

# Irradiation effects on polycaprolactone

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(Received 20 March 1984)

The structure and some physical properties of  $\gamma$ -irradiated polycaprolactone (PCL), a semi-crystalline linear saturated polyester, were studied as function of the irradiation dose level. The critical dose level for gel formation is 26 Mrad and above this irradiation dose the number of scission events is similar to the number of crosslinking events. G.p.c. results show that the initial rather narrow molecular weight distribution gradually widens with increasing dose in the pre-gelation region. A significant difference between first and second d.s.c. scans of irradiated PCL is shown and explained. Scission and crosslinking reactions associated with the irradiation process occur preferentially in the non-ordered regions. Small irradiation doses, 2-5 Mrad, are shown to have a dramatic effect on the tensile elongation at break by converting ductile PCL samples into brittle materials.

(Keywords: irradiation effects; polycaprolactone; gamma irradiation; gel formation)

## INTRODUCTION

Irradiation of polymers may cause crosslinking, chain scission or both depending mainly on the chemical structure of the polymer<sup>1-3</sup>. For example, polypropylene may be considered as intermediate in structure between polyethylene which predominantly crosslinks and polyisobutylene which only degrades by radiation. The resulting structure and properties are determined by the dominating degradation or crosslinking reactions. The overall net radiation effect in saturated linear polyesters was found to depend on the specific chemical structure such as the methylene/ester group ratio<sup>4</sup>. PET, a saturated aromatic polyester, undergoes both scission and crosslinking and at high dose rates even gel formation is observed<sup>3</sup>. PGA, poly(glycolic acid) and PLA, poly(lactic acid) are two biocompatible polyesters, which are also found to cleave and crosslink. PGA degrades and crosslinks at about the same rate<sup>5,6</sup> whereas PLA<sup>7</sup> predominantly degrades.

The present work concentrates on PCL, polycaprolactone  $\{(\text{CH}_2)_5\text{COO}\}_x$  a linear saturated polyester belonging to the PGA  $\{[\text{CH}_2\text{COO}]\}_x$  and PLA  $\{[\text{CHCH}_3\text{COO}]\}_x$  polyester series.  $\gamma$ -radiation effects on the structure and some physical properties of PCL are reported and analysed.

## EXPERIMENTAL

Polycaprolactone PCL-700, Union Carbide) having the following g.p.c. average molecular weights:  $\bar{M}_w = 56\,800$ ,  $\bar{M}_n = 34\,500$ ,  $\bar{M}_w/\bar{M}_n = 1.64$  was compression moulded into 1 mm thick plates. Specimens cut from the plaques

were  $\gamma$  irradiated in vacuum at 0.136 Mrad/h. Gel contents were determined in boiling benzene. G.p.c. runs were carried out in THF for PCL samples irradiated below the critical dose for gel formation, 26 Mrad. These PCL samples were also dissolved in benzene (2 g/dl) and their viscosity was determined. D.s.c. thermograms were obtained using a Perkin Elmer 2B DSC at a heating rate of  $20^\circ\text{C min}^{-1}$ . The specimens were quenched in the instrument at the end of the 1st run and then reheated (the 2nd run). X-ray diffraction diagrams were obtained using  $\text{CuK}\alpha_1$  radiation in the reflection mode. Tensile properties were determined with an Instron machine ( $5\text{ cm min}^{-1}$ , gauge length = 7 cm).

The tensile behaviour of another PCL batch ( $\bar{M}_w = 41\,400$ ,  $\bar{M}_n = 22\,800$ ,  $\bar{M}_w/\bar{M}_n = 1.82$ , obtained from the same source) irradiated in identical conditions was also studied. No other studies were performed on this second PCL batch.

