

Ultrasonic and Thermal Properties of γ -Irradiated Low-Density Polyethylene

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SYNOPSIS

The ultrasonic pulse-echo technique and differential thermal analysis were utilized to characterize and to monitor the effect of γ -irradiation on the sonic modulus and the heat effect of low-density polyethylene. The sonic wave velocity, sonic modulus, and specific gravity exhibit a minimum for samples irradiated at 10 Mrad. A minimum in the heat capacity was observed at 1 Mrad. The estimated relative change of the activation energy of ordering exhibits a minimum at 100 Mrad. Below 10 Mrad, the perturbation and the loss of the crystalline phase override the effect of radiation cross-linking. From 10 to 100 Mrad, the effect of cross-linking as well as that of crystallinity are prevailing. Oxidative degradation is dominating above 100 Mrad. © 1993 John Wiley & Sons, Inc.

1. INTRODUCTION

Engineering polymers are progressively replacing metals and other conventional materials in many engineering applications. Physical, mechanical, and chemical properties of the polymeric materials are crucial in assessing their fields of applicability. For instance, many of the properties of low-density polyethylene (LDPE) have been thoroughly investigated; to mention but a few, the thermal expansion,^{1,2} heat capacity,³ thermal and electrical conductivities,^{4,5} and mechanical properties^{6,7} of LDPE were rigorously studied in the sense of relating these properties to its internal structure.

The action of ionization radiation is known to be one of the major sources of altering the internal structure of polymers and, hence, leading to a wide span of interrelated changes in their properties. It may result in cross-linking of the molecular chains,^{8,9} destruction and degradation of the macromolecules with the simultaneous formation of molecules with smaller chain lengths,^{9,10} and, possibly, a change in the number and nature of double bonds.^{11,12} Cross-linking of polymers under the action of ionizing radiation is known as "radiation

cross-linking." For polyethylene, the irradiation leads to the elimination of hydrogen and increases the degree of unsaturation of the molecule.¹³ Radiation cross-linking of polyethylene gives a material of increased thermal stability, insoluble in organic solvents and possessing a number of valuable properties. If the number of cross-links is small (low network density), the product will be soft and flexible; increasing the network density increases the stiffness of the polymeric material. A very large number of cross-links gives a very hard material.^{13,14} Radiation cross-linking of polyethylene has been utilized for the commercial production of films, combining the properties typical of polyethylene with form stability up to 200°C and a significant increase in tensile strength.¹⁵

It is pertinent to mention that the velocity and the attenuation of elastic waves at ultrasonic frequencies can be used for the determination of mechanical properties of crystalline polymers. The sonic pulse, in the MHz range, causes real displacements of the molecules from their equilibrium positions as it passes through the sample.¹⁶ Generally, the magnitude of the velocity of an ultrasonic wave traveling in the material is related to its density and one or more elastic stiffness constants. The form of the relationship between the velocity and the stiffness depends on the direction of propagation, the material's symmetry, and the character of the

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wave.¹⁷ For a wave propagation along the symmetry direction, the relation can be expressed as

$$C_{ii} = \rho V_{ii}^2 \quad (1)$$

where C_{ii} is the stiffness constant in a particular direction; ρ , the density of the material; and V_{ii} , the velocity of a particular wave propagating in a particular direction and $i = 1, 2, \dots, 6$.

The objective of the present work was to investigate the effect of the radiation dose on the propagation of ultrasonic waves through γ -irradiated LDPE and its sonic modulus. Furthermore, the effect of γ -irradiation on some of the thermal properties of LDPE, viz., heat capacity, is also highlighted.

2. EXPERIMENTAL

The raw material used throughout this work was low-density polyethylene Lotrene FB 3003 LDPE produced by Qatar Petrochemicals Co., the properties of which are listed in Table I.

