[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY AND FROM THE POLYMER STRUCTURE SECTION, NATIONAL BUREAU OF STANDARDS]

Fusion of Polymer Networks Formed from Linear Polyethylene: Effect of Intermolecular Order

BY L. MANDELKERN, D. E. ROBERTS, J. C. HALPIN AND F. P. PRICE

RECEIVED JUNE 11, 1959

Specimens of linear polyethylene have been crosslinked at a variety of temperatures both above and below the melting point by either high energy electrons or by Co^{60} γ-rays. The melting points and the specific volume–temperature behavior of these specimens have been examined as functions of radiation dose and irradiation temperature. In general, the two types of radiation give the same results. Both the melting point depression and the reduction in crystallinity are more sensitive to radiation dose when the irradiation is carried out above the melting temperature than when it is performed below this temperature. The observed effects are explicable in terms of a recent theory of Flory which envisages that the configurational entropy of an amorphous polymer network is sensitive to the degree of order present when the crosslinks were introduced. These considerations lead to the conclusion that intermolecular order present in a highly crystalline polymer is maintained to some degree in the melt, if the crosslinks are introduced in the crystalline state. Consequently the melting temperatures of networks formed in this manner are significantly higher than those of networks formed from randomly arrayed chains. Furthermore, it was found that the melting temperatures of both types of networks, when immersed in a large excess of liquid, are depressed in accordance with the well known melting point relation, provided cognizance is taken of the amount of liquid inbibed.

Introduction

The intermolecular crosslinking of a collection of linear polymer chains results in a three dimensional network of vastly different properties from the original system of polymer chains from which it was formed. Recent theoretical considerations by Flory[1] have indicated that even though crosslinks are introduced randomly in space, many of the resulting network properties will depend to a marked extent on the arrangement of the polymer chains relative to one another at the time the crosslinks are introduced. In particular, differences in intermolecular order, present when the crosslinks are introduced, should be reflected in the resulting network properties. This recently has been shown to be the case by the comparison of the effects of crosslinking highly oriented or unoriented natural rubber[2] with Co^{60} γ-rays. In this study it was found that the isotropic length, the isotropic melting temperature and the equilibrium swelling ratio differed for the two types of networks when comparison was made at the same values of the fractions of units crosslinked. In this system and in others, in which crosslinking was effected by chemical means, the orientation of the polymer chains was brought about by mechanically elongating the polymer specimen. This resulted in a specimen which was anisotropic on a macroscopic scale.

In a specimen of undeformed crystalline polymer, wherein portions of polymer molecules are constrained to be parallel to one another in a three dimensional array, there exists a large amount of intermolecular order. This order is, however, on a submicroscopic scale, and the relatively small ordered regions are randomly oriented with respect to each other. It is of some interest to inquire whether the crosslinking of such a polymer in the crystalline state will produce a network which differs in properties from that produced by crosslinking the system when it is in the amorphous state. That crosslinking of crystalline polymers could produce unusual effects was illustrated recently by the observation that polyethylene which was crosslinked by irradiation at room temperature, upon subsequent heating to temperatures above the crystal melting point showed persistent birefringence in a spherulitic pattern.[3] This investigation showed that the birefringence was not due to the presence of crystallites. This work has been confirmed by one of us (F.P.P.), who found that the massive doses used by Hammer and his associates are not necessary to give the effect. In fact, specimens irradiated with 800 KV. peak electrons to doses as small as 40 megarads showed birefringence in the range of 150–200°. A photomicrograph of one such irradiated specimen is shown in Fig. 1. The spherulitic pattern is obvious and even the internal structure of the spherulites is still visible at some points. It was further found by us that polyethylene specimens that were irradiated when molten did not show birefringence upon subsequent melting after recrystallization. This demonstrates unambiguously that the presence of birefringence above the crystal melting point is due to the presence of the ordered crystalline regions during the irradiation.

In the present paper we consider the effect of introducing crosslinks into linear polyethylene when it is either in the crystalline state or in the amorphous state. The latter state is characterized by the fact that the polymer chains are randomly arranged relative to one another. It is well known[4] that subjecting polyethylene to high-energy irradiation results primarily in the introduction of intermolecular crosslinks. The crosslinking was thus accomplished by subjecting the polymer to either high-energy electrons or to Co^{60} γ-radiation. The physical state of this system at the time of crosslinking was controlled simply by suitable selection of the temperature at which the polymer was irradiated. The specific volume–temperature relations and the isotropic melting temperature of the resulting networks were the physical properties selected for initial study.

---

(1) P. J. Flory, THIS JOURNAL, **78**, 5222 (1956).

(2) D. E. Roberts and L. Mandelkern, *ibid.*, **80**, 1289 (1958).

(3) C. F. Hammer, W. W. Brandt and W. L. Peticolas, *J. Polymer Sci.*, **24**, 291 (1957).

(4) E. J. Lawton, J. S. Balwit and R. S. Powell, *ibid.*, **32**, 257 (1958).