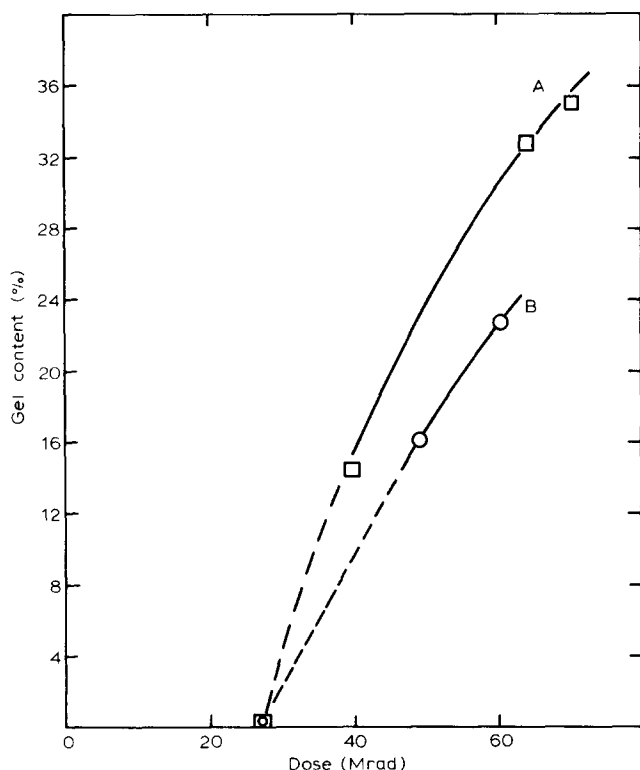
## RESULTS AND DISCUSSION

The formation of gel by irradiation of PCL in air and vacuum is shown in *Figure 1*. The critical radiation dose required to form measurable gel contents is about 26 Mrad in both environments, however the rate of gel formation is faster in vacuum. All the specimens analysed in the present work were irradiated in vacuum. It should be pointed out that, as shown in *Figure 1*, relatively high doses produce rather low gel contents. D'Alerio *et al.*<sup>4</sup> have shown that for a series of linear polyesters more gel is formed, for a given radiation dose, as the  $\text{CH}_2/\text{COO}$  ratio increases. PGA<sup>5</sup> representing the linear polyester having the minimum  $\text{CH}_2/\text{COO}$  unity ratio and PLA<sup>7</sup> representing the first member of the branched polyesters predominantly degrade and apparently start to gel only after very high radiation doses. High density polyethylene (HDPE), in the other extreme, which can be visualized as

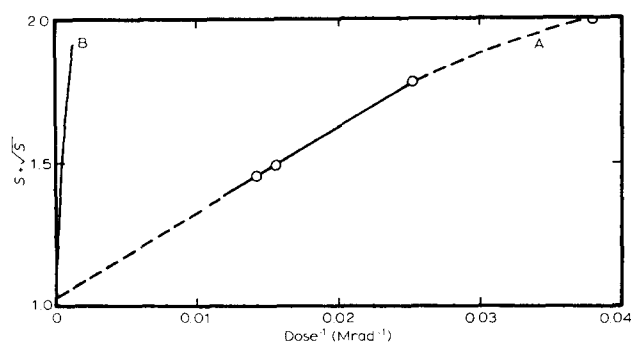
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**Figure 1** Gel content of irradiated PCL as function of radiation dose. Curve (A): vacuum; curve (B): air



**Figure 2**  $S + \sqrt{S}$  vs. radiation dose<sup>-1</sup> of curve (A): PCL and curve (B): PET<sup>2</sup>

having  $\text{CH}_2/\text{COO}$  ratio of infinity undergoes only crosslinking reactions; gel formation is found from the very beginning of the irradiation process if the starting molecular weight is not too low<sup>8</sup>. Moreover, only about 20 Mrad are required to convert a commercial HDPE into a well-crosslinked polyethylene containing 60–80% gel<sup>9</sup>. The typical critical doses (20–30 Mrad) which were required to initiate gel formation in linear polyesters containing 3–7 methylene groups per ester group<sup>4</sup> are similar to the value found for PCL ( $\text{CH}_2/\text{COO} = 5/1$ ) in the present work (26 Mrad).