2.1. Sample Preparation

LDPE pellets were compression-molded into a disc-like shape (25 mm diameter \times 2 mm thick) in a compression-molding machine at 30 MPa and 165°C for 20 min. The disc-like specimens were γ -irradiated at room temperature in air using a gamma cell 220 manufactured by Atomic Energy Canada. The operating dose rate was 1.5 Mrad/h and a set of samples spanning an integrated dose from 1 to 300 Mrad was prepared. The prepared samples were utilized for ultrasonic measurements to obtain the sonic modulus. The samples were also subjected to differential thermal analysis to determine their crystallinity and density as well as their specific heat. Finally, the degree of cross-linking of the γ -irradiated samples was monitored by determining their gel content.

Table I Properties of Loterne FB 3003 LDPE Resin

Density	0.921–0.923 g/cm ³
Crystalline melting point	115°C
Tensile strength	20 MPa
Melt index	0.24–0.30g

2.2. Ultrasonic Measurements

The sonic velocity is usually determined by measuring the transit time of a pulse using the pulse-echo technique. Pulse frequencies around 5 MHz allow accurate transit times to be measured on a sample whose dimension in the propagation direction may be as small as 2 mm.

Generally speaking, once the stiffness matrix components, C_{ij} , are obtained, the compliance matrix components, S_{ij} , can be readily calculated. Therefore, for an isotropic specimen, the sonic modulus may be given by the following relation^{17,18}:

$$E = E_{11} = 1/S_{11} \\ = [C_{11}(C_{11} + C_{12}) - 2C_{12}^2]/(C_{11} + C_{12}) \quad (2)$$

Nevertheless, a problem appears when applying this equation since C_{12} is unknown. For isotropic bodies, however, C_{12} can be deduced from the following equation^{17,18}:

$$\nu_{12} = C_{12}(C_{11} - C_{12})/(C_{11}^2 - C_{12}^2) \quad (3)$$

where ν_{12} is the in-plane Poisson's ratio, which for the LDPE utilized may be taken as 0.315.^{19,20} Measurements were then performed using the contact (transmitter-receiver) probe on the disc-like specimens with optically parallel surfaces. A slight smear of silicone grease was utilized to ensure good contact. All the measurements were performed at a frequency of 4 MHz. The velocity of sound propagation, V_{sp} (mm/s), through the sample can be determined from the relation

$$V_{sp} = 2D/\tau \quad (4)$$

where D = length of test specimen in the direction measurement, mm, and τ = transit time, s. Using eq. (1), one can then calculate the stiffness constant C_{11} from the relation

$$C_{11} = \rho(V_{sp})^2 \quad (5)$$

The density, ρ , was experimentally determined using thermal analysis, as indicated in the next section. C_{12} was obtained using eq. (3), and, finally, the sonic modulus was obtained from eq. (2).

2.3. Differential Thermal Analysis

DTA measurements were performed with the intention of following up the variation of the enthalpy of fusion, crystallinity, density, and heat capacity of

the irradiated LDPE samples with the radiation dose.

The melting endotherms were obtained using a Shimadzu thermal analyzer, DT-30, operating in the DTA heat mode. The heating cell was loaded with two platinum crucibles, one of which contained the reference material (alumina powder), while the other contained the test specimen. A typical specimen weight was about 10 mg. The heating rate was set at 10°C/min, starting from room temperature to 150°C. The obtained endotherms were utilized to determine the enthalpy of fusion, crystallinity, density, and specific heat of the prepared samples. High-purity benzoic acid and indium were utilized as reference materials for calibration purposes. Details of calculations are outlined elsewhere.²¹

2.4. Gel Content

A gel is a connected network extending through the polymer sample and which removes fluidity. The degree of cross-linking may be expressed as gel content by extraction with boiling xylene in a Soxhlet extractor.²² The extraction was allowed to be carried for five cycles over a period of 2 h. The sample was weighed before and after extraction and the gel content reported as wt %. It is pertinent to mention that the samples were vacuum-dried immediately after the extraction at 1 bar and 35°C and then weighed. The drying–weighing process was repeated until a constant weight was obtained.

3. RESULTS AND DISCUSSION

3.1. Ultrasonic Measurements

The sonic modulus is found to be sensitive to the irradiation dose, as shown in Figure 1. The figure shows that the sonic modulus decreases rapidly with increasing irradiation dose until a minimum value is reached at approximately 10 Mrad (stage I). Beyond this value, the sonic modulus increases until approximately 100 Mrad (stage II). At higher levels of irradiation, the modulus tends to decrease (stage III).