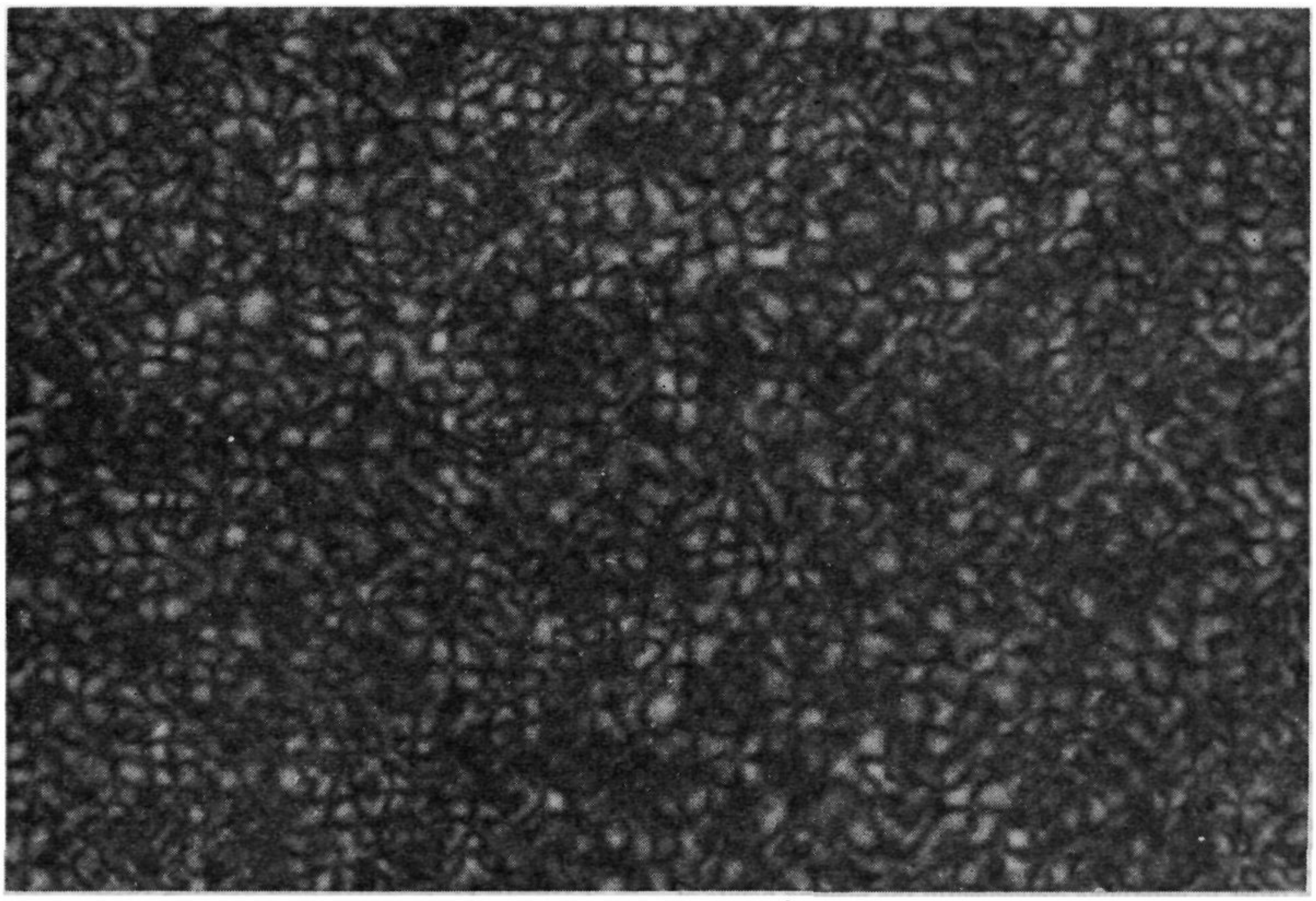

Fig. 1.—Photomicrograph of Marlex 50 irradiated 120 megarads at 25°: picture taken at 150° after one-half hour at that temperature; crossed Nicols and 300 ×.

Experimental

The polymer selected for study was a polyethylene manufactured by the Phillips Petroleum Company, Bartlesville, Oklahoma, under the name Marlex-50. Published infrared data[5] and a recent thermodynamic analysis of the fusion of this polymer[6] indicate that except for the end groups it consists primarily of unbranched polymethylene chains. The unfractionated polymer was used in this study; the weight average molecular weight as determined by light scattering techniques was found to be 130,000. Throughout this paper irradiation doses are reported in megarads.

That part of the work done at the National Bureau of Standards will be described first. Molded sheets of the polymer, $^1/_8''$ thick, were placed in Pyrex ampoules and heated at 145° *in vacuo* for 20 hr. The ampoules were then sealed and placed in the Co^{60} γ-ray source at the desired temperature for the required length of time. Irradiation temperatures of 17 and 175° were used. After irradiation the 175° specimens were allowed to cool slowly to room temperature and the ampoules then were opened. After irradiation the 17° specimens were heated at 145° for 60–120 min. and then allowed to cool slowly to room temperature before opening. It was found necessary to exclude rigidly oxygen from the polymer during the long irradiation in order to obtain consistent results.

After removal from the ampoules the irradiated polymers were extracted to constant weight with hot (135°) xylene. Removal of the imbibed xylene was effected by heating at 138° *in vacuo* (0.2–0.05 μ) for 24 hr. The volume–temperature behavior of the extracted specimens was determined using mercury filled dilatometers of the type previously described.[7] Measurements of the absolute specific volume of the extracted, recrystallized polymers were made at 25°, using the flotation method. All the dry melting points of the polymers irradiated with Co^{60} γ-rays were determined dilatometrically employing slow heating rates.[6]

Wet melting points were determined by immersing about 0.1 g. of the specimen in a large volume (50–100 ml.) of xylene, slowly raising the temperature ($^1/_4$° min.$^{-1}$) and observing the disappearance of cloudiness in the specimen. The volume fraction of imbibed solvent at the melting point was determined by removing the specimens from xylene, blotting with filter paper and weighing in closed weighing bottles.