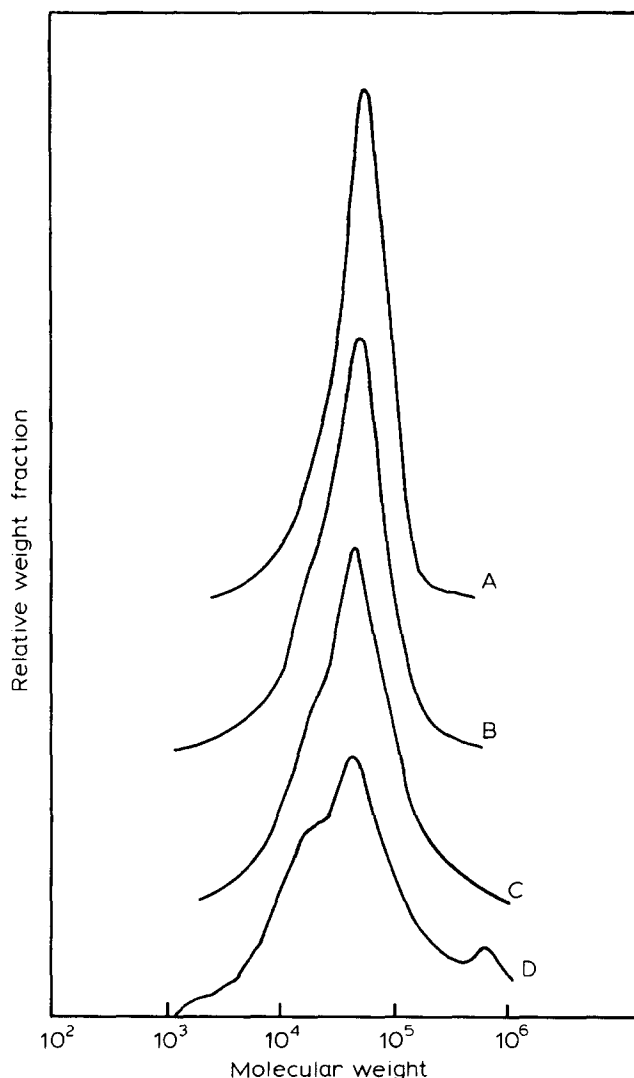
The probabilities of degradation ( $p_0$ ) and crosslinking ( $q_0$ ) per monomer unit per unit dose were derived by Charlesby and Pinner as follows:

$$S + \sqrt{S} = p_0/q_0 + 1/(q_0 \bar{y}_n D) \quad (1)$$

where  $S$  is the sol fraction at dose  $D$  and  $\bar{y}_n$  is the number average degree of polymerization. This equation assumes that the unirradiated polymer has a random distribution of chain lengths. The equation holds for radiation doses

larger than the critical dose required for gel formation. The data of *Figure 1* are replotted in *Figure 2* using the Charlesby and Pinner equation. An extrapolated intercept of  $p_0/q_0 \approx 1$  is obtained, implying that the number of scission events is similar to crosslinking events in PCL. For comparison, an intercept of  $p_0/q_0 \approx 0$  was reported by Lyons<sup>11</sup> for HDPE, thus the number of scission events in HDPE is negligible and the crosslinking events dominate. Interestingly, PET<sup>2</sup>, an aromatic linear polyester, exhibits also, like PCL, an intercept  $p_0/q_0 \approx 1$ . However, for PET the number of scission and crosslinking events per unit dose and per monomer unit are extremely low compared to those in PCL as shown by the line slopes in *Figure 2* (see also ref. 12).