In stage I, such a peculiar behavior was also detected for the elastic modulus of LDPE obtained by tensile testing.⁷ It is assumed that two opposing processes are taking place simultaneously: A decrease in the polymer's density is accompanied by an increase in the degree of cross-linking. The density of the irradiated samples (and, hence, their crystallinity) decreases with irradiation doses up to

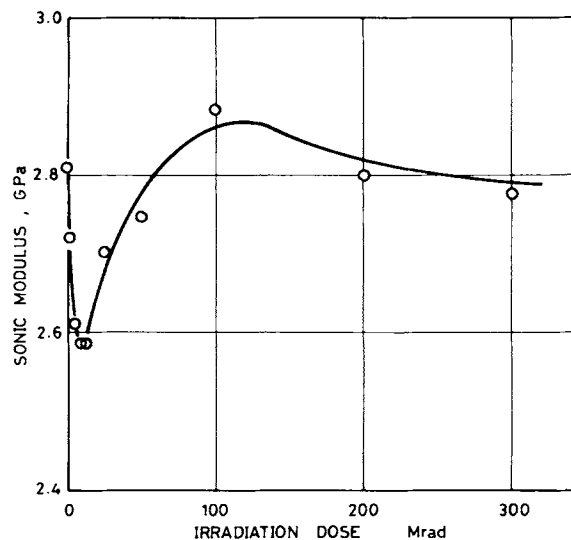


Figure 1 Variation of the sonic modulus of LDPE with irradiation dose.

approximately 10 Mrad, as shown in Figure 2. A similar behavior in this dose range was also recorded by Sangster and Barry.²³ This is in contradiction to the reported effect of irradiation on isotropic polyethylene,^{24,25} where an increase in density with irradiation dose was reported. That increase was attributed to chain scission followed by recrystallization. In our case, as will be shown later, the probability of scission is much less than that of cross-linking. Nevertheless, the present results indicate that there is a net increase in density (and therefore crystallinity) as shown in Figure 2: Compare the density at 0 Mrad to that at 300 Mrad. Furthermore, Figure 3 shows that the gel content increases in this irradiation range (0–10 Mrad) and, accordingly, the degree of cross-linking is also increasing. The gelation data may be analyzed in terms of the Charlesby–Pinner equation²⁶:

$$s + s^{1/2} = G(s)/2G(x) + K/[G(x) \cdot M_w \cdot r] \quad (6)$$

where s is the soluble fraction of the cross-linked polymer; r , the irradiation dose; $G(s)$, the number of main-chain scission events; $G(x)$, the number of cross-links produced; K , a constant; and M_w , the molecular weight. The equation predicts that a plot of $(s + s^{1/2})$ vs. $(1/r)$ should be linear. The ratio $G(s)/2G(x)$ is the intercept and the slope is proportional to $1/G(x)$. Such a plot, for relatively low irradiation doses, is illustrated in Figure 4. A linear relationship is observed up to about 10 Mrad, after which a deviation from linearity is manifested. Obviously, this is the dose at which cross-linking be-

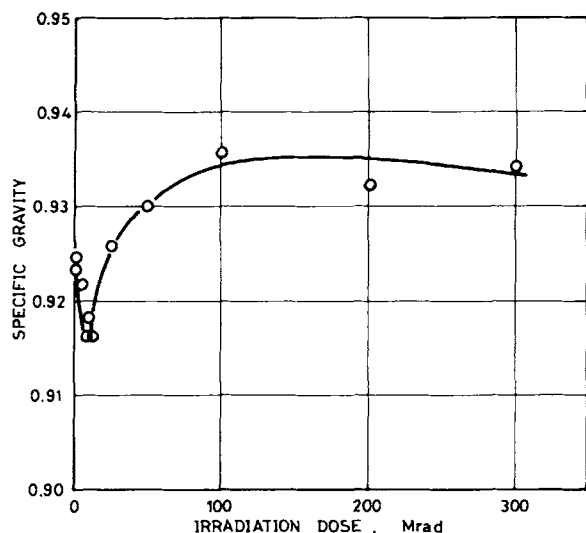


Figure 2 Effect of irradiation dose on the specific gravity of LDPE.

