The intermolecular potential was derived on the assumption that the free energy of mixing the solution for a given configuration of polymer centers is an integral of $\epsilon[f(R)]$ over the solution volume, where $f(R)$ is the local volume fraction of segments. It was further assumed that $\epsilon(f)$ could be expanded in powers of $(f - v_2)$ and that terms higher than quadratic could be suppressed. The last assumption is responsible for the existence of a pair potential. If cubic and higher powers of $(f - v_2)$ were retained, not only would the concentration dependence of the pair potential be modified, but three-body and, in general, n-body potentials would be introduced. The concept of interacting polymer molecules would become useless and a return to explicit consideration of segment–segment interactions would be necessary. The unfortunate failure of $h(r)$ to stay near unity makes probable the

failure of the quadratic expansion, but the neglect of fluctuations in the gaussian segment distribution must also become serious at very high concentrations as follows from the analysis of the segment concentration after eq. 30. We know of no experiments to test directly the theory of α. Some related possibilities are light scattering studies of a polymer A in a solution of polymer B, such that B and the solvent have the same refractive index,[9] and studies of polymer solutions in the critical region,[10] where the theory of intermolecular interference might be simple enough to allow extraction of polymer dimensions. The former experiment would require minor and the latter experiment major extensions of the theory.

(9) Preliminary attacks on this difficult experiment were made some time ago by W. H. Stockmayer, private communication.

(10) P. Debye, B. Chu, and D. Woermann, *J. Chem. Phys.*, **36**, 1803 (1962).

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Irradiation Cross Linking of Polyethylene. The Temperature Dependence of Cross Linking in the Crystalline and Amorphous States[1]

BY R. KITAMARU AND L. MANDELKERN

The irradiation cross linking of molecular weight fractions of polyethylene has been studied as a function of the temperature and state of the system. In general it is found that a definite distinction must be made between the temperature and the state of the system since the irradiation temperature has a different effect on the crystalline and amorphous regions. At low temperatures there is essentially no difference in the cross-linking efficiency of a highly crystalline bulk specimen when compared with one in which the crystallinity is not as well developed. However, at temperatures exceeding 100° the efficiency of cross linking the highly crystallized specimen increases by a factor of two while the efficiency for the other specimen remains essentially constant. An explanation of these results is offered in terms of the onset of molecular motion among the chain units in the crystalline sequences at this temperature. In addition, it is found that at temperatures where a direct comparison can be made, intermolecular cross linking is much more easily accomplished in the highly crystalline specimen than in a completely amorphous one. Experiments on the partitioning between sol and gel subsequent to the irradiation of crystals formed from dilute solution are interpreted in terms of these results.

Although the effect of high energy ionizing irradiation on polyethylene has been extensively studied many fundamental questions still remain unresolved.[2] The problems of concern include the efficiency of the cross-linking process, particularly as it depends on the state of the system, the partitioning between sol and gel, the elastic and thermodynamic properties of the resulting network structures, as well as the mechanistic details of the radiation chemistry involved. These difficulties in interpretation still are present even if consideration is limited to linear polyethylene. One major reason for these problems can be attributed to the very broad molecular weight distribution in the samples that have been studied which in turn makes difficult any detailed interpretation of the sol–gel curve. In addition, the crystallization of polyethylene at the usual irradiation temperatures introduces into the sample distinctly different coexisting chain configurations as a result of the polycrystalline and partially crystalline character of the system. Since it can be anticipated[3–6] that the efficiency of the cross-linking

process as well as the properties of the resultant isotropic network will depend on the chain configuration and hence the state of the system at the time cross links are introduced, obviously complication in analyses will inherently exist unless the level and type of crystallization can be quantitatively described. This requirement involves, as a minimum condition, the controlled crystallization of samples prior to irradiation as well as the control of the sample temperature during the irradiation process.