In the work done at the General Electric Research Laboratory high energy electrons were used as the ionizing radiation. These were produced by a G.E. resonant transformer type electron generator and had 800 KV. peak energy. The specimens were sheets of polymer, 40 mils thick for the dilatometry experiments, 10 mils thick for the melting point determination by the polarized light apparatus described below and about 2 mils thick for the microscopic observation of melting point. Irradiations were carried out in a nitrogen filled chamber, but no rigid precautions were taken to remove dissolved oxygen from the samples. With the electron generator the dose rate is 1030 megarads/hr. as compared to 0.57 megarad/hr. for the Nat. Bur. Standards Co^{60} γ-ray source. Thus in the electron irradiation the exposure time is quite short. The rigid precautions for exclusion of oxygen thus were not deemed necessary when the electron source was used. Electron irradiation was carried out at a variety of temperatures. When irradiation was performed at temperatures below 150°, the samples after irradiation were placed immediately in an air oven at 150° for 15–20 min. to destroy any radicals trapped in the crystalline portions. In the work with the electron irradiated specimens no attempt was made to remove the sol fraction prior to determination of melting point or specific volume.

The volume–temperature behavior of the electron irradiated samples was determined with the conventional sealed off mercury-filled dilatometers. In this work the temperature of the thermostat containing the dilatometers was raised stepwise in 2° increments at the rate of 2° per day. The absolute specific volumes of the samples were determined at one temperature between 140 and 150° using silicone oil-filled pycnometers.

The specific volume–temperature relationships gave values of the melting points of the irradiated polyethylenes. Melting points were also determined using two other techniques:

---

[5] D. C. Smith, *Ind. Eng. Chem.*, **48**, 1161 (1956).

[6] F. A. Quinn, Jr., and L. Mandelkern, THIS JOURNAL, **80**, 3178 (1958).

[7] P. J. Flory, L. Mandelkern and H. K. Hall, *ibid.*, **73**, 2532 (1951).

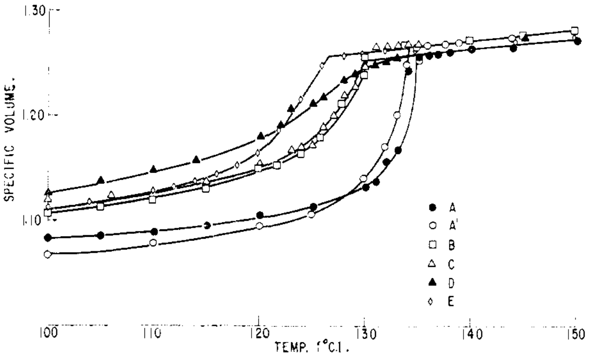

Fig. 2.—Effect of radiation dose below T_m^0 on specific volume–temperature behavior of Marlex 50: curve A, no irradiation (N.B.S.); curve A′, no irradiation (G.E.); curve B, 50 megarads electrons at −190°; curve C, 55 megarads Co^{60} γ at 17°; curve D, 607 megarads Co^{60} γ at 17°; curve E, 100 megarads electrons at −190°.

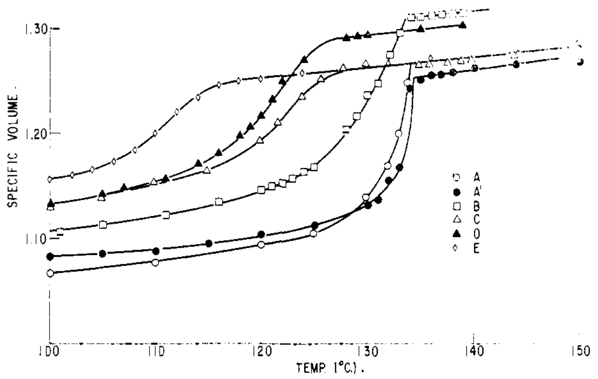

Fig. 3.—Effect of radiation dose above T_m^0 on specific volume–temperature behavior of Marlex 50: curves A and A′ as in Fig. 2; curve B, 5.7 megarads Co^{60} γ at 175°; curve C, 20 megarads electrons at 150°; curve D, 27.4 megarads Co^{60} γ at 175°; curve E, 45 megarads electrons at 150°.

(1) the polarizing microscope and (2) a polarized light apparatus described below. In the determination of the melting point using the polarizing microscope, the specimen (2 mils thick) was placed between cover slips on the microscope hot stage. The temperature was raised at the rate of 0.1°/min. The melting temperature was taken as that at which the last observable crystallites disappeared. The melting points thus determined agree quite well with those determined dilatometrically, presumably due to the ability of the observer to see the last remnants of crystallinity.

In order to determine conveniently the melting points of specimens irradiated under a wide variety of temperatures and doses, a special polarized light apparatus was constructed. It consisted of a silicone oil-filled thermostat fitted with glass ports so that a beam of light could pass through the thermostating liquid. The specimen under investigation was pressed between two thin optical quartz plates and mounted in the light beam in the silicone oil. Two crossed Nicol prisms were mounted in the light beam on either side of the thermostat and the light from an AH4 low pressure Hg lamp, filtered through Wratten 77 filter to give the 5461 Å. Hg line, passed through the system and fell on a 929 phototube. The output of the phototube was registered by a galvanometer. The output of the phototube was plotted as a function of the thermostat temperature. The melting point of the sample was taken as that temperature at which the output fell to a constant value. The polyethylene specimen was kept at each temperature about one half hour before readings were taken. The melting points could be estimated to ±0.5°. Because of the relatively rapid rate of heating, these melting points tend to be lower than those obtained from volume–temperature determinations.