comes effective and the spatial network will start contributing to the properties of irradiated LDPE. The intercept on the $(s + s^{1/2})$ axis indicates that the probability of chain scission to cross-linking is about 1/3. Therefore, the opportunity of chain scission and possible recrystallization is limited and, hence, there will be no reason to believe that an increase in the density will accompany the increase in irradiation dose, as reported elsewhere.^{24,25}

Therefore, when LDPE is subjected to relatively low levels of irradiation doses, up to 10 Mrad, a loss of crystallinity is observed and the crystalline struc-

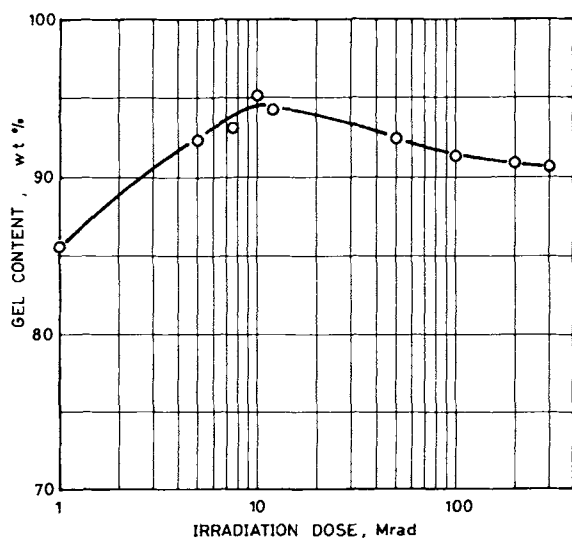


Figure 3 Relationship between gel content of LDPE and the irradiation dose.

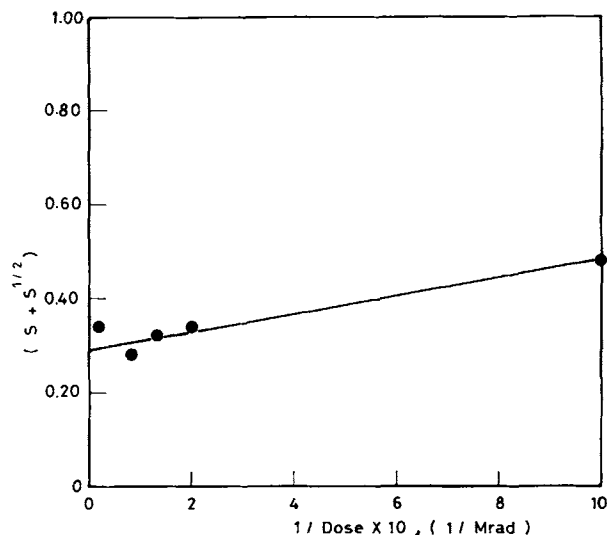


Figure 4 Plot of the Chalesby-Pinner equation for irradiated LDPE at relatively low irradiation doses.

ture is perturbed and disorganized. Such phenomena are expected to lower its density, as depicted in Figure 2. Simultaneously, cross-linking, which is normally confined to the interfacial regions of lamellae at or near fold surfaces,²⁷ is taking place as indicated by the increase in gel content. In this range of irradiation doses, the perturbation of the crystalline phase and the loss of crystallinity are assumed to be dominant and the entire internal structure is disturbed with a consequent increase in the free volume. For this reason, the velocity of the traveling sonic wave decreases with irradiation dose until a minimum value is reached at approximately 10 Mrad, as shown in Figure 5.