In an effort to sort out these various complexities, we have investigated the effects of high energy ionizing radiation on molecular weight fractions of linear polyethylene. The samples were prepared under prescribed crystallization conditions with an attempt being made to take advantage of other investigations involving a description and analysis of the thermodynamics of the fusion process[7] as well as the crystallization kinetics from the melt of fractions.[8,9] We have reported[10]

(2) A. Chapiro, "Radiation Chemistry of Polymer Systems," Interscience Publishers, Inc., New York, N. Y., 1962, pp. 385–405.

(3) L. Mandelkern, D. E. Roberts, A. F. Diorio, and A. S. Posner, *J. Am. Chem. Soc.*, **81**, 4148 (1959).

(4) L. Mandelkern, D. E. Roberts, J. C. Halpin, and F. P. Price, *ibid.*, **82**, 46 (1960).

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

(6) J. C. Halpin and L. Mandelkern, *J. Polymer Sci.*, **2B**, 139 (1964).

(7) R. Chiang and P. J. Flory, *J. Am. Chem. Soc.*, **83**, 2857 (1961).

(8) W. Banks, M. Gordon, R. J. Roe, and A. Sharples, *Polymer*, **4**, 61 (1963).

(9) J. Fatou and L. Mandelkern, to be published.

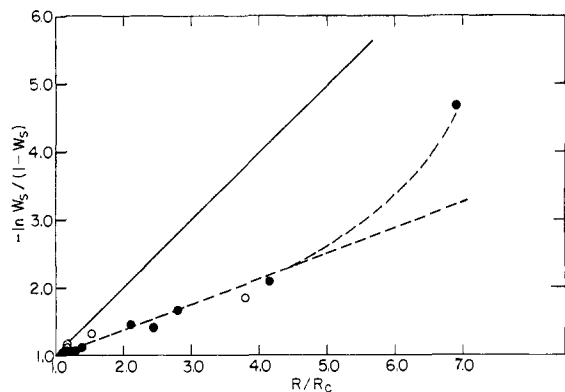(10) R. Kitamaru, L. Mandelkern, and J. Fatou, *J. Polymer Sci.*, in press.

Fig. 1.—Plot of the quantity $-\ln W_s/(1 - W_s)$ against the ratio R/R_c: solid line, theoretical curve calculated according to eq. 2; dashed line, representation of experimental results for irradiation of molecular weight fraction $M_\eta = 182{,}000$ at $133°$; ●, highly crystalline sample; ○, completely amorphous sample.

that for the irradiation of completely amorphous polyethylene the dosage required for incipient gelation is inversely proportional to molecular weight, over a wide molecular weight range, in accord with classical theory.[11,12] Moreover, a study of the partitioning between sol and gel of a highly crystalline polymer and the same sample in the completely amorphous state, both samples being irradiated at 133°, has demonstrated that cross linking occurs much more effectively in the crystalline state at this temperature. In the present work, we have extended these studies to encompass a wider temperature range, from room temperature to above the melting temperature of the polymer, and have also investigated gel formation in polyethylene crystals formed from very dilute solutions.

Experimental

Materials.—Molecular weight fractions were obtained by conventional column elution techniques with unfractionated Marlex-50 being used as the starting material. Viscosity-average molecular weights of the fractions were obtained from intrinsic viscosity measurements in decalin at 135° using the relation $[\eta] = 6.2 \times 10^{-4}M^{0.70}$ obtained by Chiang.[13] Three types of specimens were utilized for the irradiation studies of the fractions. These were a highly crystalline sample prepared in bulk by isothermally crystallizing at 130° for 40 days and slowly cooling to room temperature,[7,14] a much less crystalline sample of the same molecular weight fractions prepared by molding a film at 205° and quickly cooling to room temperature, and crystals obtained from a 0.3% xylene solution after isothermal crystallization at 85° for 2 days. The crystalline materials prepared from dilute solution were filtered on sintered glass under vacuum and then vacuum dried for 4 days at 50°.