The wide angle X-ray diffraction patterns were obtained using General Electric XRD-5 diffraction equipment. Scans were made at a slow speed so that 0.1 inch of chart paper corresponded to 0.05° in 2θ. A linear intensity scale was used. With this equipment a line width at half height (half width) of 0.12° was obtained with finely divided (325 mesh) quartz in a film a few mils thick. The polymer samples and the paraffin specimen used for comparison were all 18 mils thick.

Results and Discussion

Specific Volume Measurements.—The pertinent results of the effects of irradiation with either electrons or Co^{60} γ-rays on the specific volume–temperature behavior are indicated in Figs. 2 and 3, with plots of some typical experimental results. The results of irradiation at temperatures well below the crystalline melting point which are displayed in Fig. 2 will be discussed first. It must be emphasized that after being irradiated, these samples were melted and then allowed to recrystallize slowly before the dilatometric measurements were made. Comparison of curves A and A′ for the unirradiated polymer shows that the techniques used in the two laboratories give the same results. The difference between the two curves above the melting point is negligible, the melting points are identical and the differences below the melting point easily can be attributed to differences in specimen preparation and heating rates. Above the melting points the data for all the samples fall on essentially the same volume–temperature curve. This leads to the conclusion that when crystalline polyethylene is irradiated the specific volume of the melt of this polymer is independent of the absorbed radiation dose, the irradiation temperature, the dose rate and the type of radiation used. Below the melting temperature the irradiation decreases the amount of crystallinity rather abruptly at the start and then the effect of absorbed dose on crystallinity levels off. The melting point of the irradiated polymer also decreases somewhat with increasing dose but the effect is not very marked and it too seems to level off at a rather low dose. The melting point results will be discussed in more detail below. Further, only at very high irradiation doses, as is illustrated in curve D of this plot, is there any significant broadening of the melting range.

The effects of irradiation dose at temperatures above the melting point on the specific volume–temperature relations are shown in Fig. 3. Here it is seen that, whereas irradiation with electrons at 150° has no effect on the volume–temperature behavior of the molten irradiated polymer, irradiation with Co^{60} γ-rays at 175° produces first a rise and then a fall in the specific volume of the molten polymer at a fixed temperature. The difference cannot be attributed to the different irradiation temperatures, 150° for the electrons and 175° for the Co^{60} γ-rays, as the polymer is molten at both temperatures. The effect is well outside experimental error and must be real. It has been shown[8] that massive doses of ionizing radiation will eventually produce a more dense polymer. However,

---

(8) A. Charlesby and L. Callaghan, *J. Phys. Chem. Solids*, **4**, 306 (1958).

the initial decrease in density is puzzling. It may be due to the presence of either vinylene groups or branching introduced by the irradiation. The density lowering effect of these groups is eventually overcome by the density raising effect of the crosslinks. Why such effects should be more pronounced with Co^{60} γ-rays than with electrons is not known, though the more rigid exclusion of oxygen with the former type of irradiation may be a factor. Even though the absolute specific volume of the polymer changes with the dose in the case of Co^{60} γ-rays, the temperature coefficient of the specific volume is unaltered and is the same as that shown by the electron-irradiated polymers. The melting point behavior of these polymers will be discussed in detail below. Here suffice it to say that, in spite of the above mentioned differences, the depression of the melting point by a given irradiation dose is independent of whether the source is electrons or Co^{60} γ-rays. The effect of irradiation in depressing both the melting point and the crystallinity is much more marked here than in Fig. 2. Comparison of curve D in Fig. 2 with curve E in Fig. 3 shows that 607 megarads of Co^{60} γ-radiation at room temperature lowers the melting point only about 5° and gives a specific volume at 100° of 1.125 while a dose of only 45 megarads of electrons at 150° lowers the melting point 20° and gives a specific volume at 100° of 1.158. Furthermore, the polymers irradiated above the melting point show a continuous increase in specific volume below the melting point as the absorbed dose is increased in contradistinction to the leveling off shown by the polymers irradiated in the crystalline state. These results imply a continuous and larger decrease in the amount of crystallinity of the networks formed from amorphous chains as compared to those formed from crystallized chains. Also in contrast with the low temperature irradiated polymers the melting range of the polymers irradiated at high temperatures shows a marked tendency to broaden with increasing dose. Further, there is considerable rounding off of the curves in the region of the melting points. This type of melting behavior is reminiscent of the effects observed in the melting of copolymers.[9,10]

Dry Melting Point Measurements.—In the following discussion we define T_m^0 as the melting point of the unirradiated non-crosslinked polymer and T_m as the melting point of the irradiated crosslinked polymer. The results of the investigation of the effect of irradiation dose and irradiation temperature on melting point depression, $T_m^0 - T_m$ when the electron irradiation was carried out at temperatures below T_m^0 are shown in Table I. Here it is seen that the melting point depressions are small and that they are essentially independent of the irradiation temperature as long as this temperature is below the melting point of the polymer. The value of the melting point of the unirradiated polymer, 133°, determined with the polarized light apparatus is lower than the value of 137.5° determined by careful dilatometry.[6] This is due to the rapid heating rate (2°/hr.) with the polarized light apparatus compared to about 1°/day for the dilatometric techniques. In spite of differences in the absolute value of T_m as determined by the two methods, the depression of the melting point, $T_m^0 - T_m$, shows good agreement. Irradiation with Co^{60} γ-rays at 17° gave a constant melting point depression of 6.5° in the dose range of 14–607 megarads with indications that the sample which received the largest irradiation dose (curve D of Fig. 2) has a melting point depression slightly less than this value. These melting points were determined using dilatometric techniques and slow heating rates. The relative efficiency of crosslinking crystalline polyethylene by ionizing irradiation has been shown[4] to be much less than that for the corresponding amorphous polymer. However, the small but constant depression of the melting point that is observed is not due to a negligible change in the fraction of the units crosslinked with increasing radiation dose. This statement is supported by the fact that the gel fraction rose from 0.73 to 0.95 over the dose range studied and concomitantly the equilibrium swelling ratios of the networks formed decreased from 20.0 to 1.4. Both these facts indicate that a substantial number of crosslinks are introduced when the radiation occurs below T_m^0.