Literature sol-gel data for other polyesters irradiated above the critical dose for gel formation are not available. Some information however does exist<sup>6</sup> for polyester irradiated below the critical gelation dose. In this region molecular weight changes as determined by g.p.c., or other solution methods, can be employed for calculation of the ratio of scission to crosslinking events. *Figure 3* depicts g.p.c. molecular weight distributions as a function of the irradiation dose in the pregelation stage of PCL ( $D < 26$  Mrad). Number and weight average molecular



**Figure 3** G.p.c. molecular weight distribution curves of PCL as function of radiation dose. Curve (A): 0 Mrad; curve (B): 5 Mrad; curve (C): 10 Mrad; curve (D): 20 Mrad

**Table 1** Summary of g.p.c. molecular weights of irradiated PCL

Dose (Mrad)	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
0	56 800	34 500	1.62
5	52 000	26 500	1.97
10	64 000	26 000	2.46
20	744 000	19 400	38.4

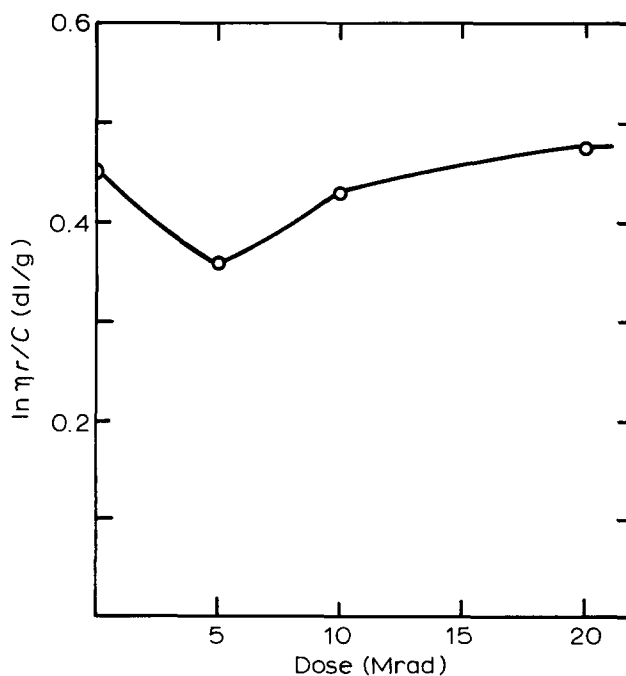
weights and distribution widths derived from the distribution curves are summarized in *Table 1*. Additional manifestation of the radiation effects on molecular weight changes is shown in *Figure 4* by plotting  $(\ln \eta t)/c$  (an approximation of  $[\eta]$ , the intrinsic viscosity) versus  $D$ . The initial rather narrow molecular weight distribution gradually widens with increasing  $D$ , as shown in *Figure 3* and low and high molecular weight tails are formed. Toward the critical gelation dose a new well-defined high molecular weight peak is observed. These long chains will be transformed from the sol to the gel fraction upon further irradiation. The continuous decline in  $\bar{M}_n$  (see *Table 1*) indicates that in the pregelation stage the number of molecules increases, thus chain scission events dominate. In this region, however, long chains are also formed by the crosslinking events, thus  $\bar{M}_w$  and  $(\ln \eta t)/c$  go through minimum values at about 5 Mrad dose (*Figure 4* and *Table 1*).