Upon further increase in the irradiation dose, stage II, the perturbation of the crystalline lattice is no longer observed, but, instead, an increase in the material's density (and, hence, its crystallinity) is observed, as depicted in Figure 2. It was pointed out earlier that it is around 10 Mrad that cross-linking becomes effective. Nonetheless, although relatively high, the degree of cross-linking slightly decreases with the irradiation dose in this stage. Such an observation was also reported in the work of Spadaro et al.²⁸ Therefore, the spatial three-dimensional lattice formation is accompanied by an increase in the material's crystallinity and the densification in stage II is not only due to the reduction of the free volume as a result of cross-linking but is also due to the increase in crystallinity. Such a densification is confirmed by the increase in the sonic velocity during this stage, as shown in Figure 5. Conceivably, the combined variations of the density

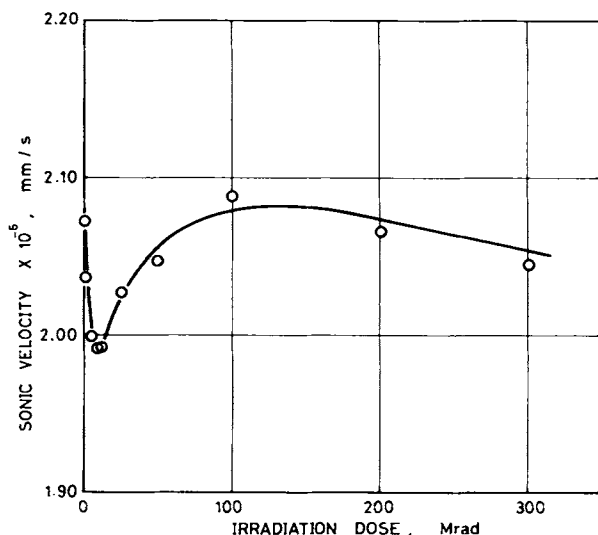


Figure 5 Effect of irradiation dose on the velocity of sonic-wave propagation in LDPE.

and the sonic velocity are expected to increase the sonic modulus of LDPE, as shown in Figure 1.

Irradiation doses greater than 100 Mrad seem not to improve the sonic modulus of LDPE. At such high doses (stage III), yellowing is observed to occur and this indicates that the specimens are oxidized.^{29,30} It is pertinent to point out, however, that those highly irradiated samples were left overnight at 45°C and the yellowing did not vanish. Furthermore, in spite of the relatively high degree of cross-linking, at this stage the velocity of the sonic wave tends to decrease and results in a lowered sonic modulus. The decrease in the sonic velocity may be attributed to the oxidative degradation taking place at relatively high levels of irradiation doses. Such phenomena were also quoted by Spadaro et al.²⁸ They reported that irradiation of polyethylene in air causes two competitive phenomena, viz., cross-linking and oxidative degradation, the kinetics of which are controlled by atmospheric oxygen diffusion: The former prevails at high dose rates and the latter at low dose rates. The dose rate used in this work is relatively high, and for this reason, cross-linking took place, even at integrated doses less than 50 Mrad. This contradicts the work of Torikai et al.³¹ because of the differences in applied dose rates and the polyethylene used in their work was linear low-density polyethylene and not LDPE. Furthermore, the reduction in gel content (and, hence, the degree of cross-linking) above 100 Mrad is to be expected at such high integrated irradiation doses, during which the oxidative degradation prevails when compared to cross-linking.²⁸ Figure 6 is a

schematic summarizing the various stages and the accompanied prevailing phenomena within the examined range of irradiation for the LDPE.

3.2. Thermal Measurements

The specific heat at constant pressure, C_p of unirradiated and γ -irradiated LDPE was obtained from the endotherm of the thermograms generated by thermal analysis. C_p was examined as a function of temperature to illustrate the effect of γ -irradiation on some thermodynamic properties. Figure 7 represents the temperature dependence of the specific heat, C_p , at total integrated doses of 0, 1, 10, and 300 Mrad. As expected, C_p reaches a maximum at temperatures near the fusion temperature of the unirradiated material, T_f ($T_f = 388\text{K}$). The fusion temperature of the 1 Mrad specimen is somewhat higher than that of the unirradiated specimen, whereas higher radiation doses do not seem to cause significant changes to the fusion temperature. The specific heat at the fusion temperature, C_p^{max} , is plotted in Figure 8. The values decrease at 1 Mrad and then suddenly increase at 10 Mrad to a value higher than that of the unirradiated material. Beyond 10 Mrad, the specific heat tends to increase very slightly. The initial decrease in C_p^{max} for the lower irradiation doses (1 Mrad) may be attributed not only to the dominant perturbation and the loss of the crystalline phase as mentioned earlier, but also to the formation of different types of radicals when irradiation is carried out in air.³² On the other hand, at sufficiently high doses, the effect of cross-linking is overridden by that of atmospheric oxygen