TABLE I

EFFECT OF ELECTRON IRRADIATION AT TEMPERATURE BELOW T_m^0 ON MELTING POINT DEPRESSION[a]

Dose (megarads)	Irrad. temp. (°C.)	$T_m^0 - T_m$ (°C.)
10		1
20	−190	3
50		5
10		1
20	25	4
50		5
10		3
20	75	4
50		6
10		3
20	125	5
50		6

[a] Melting points determined with polarized light apparatus. M.p. of unirradiated polymer was 133°.

The results of the effect on melting point depression of radiation administered above T_m^0 are presented in Fig. 4. The ratio of the melting point depression to the melting point of the irradiated polymer is plotted as a function of dose. The melting points were determined using a variety of techniques and the results of both the electron and the Co^{60} γ-ray irradiation are included. The melting points determined using the polarizing microscope are in good agreement with those determined using the dilatometric method. It can be seen that at doses below 50 megarads all the points fall on a good straight line. Above 50 megarads the Co^{60} γ-radiation is more effective in depressing the melting point than is the electron radiation. It is not known why this should be so, although it is possible that the 1500-fold difference in dose rates (0.57 megarad/hr. for Co^{60} γ, 1030 megarads/hr. for electrons) is responsible. The difference is not due to differences in the dose temperature, for speci-

---

(9) P. J. Flory, *Trans. Faraday Soc.*, **51**, 848 (1955).

(10) L. Mandelkern, *Chem. Revs.*, **56**, 903 (1956).

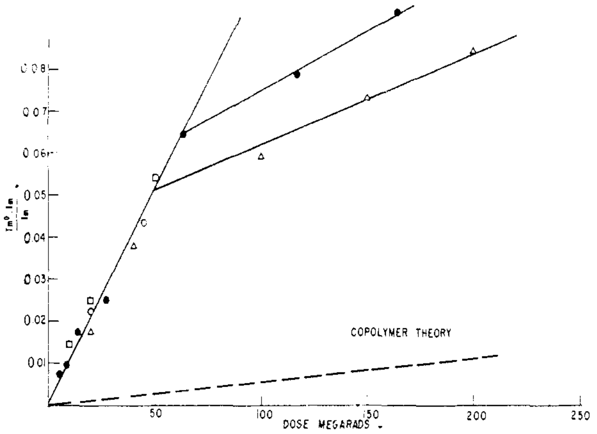

Fig. 4.—Influence of dose on melting point of Marlex 50 for irradiation above T_m^0: ●, Co^{60} γ at 175° determined dilatometrically; ○, electrons at 150° determined dilatometrically; △, electrons at 150° determined with polarizing microscope; □, electrons at 150° determined with polarized light apparatus.

mens irradiated with electrons to 100 megarads at 175 and 200° gave values of $(T_m^0 - T_m)/T_m$ of 0.065 and 0.071, respectively. It should be noted here that, as will be discussed below, the observed depression of the melting point is surprisingly large, and in contrast to the samples irradiated below T_m^0, a continuous depression of the melting point is observed with increasing radiation dose.

The random introduction of crosslinks into a collection of random chains, a situation which corresponds to the subjecting of polyethylene to ionizing radiation above T_m^0, results in no change in the configuration entropy of the liquid state since units are selected and paired at random.[1] However, the introduction of the crosslinks does produce an increased randomness of the liquid which, in the case where the fraction of crosslinks is small, results in an increase in entropy of the liquid per mole of repeating unit of $R\rho$ (R = gas constant, ρ = fraction of units involved in crosslinks). Upon crystallization it might be expected in general that due to steric requirements, chain units involved in crosslinkages would be excluded from the crystalline regions. This will result in a somewhat more positive entropy per repeating unit for the crystalline units. Thus the introduction of crosslinks will increase the entropy of fusion per mole of repeating units by $R\rho$ at a maximum. On the other hand, the heat of fusion per polymer unit ΔH_u would not be expected to be significantly altered, particularly since the crystal structure is not changed. Under equilibrium conditions, therefore, wherein no restraints are placed on the development of crystallinity except for interruptions along the chain direction due to the presence of crosslinks it might be expected that the melting point of a network, formed by the random crosslinking of random chains would obey the relation

$$1/T_m - 1/T_m^0 = (R/\Delta H_u)\rho \qquad (1)$$

when the fraction of units crosslinked is small. This equation is identical to the limiting form of the expression previously derived[9] for the melting temperature of a random type copolymer containing non-crystallizing units. In the latter case, however, this equation is valid only when no restrictions are placed on the development of crystallinity in directions transverse to the chain direction.[11]

The fraction of the units crosslinked, when polyethylene is irradiated above its melting temperature, can be estimated from the following considerations. Since the weight average molecular weight is 130,000, it is found by applying the critical conditions required for gel formation[12,13] that the fraction of the repeating units crosslinked at the gel point is 1.1×10^{-4}. It has been determined that a dose of 2.74 megarads is just sufficient to produce gel, by the Co^{60} irradiation of the unfractionated polymer at 175°.[14] If it is assumed that the fraction of units crosslinked in the entire system is proportional to the irradiation dose, then 4×10^{-5} units are involved in crosslinkages per megarad of irradiation. The published value of G = 3 crosslinks/100 e.v., which was obtained by less direct methods,[4] yields a comparable value for the crosslinks per megarad if it is assumed that there are 30 e.v./ion-pair and 1.51×10^{15} ion pairs/(megarad g.).