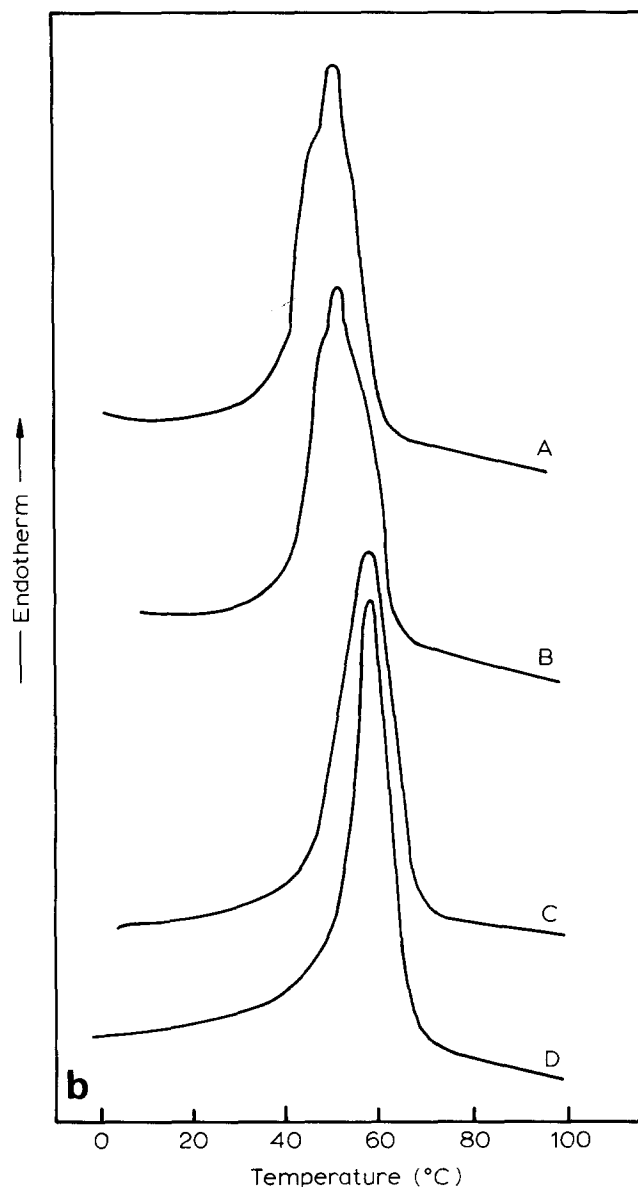
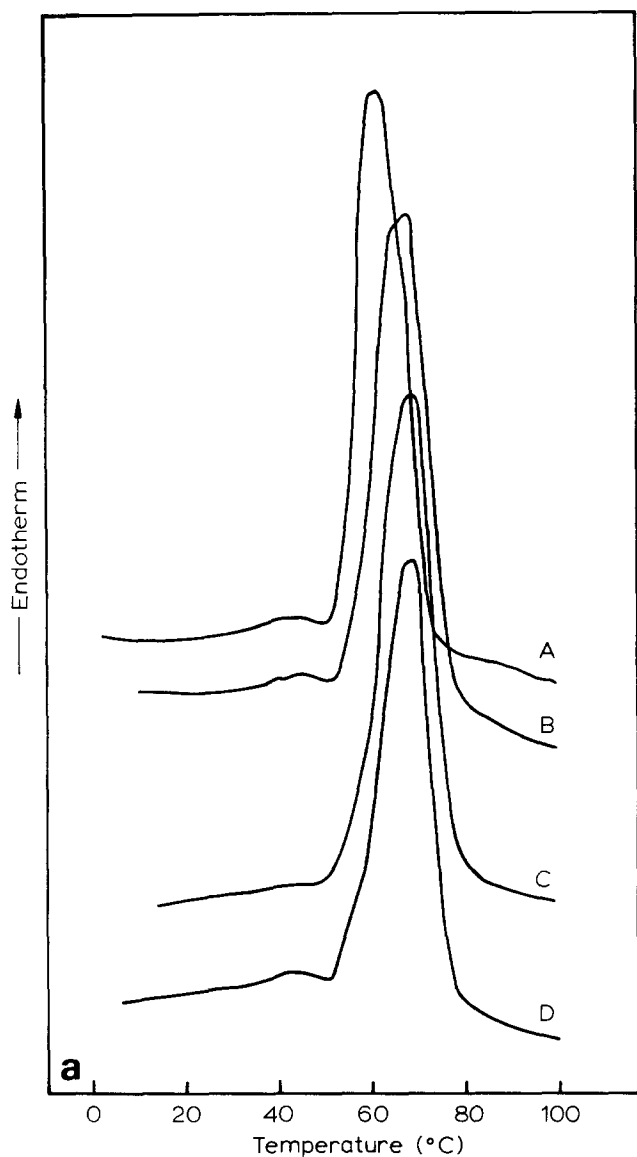
The effect of  $\gamma$  irradiation on the thermal behaviour of PCL is shown in *Figure 5*. The first d.s.c. runs show a significant melting point depression only at 50 Mrad dose. The second runs, performed immediately after melt quenching in the instrument, show a significantly different behaviour. The melting temperature of 40 Mrad irradiated PCL and subsequently recrystallized has been markedly depressed. Its thermogram consists of a shoulder at the melting temperature ( $T_m$ ) of the original PCL and an additional one at temperature below the main peak. The peak  $T_m$  of the 50 Mrad PCL is 8°C lower than that of the unirradiated PCL. In addition, the 40 and 50 Mrad recrystallized sample thermograms (*Figure 5b*) are much wider and less intense compared with the lower dose specimens. Similar  $T_m$  depressions in other irradiated polymers such as HDPE<sup>2</sup> and PLA<sup>7</sup> were also recently reported. Comparison of peak areas of the first and second d.s.c. runs for identical doses reveals an approximately 25% crystallinity decrease in the irradiated and subsequently crystallized melts. The degree of crystallinity (1st d.s.c. runs,  $\Delta H_f = 33.4 \text{ cal g}^{-1}$ ) as a function of the radiation dose is shown in *Figure 6*. The crystallinity increases from 52% to about 65% upon irradiation up to 50 Mrad dose and then tends to slightly decrease. The X-ray degree of crystallinity, however, is unchanged up to 60 Mrad dose. The wide angle X-ray diffraction peaks become narrower with radiation dose increase, thus the polymer crystallite size in both 110 and 200 directions (the third *lll* reflection appears only as a shoulder) gradually increases (see *Table 2*).