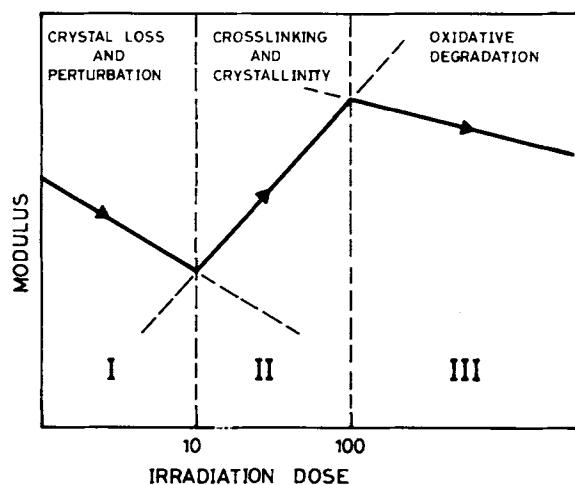


Figure 6 Dominating phenomena at different irradiation levels for LDPE.

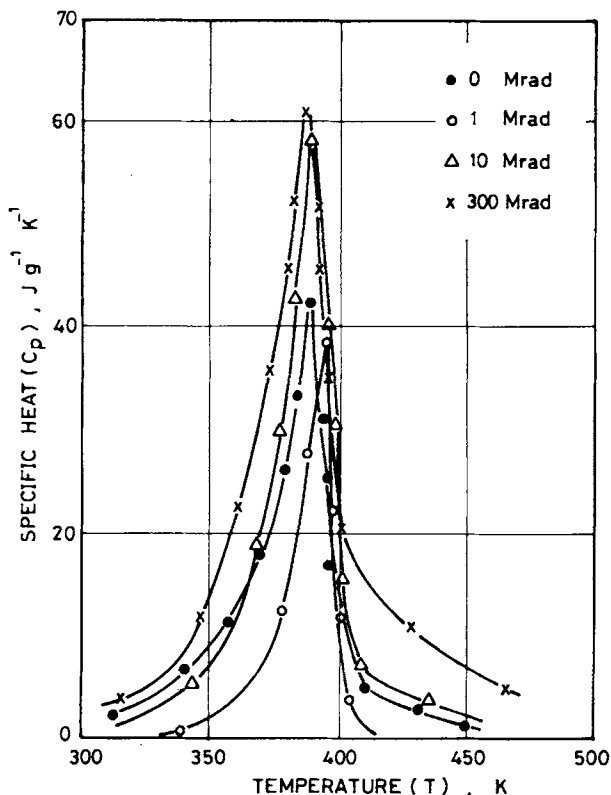


Figure 7 Variation of the specific heat of LDPE with temperature at various irradiation doses.

diffusion and oxidative degradation prevails as explained earlier (see diagram of Fig. 6).

The activation energy of ordering transition, u , could be estimated by applying the exponential relation³³

$$\Delta C_p = Z (Nu^2/RT^2) e^{-u/RT} \quad (7)$$

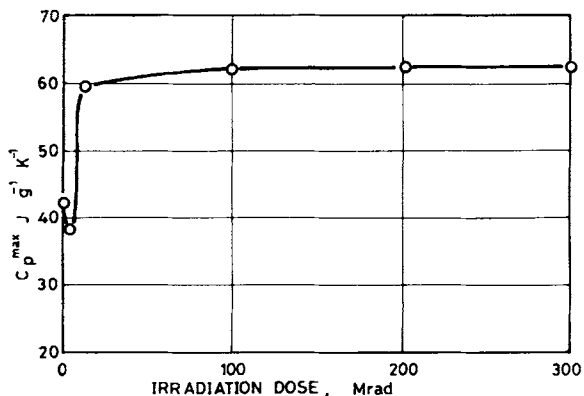


Figure 8 Relationship between the specific heat of LDPE at fusion (C_p^{\max}) and irradiation dose.