The value of the quantity $(T_m^0 - T_m)/T_m$ to be expected according to equation 1 can be calculated by utilizing the relation $\rho = 4 \times 10^{-5} D$, where D is the absorbed dose in megarads and the previously determined[6] value of 940 cal./mole of methylene units for ΔH_u. The results of this calculation are indicated by the dashed line in Fig. 4. It is obvious from this plot that the observed melting point depression over the complete crosslinking range is many times greater than that calculated by means of equation 1. Thus, for example, for a network formed at a radiation dose of 116 megarads corresponding to a value of ρ equal to 4.65×10^{-3}, a melting point depression of 30° is observed, while according to equation 1 a depression of only one to two degrees is calculated. Qualitatively similar results have been obtained over the same crosslinking range for the melting points of networks formed from amorphous chains of natural rubber by either chemical means[15] or by means of ionizing radiation.[2]

It has been observed frequently in considering the melting point depression of random copolymers that the actual depression is greater by a factor of about two than that theoretically expected.[9,10] These observations have been made on systems in which the concentration of chain irregularities (non-crystallizing copolymeric units) was substantially greater than those considered here. The discrepancy in that case can be attributed to the fact that in the true copolymer systems studied, it is extremely difficult to determine the required equilibrium melting temperature.[9,10] The presently observed discrepancy for randomly crosslinked systems cannot, however, be explained on this basis, and these results are clearly incompatible

---

(11) P. J. Flory and L. Mandelkern, *J. Polymer Sci.*, **21**, 315 (1956).

(12) P. J. Flory, THIS JOURNAL, **63**, 3097 (1941).

(13) W. H. Stockmayer, *J. Chem. Phys.*, **12**, 125 (1944).

(14) L. Mandelkern, D. E. Roberts and J. C. Halpin, unpublished results.

(15) D. E. Roberts and L. Mandelkern, *Bull. Am. Phys. Soc.*, Series II, **1** (March 1956).

with the copolymer melting point equation. In a formal fashion, this type of result has been rationalized[16] by assuming that the number of units that are restricted from participating in the development of crystallinity is appreciably greater than the number of units that are actually intermolecularly crosslinked. Since the crosslinks are tetrafunctional, a small part of the observed discrepancy might be accounted for by allowing that nearest neighbor units are also prevented from participating in the crystallization. Even if this were allowed, a major discrepancy would still exist if adherence of the experimental results to equation 1 is demanded.

Equation 1, however, is derived on the basis that crystallinity be allowed to develop in an ideal fashion in directions lateral to the chain direction, no imperfections being allowed and no restrictions being placed on the size of the crystallites that develop. If these conditions are not fulfilled, then substantial alterations of equation 1 must be made.[11] Though, in true copolymer systems there are, in principle, no restrictions to the development of crystallinity in the lateral directions, the distinct possibility exists that in crosslinked systems, since the complete rearrangement of polymer chains cannot occur, a restriction on the lateral development of crystallinity may be imposed.

The possibility of restricted development of crystallinity in the lateral direction was investigated by examining the half width of the wide angle X-ray reflection of the 110 plane for specimens subjected to irradiation while either crystalline or molten. The specimens that were irradiated with electrons (a) to 100 megarads at 25° and (b) to 50 megarads at 150° gave half widths of 0.47 and 0.60°, respectively. A sample of unirradiated polyethylene gave a half width of 0.36° while a block of crystalline paraffin of the same thickness gave a half width of 0.30° for the 110 reflection. It should be noted that the differences between the two irradiated specimens cannot be due to major differences in the crosslinking, since the gel content in each case was well over 90%. It should further be noted that in this dose range there was no detectable change in all the recorded Bragg spacings. This observation is at variance with results of a previous investigation[17] wherein, however, much larger irradiation doses were used. The increased breadth of the 110 reflections of the irradiated specimens might be attributed to strain, to imperfections within the crystallites, or to decrease in the crystallite size in the lateral direction.

The magnitudes of the differences among the various half widths are sufficient to account for significant differences in extent of lateral order provided that all the broadening is due to changes in crystal size.[18] However, regardless of which if any of these effects is dominant, each individually or in combination will act to cause a severe depression of the melting temperature. Since in the well annealed crosslinked specimens line widths (for reflections representing lateral crystalline planes) comparable to those observed in the non-crosslinked polymer cannot be attained, a systematic depression of T_m with crosslinking should be expected. A similar result has been obtained for crosslinked natural rubber and will be reported shortly.[19]

It is worth noting that the excessive depression of the melting point resulting from decreases in crystallite size or perfection comes about from the fact that the net heat of fusion becomes negative at a greater rate than does the net entropy of fusion. This is a direct consequence of the fact that the free energy associated with the crystallite surfaces becomes a significant fraction of the total free energy of fusion. Further, in the range of melting temperatures here discussed, a decrease of 10% in the heat of fusion is sufficient to decrease the melting point about 40°. Thus, changes in heats of fusion that are undetectable by conventional polymer techniques are capable of producing the changes in melting point noted here. The broader melting range that is observed for networks formed above T_m^0, compared to those formed below T_m^0, can thus be attributed to the preferential melting of small and imperfect crystallites as the temperature is increased. Thus, it can be concluded that the random introduction of crosslinks into amorphous polymer chains retards the development on subsequent recrystallization of the more perfect crystallites required by the equilibrium theory. Since the fraction of the units crosslinked is so relatively small compared to the observed melting point depression, the role played by chain irregularities must be secondary in this respect.