Bassett<sup>13</sup> already in 1964 showed by X-ray diffraction that the attack of oxygen and chlorine on single crystals of poly(4-methyl pentene-1) occurs preferentially at chain folds. Wide angle X-ray diffraction of this polymer was not altered during oxidation, but the low angle diffraction, which emphasizes reactions at the crystal surface, where folds are located, was changed by a factor of 20. It has been

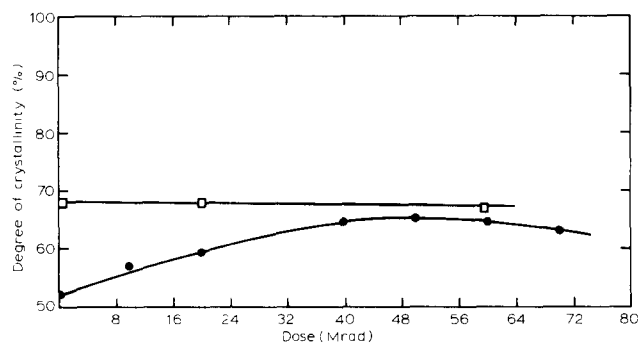
suggested that molecules are strained at the folds, thus lowering their bond energy and facilitating their oxidative attack. Salovey and Bassett<sup>14</sup> studied solution grown crystals and found that crosslinking induced by radiation occurred preferentially between chain folds of adjacent lamellae. We will now consider semi-crystalline polymers which are well known to contain chain folds, tie molecules, chain ends and some entanglements which are preferentially susceptible to chemical and radiation effects. Thus, scission and crosslinking reactions occur preferentially in these non-ordered sites. As a result, the thermal and mechanical properties of semi-crystalline materials are expected to change upon irradiation. Consequently, highly ductile materials may become very brittle after even small radiation doses, as will be shown later. It should be emphasized that the level of these changes strongly depends on whether the irradiated material is tested as such or as irradiated samples which have subsequently been melted and recrystallized. This is well demonstrated in *Figures 5a* and *5b*.

