}) = 22.4$, and $Q = G(-\text{CH}_2\text{CH}_2-) = 6.5$). Therefore, after a sufficient dose to make negligible the influence of the initial end groups in the polymer, it is expected that about three-quarters of the irradiated polymer has sufficient thermal stability to allow measurement of the melting point.

A more fundamental question concerning depolymerization is whether loss of monomer should be included, along with fractures and cross-links, as contributing toward a depression of the melting point. This is not easily decided from a theoretical point of view but experimental data indicate that, within the range of doses of present interest

(100–300 Mrad), depolymerization can occur without significant changes in the melting point. For example, Figure 7 shows results of experiments in which two samples undergoing postirradiation depolymerization at room temperature were examined by DTA after various times. The results obtained after a dose of 138 Mrad in air show that a loss of 8% in weight is accompanied by a change in melting point from 141 to 143°. Another sample which had received the same dose under vacuum lost 3% in weight with a change in melting point from 142° to 143°. These results, along with ones obtained after a dose of 101 Mrad, show that these changes in melting point are unimportant relative to the large depressions due to irradiation (*cf.* Figure 4).

One clue to the physical nature of radiation damage has been obtained by Jaffe and Wunderlich.[4] These authors calculated values of density changes from measurements of refractive index. A decrease from 1.480 to 1.449 g cm^{-3} was calculated after a dose of 45 Mrad. It was suggested that this was due to the formation of holes and disordering. This large decrease which is equivalent to a loss of 2% by weight is presumably due, largely, to depolymerization. Possibly, the holes do not affect melting behavior through being annealed during the DTA scan.

Conclusion

(1) After doses in the range 100–300 Mrad, under vacuum, the depression of the melting point of polyoxymethylene lies in the range 0.115 to 0.160°C/Mrad. This value is in agreement with a value of 0.154°C/Mrad deduced from data reported by Jaffe and Wunderlich for a sample irradiated in air.

(2) Substitution of the values 0.115 and 0.160°C/Mrad in an equation derived from the Clapeyron–Clausius equation, along with a value for the enthalpy of fusion of 53.3 cal/g, gives values for units excluded from the crystal lattice by irradiation of $G(\text{–units}) \simeq 17$ to 23.

(3) A value of $G(\text{units chemically changed}) \simeq G(\text{fractures}) + 2G(\text{cross-links} = -CH_2CH_2- \text{ groups}) = 24 \pm 1.0$ was calculated from chemical analyses reported by Fischer and Langbein for polyoxymethylene irradiated under vacuum at dose rates three orders of magnitude higher than in the cryoscopical studies.

(4) There is good agreement between the chemical and cryoscopic studies but the former relate to doses documented up to 100 Mrad whereas the latter have been demonstrated only for doses in the range 100–300 Mrad.

(5) At doses <100 Mrad the cryoscopic methods give values of $G(\text{units}) > G(\text{units chemically changed})$. It is suggested that a complication is involved at low doses because of thermal instability of the irradiated polymer. At doses >100 Mrad a sufficient amount of thermally stable polymer is formed to allow monitoring of the melting point.

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Cocrystallization in Polyamides from Bis(4-aminocyclohexyl)methane

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ABSTRACT: A study was made of the crystallinity of polyamide copolymers derived from mixtures of bis(4-aminocyclohexyl)methane (PACM) and various acyclic diamines with dodecanedioic acid or suberic acid. The highest degree of cocrystallization was observed when 1,9-nonanediamine or 5-methyl-1,9-nonanediamine was used as the second diamine component. Evidence of this was obtained from plots of crystalline melting point *vs.* composition and from heats of fusion of copolymers derived from equimolar mixtures of diamines. All α,ω straight chain diamines in the range of 6 to 12 carbon atoms showed varying degrees of crystallinity retention, with those longer than nine carbon atoms exhibiting greater retention than those shorter. X-Ray diffraction data indicated that while 1,12-dodecanediamine derived copolymers cocrystallize, those obtained using 1,6-hexanediamine do not. Other ring-containing monomers (*e.g*, 1,4-bis(aminomethyl)cyclohexane, 1,3-bis(4-piperidyl)propane, and *p,p′*-methylenedianiline) did not cocrystallize with PACM when used to prepare polyamide copolymers.

The ability of polymer repeat units to cocrystallize has been a matter of considerable interest and importance in the area of polyamides derived from alicyclic diamines, due largely to the presence of cis and trans isomers in these systems and their effect on polymer properties. Previous work has shown[1] that *cis*- and *trans*-1,4-bis(aminomethyl)cyclohexane cocrystallize with very little lattice distortion when polymerized with a dicarboxylic acid having from 6 to 12 carbon atoms. In similar polyamides derived from bis(4-aminocyclohexyl)methane, the *trans,trans* and *cis,trans* isomers cocrystallize with significant lattice distortion.[2,3] The behavior of copolymer systems derived from these di-