It already has been indicated that the melting temperatures of networks formed by irradiation below T_m^0 vary in a markedly different fashion with radiation dose than those of networks formed above T_m^0. In the former case a depression of only about 6° in the melting point is observed, even for a radiation dose as high as 605 megarads. A quantitative evaluation of the number of crosslinks introduced when the irradiation takes place in the crystalline state is difficult to make for this polymer due to the fact that the partitioning of the polymer between sol and gel with increasing dose does not follow the same course as when the amorphous polymer is crosslinked.[14] Thus the same methods used previously to determine the quantity ρ for the irradiation of crystalline natural rubber[2] cannot be used. Furthermore it is now well recognized[2,20] that the measurement of certain network properties as elastic modulus or swelling ratio in the amorphous state of networks formed from ordered chains does not unambiguously give the desired quantity ρ, due to the necessity of specifying the network dilation factor $<\alpha>$.[1] This latter quantity has as yet not been susceptible to direct calculation. In spite of these difficulties, the observed sol–gel relations and the drastic changes that occur in the equilibrium swelling ratio with progressively increasing radiation dose indicate that an appreciable number of crosslinks are introduced. Thus, though higher radiation

---

[16] A. W. Gent, *J. Polymer Sci.*, **18**, 321 (1955).

[17] W. P. Slichter and E. R. Mandell, *J. Phys. Chem.*, **62**, 334 (1958).

[18] W. H. Bragg and W. L. Bragg, "The Crystalline State," Vol. I, G. Bell and Sons, Ltd., London, 1949, p. 189 ff.

[19] D. E. Roberts and L. Mandelkern, publication in preparation.

[20] J. F. M. Oth and P. J. Flory, THIS JOURNAL, **80**, 1297 (1958).

doses need be employed, the values of ρ for the networks formed from the crystalline chains are comparable to those formed from the amorphous chains.

In contrast to the crosslinking of randomly disposed polymer chains, the crosslinking of an ordered system, *i.e.*, one in which portions of polymer chains are constrained to lie in parallel array, results in a decrease in the chain configurational entropy in the liquid state.[1] This situation arises because, even though crosslinks may be distributed randomly in space, the crosslinking process does not involve the random selection of pairs of units. Thus the units that can be paired are severely restricted, since the maintenance of the regular chain array specifies and limits the pairing process. As Flory has shown,[1] this process necessarily decreases the configurational entropy in the liquid state; a more ordered liquid can be considered to be formed, and a decrease in the entropy of fusion must result. Insofar as ΔH_u will not be altered by the crosslinking process, if the above were the sole consideration, a continuous increase of T_m with crosslinking density should be expected for networks formed from ordered chains. However, any restrictions on the development of crystallinity imposed by the crosslinks must also be considered.

The photomicrograph of Fig. 1 indicates that when the highly crystalline, but not mechanically oriented, polyethylene is crosslinked considerable order is maintained in the liquid state. The above considerations might therefore also apply to chains ordered on a microscopic scale. The change in line width of the 110 reflection for the network formed in this manner has been noted above. The broadening of the 110 reflection with radiation dose in this case indicates that the development of crystallinity comparable to the non-crosslinked polymer is again considerably restrained. However, the line broadening is not as great as when random chains are crosslinked. This difference is due to the fact that crystallization takes place from an ordered liquid with consequent differences in the recrystallization mechanism.

The differences between the melting points of networks formed from ordered chains and that of the amorphous polymer will depend on two additional contributions to the free energy of fusion due to the introduction of crosslinks. One effect will be an alteration of the entropy of fusion due to a decrease of chain configurational entropy in the melt. This factor will tend to raise the melting point. On the other hand, the fact that the development of crystallinity in the lateral direction is retarded will tend to lower the melting point. These two factors will tend to compensate each other and in the case of crosslinking crystalline polyethylene a small melting point depression, which is invariant with radiation dose, results. This is in marked contrast to the crosslinking of amorphous chains, where the chain configurational entropy in the melt is unaltered by the crosslinking process and a continuous decrease in T_m with irradiation dose occurs. Similar differences in the melting points of networks formed from amorphous natural rubber and of fibrous natural rubber have been reported.[2] Thus, it can be concluded that the mechanical orientation of polymer chains is not required in order for differences to be observed in the properties of the resulting network. The microscopic orientation developed by the random crystallization of portions of the chains introduces sufficient order into the system so that the melting temperature and melting behavior following crosslinking is fundamentally different from that of networks formed from random chains.

Wet Melting Points.—The melting points T_m^* of some of the networks formed by means of Co^{60} γ-irradiation were measured while the specimens were in contact with a large excess of xylene. The melting points determined in this manner will be designated as wet melting points in the subsequent discussion. On melting, the networks in the amorphous state imbibe relatively large quantities of the surrounding liquid; the amount of swelling that occurs is dependent somewhat on the temperature but primarily on the crosslinking density of the system. Conversely, on crystallization from the amorphous state the diluent is excluded and an isotropic syneresis takes place. The experimentally determined melting points of the networks and v_1, the volume fraction of xylene imbibed at the transformation temperature, are given in Table II.