The results shown above indicate the following processes to occur in irradiated PCL: reorganization and ordering in the crystalline phase with little crystallization of additional molecules occurs presumably by scission of the highly constrained tie molecules and chain folds. These processes take place at room temperature which is far above the polymer  $T_g$  ( $-60^\circ\text{C}$ ) and quite close to its  $T_m$  ( $+60^\circ\text{C}$ ). We assume that the crosslinking reactions occur between chains in their relaxed states and thus have only little effect on the reorganization processes in the solid state. These crosslinks, however, play a major role if the crosslinked PCL is melted and then recrystallized. The crystal reorganization does not change the X-ray degree of crystallinity of the just irradiated polymer. It does however increase the crystal size as determined by X-ray (*Table 2*). This explains the 'discrepancy' between X-ray and d.s.c. degrees of crystallinity (*Figure 6*). The  $T_m$  of irradiated PCL remains unaffected below 40 Mrad and

**Figure 4**  $\ln \eta r/c$  (2g/dl benzene solution at 30°C) of PCL vs. radiation dose



**Figure 5** Effect of radiation dose on D.s.c. thermograms of PCL: (a) 1st heating run, (b) 2nd heating run. Curve (A): 50 Mrad; curve (B): 40 Mrad; curve (C): 20 Mrad; curve (D): 0 Mrad



**Figure 6** Effect of radiation dose on PCL crystallinity as determined by ● d.s.c., □ X-ray

only slightly declines at higher doses. This 1st run  $T_m$  behaviour is a net result of the higher order in the crystalline phase and the changes introduced in the amorphous phase.

The  $T_m$  behaviour of the irradiated and subsequently recrystallized PCL samples (Figure 5b) is very different from that of the ones irradiated only. Here, the  $T_m$  is

**Table 2** Crystallinity and crystallite size of PCL as affected by  $\gamma$ -irradiation

Irradiation dose (Mrad)	Crystallinity (%)	Crystallite size (Å)	
		110	200
0	68	27	24
20	68	38	31
60	67	42	38

affected even at low doses and larger  $T_m$  depressions are noted. These melting point depressions found in the 2nd d.s.c. scans can, according to Flory<sup>15</sup>, be explained as a result of a reduction of the concentration of crystallizable units. In addition, the presence of the crosslinks in the melt hinders crystal growth and lowers the degree of crystallinity and crystal perfection (Table 2).

The very dramatic irradiation effect on the PCL amorphous phase is demonstrated by the polymer mechanical behaviour. As shown in Figure 7, radiation doses of 2–5 Mrad (representing only small fractions of

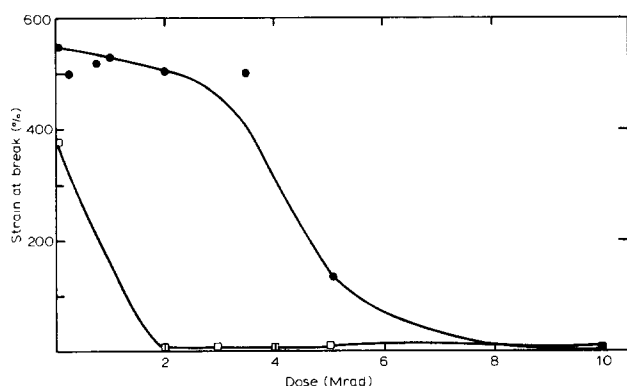


Figure 7 Effect of radiation dose on strain at break of PCL: □ batch 1 used throughout this work, ● batch 2

the critical dose for gel formation—26 Mrad) are sufficient to convert a highly ductile PCL into a very brittle one. Such doses evidently are typical in radiation sterilization treatments. This very early ductile-brittle transition stems from scission of the tie molecules leaving the crystalline domains untied, thus the load bearing elements in PCL are destroyed in a very early stage of the irradiation stage. This mechanical loss in elongation behaviour supports the foregoing discussion of the radiation effects in PCL.

#### ACKNOWLEDGEMENTS

The authors wish to thank Union Carbide for supplying the PCL-700 polymer.

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