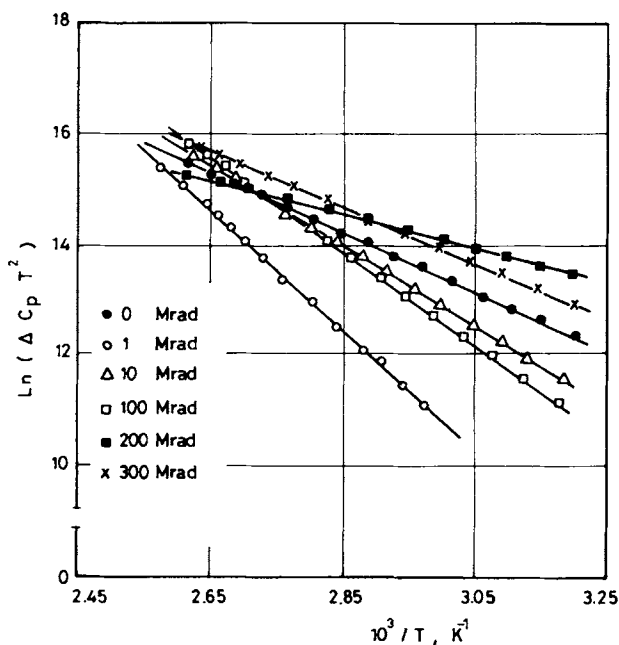


Figure 9 Effect of temperature on $\ln(\Delta C_p T^2)$ at various levels of irradiation doses.

where Z is the coordination number; N , the number of defects; and R , the universal gas constant. The activation energy of ordering, u , was obtained from the slopes of straight lines resulting from plotting $\ln(\Delta C_p T^2)$ vs. $1/T$ for different irradiation doses, as shown in Figure 9. This linear dependence is true experimentally, as long as we are away from the fusion temperature, T_f .³³ It is clear from Figure 10 that the estimated relative change of the activation energy of ordering, $\Delta u/u$, shows a minimum value at 100 Mrad. Here, Δu represents the difference between the activation energy of ordering for unirradiated samples and that of the irradiated ones and

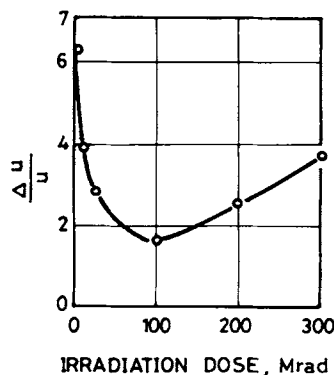


Figure 10 Effect of the irradiation dose on the relative change of the activation energy of ordering for LDPE.

u is the activation energy of ordering for the unirradiated sample. It is not surprising that the highest value occurs at 1 Mrad, since the minimum value obtained from C_p occurs at this dose, as shown in Figure 8; recall that u and C_p are inversely related. From the intersection of the straight lines of Figure 9 with the Y-axis, the relative values of defects can be estimated using eq. (7). A maximum number of defects was found to occur at 100 Mrad.

4. CONCLUSION

From the foregoing analysis, the effect of γ -irradiation on LDPE may be envisaged as a three-stage phenomenon. For doses up to 10 Mrad, the effect of radiation cross-linking is overridden by that of the perturbation and the loss of the crystalline phase. Cross-linking and crystallinity are the predominant morphological phenomena between 10 and 100 Mrad. Above 100 Mrad, oxidative degradation prevails.

The specific gravity, velocity of sound propagation, and sonic modulus show minima for the sample irradiated at 10 Mrad. Minima in the heat capacity and the estimated relative change of the activation energy of ordering are detected at 1 and 100 Mrad, respectively. The fusion temperature of the irradiated LDPE samples is not likely to be affected by the irradiation process.

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