TABLE II

MELTING POINTS OF NETWORKS IN PRESENCE OF XYLENE

Dose (megarads)	T^*_m	v_1
	17° Irradiation	
5.7	102	0.88
13.7	104	.83
27.4	105.3	.77
55.3	106.2	.69
136	110	.58
295	114	.36
	175° Irradiation	
5.7	101	.84
8.6	100.2	.85
13.7	100	.80
27.4	100.6	.71
63.3	94	.68

From this table it can be seen that the wet melting points of networks formed at 175° decrease only slightly with increasing radiation dose in contrast to the behavior of the melting points of the network formed at 17° which increase continuously and significantly with absorbed dose (crosslinking density). This behavior is to be contrasted with the melting point behavior of the undiluted networks of both the polyethylene reported here, and of natural rubber,[2] where regardless of the chain disposition prior to network formation a decrease in T_m invariably is observed. The wet melting point–crosslinking relations that are observed can be explained by considering the facts that (a) the dry melting points are decreasing at different rates and (b) the volume fraction of imbibed solvent continuously decreases with increasing crosslinking for both types of networks.

Since the diluent is excluded from the crystal lattice of the polymer, it can be supposed to a first approximation that the melting point depression of the swollen network relative to that of the undiluted network will be governed by the usual laws of phase equilibria aprpopriate to a first-order transition. Thus it will be expected that relation[21,22] (2) will be obeyed. Here χ_1 is the usual

$$\frac{1}{T_m^*} - \frac{1}{T_m} = (R/\Delta H_u)(V_u/V_1)(v_1 - \chi_1 v_1^2) \qquad (2)$$

solvent–polymer interaction parameter, V_u is the molar volume of the repeating unit and V_1 is the molar volume of the solvent. The data presented in Table I and Fig. 4 can be combined with the results of Table II to calculate the quantity on the left-hand side of eq. 2. In Fig. 5 these quantities are plotted against the appropriate values of v_1. Also in Fig. 5 the solid lines show the relationship to be expected from eq. 2 with ΔH_u = 940 cal./mole, V_u = 17.7, V_1 = 140 and χ_1 having the indicated values. The agreement between theory and experiment is satisfactory and substantiates in part the fact that ΔH_u is essentially unaffected by the presence of the crosslinks. It is noteworthy that the existing theory can encompass the apparently diverse facts that the wet melting points of the two different types of networks vary in quite different fashion with increasing amounts of crosslinkages.

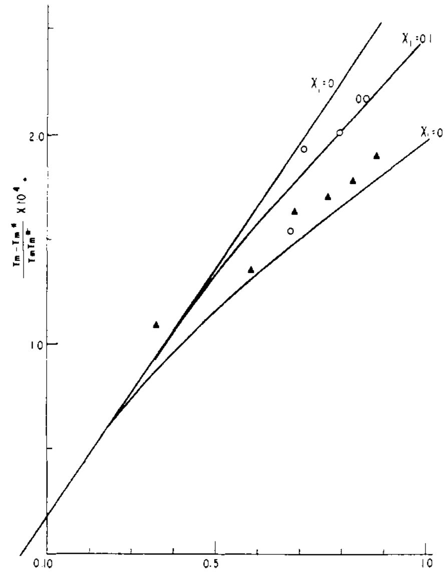

Fig. 5.—Correlation of wet melting points of Marlex 50 samples irradiated with Co^{60} γ-rays with volume fraction of xylene v_1: ○, irradiation temp. 175°; ▲, irradiation temp. 17°.

The increase of the melting temperature with crosslinking density of the wet networks formed from ordered chains is the first example of this phenomenon for the more flexible chain type molecules and is reminiscent of similar effects when fibrous proteins are crosslinked. According to the theoretical considerations of Flory[1] when highly ordered chains are crosslinked and when the crosslinking process does not interfere with the crystallization of the units involved, a continuous increase of melting temperature with crosslinking should be observed. This appears to be the case for certain of the fibrous proteins as α-keratin from various layers of epidermis and collagen crosslinked by a variety of chemical methods. For both these systems it has been reported[23,24] that the shrinkage temperature, which is closely related to the melting temperature, increases as the crosslinking is increased. However, since the melting of the fibrous proteins is always observed when the polymers are immersed in a suitable liquid medium, the change in swelling equilibrium that must occur as a result of the crystalline to amorphous transformation will also affect the melting point. From just this consideration alone an increase in melting point with crosslinking would be expected, in analogy with the wet melting points observed for polyethylene networks formed in the crystalline state. This effect could very well be of the same order as that involving alteration of the entropy of fusion by the crosslinking of oriented chains.

SCHENECTADY, NEW YORK
WASHINGTON, D. C.

---

(21) P. J. Flory, "Principles of Polymer Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, pp. 568 ff.

(22) The assumptions are made that the chemical potential of a chain repeating unit in the binary liquid phase is independent of the type of network, and that the heat of fusion per repeating unit of a network is essentially the same as for the non-crosslinked polymer.

(23) H. M. Rudall, "Symposium on Fibrous Proteins," *J. Soc. Dyers & Colorists*, 15 (1946).

(24) K. H. Gustavson, "The Chemistry & Reactivity of Collagens," Academic Press, Inc., New York, N. Y., 1956, p. 227.