The densities of the bulk crystalline specimens were determined at 25° by the gradient column method. Conventional type, mercury filled dilatometers were used to determine the densities at high temperatures. The density measurements were converted to degrees of crystallinity by utilizing the relations given by Chiang and Flory[7] and assuming the additivities of the specific volumes of the crystalline and amorphous phases.

Procedures.—X-Rays from a 3-Mev. Van de Graaff generator provided the high energy ionizing radiation. The dose rate at the sample was 1.6 or 1.8 Mrads/hr. For irradiation purposes, the polymer specimens were contained in a Pyrex tube sealed under high vacuum. The tube and its contents were placed in a silicone oil thermostat or in an air thermostat where the temperatures were maintained constant to within ±0.5° and ±1°, respectively, and the irradiations performed while the samples were maintained at a predetermined temperature.

(11) P. J. Flory, J. Am. Chem. Soc., **63**, 3097 (1941).

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

(13) R. Chiang, J. Polymer Sci., **36**, 91 (1959).

(14) L. Mandelkern, A. S. Posner, A. F. Diorio, and D. E. Roberts, J. Appl. Phys., **32**, 1509 (1961).

After irradiation, the samples were exposed to air at room temperature for 3 days and then weighed. The samples were then placed in a cylindrical cage 6.5 cm. high and 3.2 cm. in diameter which was fabricated from 0.2-mm. diameter stainless steel mesh. While in this container the samples were extracted with boiling xylene for 24 hr in a Soxhlet extractor. The nonsoluble gel portion was then dried under vacuum at 50° for 24 hr. and then reweighed. The procedures outlined thus allowed for a determination of the fraction sol and gel.

Discussion and Results

A major advantage, in principle at least, in studying the cross-linking behavior of molecular weight fractions is that the partitioning between sol and gel is simply described by the relation[15]

$$\frac{-\ln W_s}{(1 - W_s)} = \rho y \qquad (1)$$

where W_s is the weight fraction sol, ρ the fraction of units cross linked, and y is the degree of polymerization. Equation 1 is only valid for an initial collection of primary molecules of completely uniform chain length. If the usual assumption is made that ρ is proportional to the radiation dose R, and if R_c is defined as the critical dosage at the gel point, then eq. 1 can be rewritten as

$$\frac{-\ln W_s}{(1 - W_s)} = \sigma = R/R_c \qquad (2)$$

A typical set of sol–gel data for a fraction $M = 182{,}000$ irradiated at 133° in both the highly crystalline and completely amorphous states is plotted in Fig. 1 according to the suggestion of eq. 2.[16] For all but the very highest dosage the data for both states of the polymer can be well represented by the same straight line. This straight line, however, possesses a slope which is significantly less than that demanded by theory. This deviation can be attributed to the fact that even a fraction is not perfectly homogeneous in chain length. The equation in question is derived for this idealized situation and theoretically the partitioning between sol and gel is known to be very sensitive to even small amounts of polydispersity.[15] However, it is clear from an experimental point of view that for a fraction the deviations from the theory are quantitatively the same irrespective of whether the sample is in the completely amorphous or highly crystalline state. Hence, we can utilize eq. 1 or 2 with a common correction factor (multiplying the right-hand side by 0.7) to describe most of the data. At the very highest dosages, with the concomitant high cross-linking density, complete gel formation should occur in the absence of chain scission processes, and approach to the theoretical curve is expected as is observed.

For the fraction $M = 182{,}000$ the dosage required for incipient gel formation at 133° for the completely amorphous polymer is approximately twice that needed for the crystalline sample at the same temperature, where the degree of crystallinity $1 - \lambda = 0.83$. This difference in dosage is maintained over the complete

(15) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 378.

(16) This condition can be accomplished by utilizing high radiation doses and the time interval before the onset of crystallization for the amorphous polymer and the fact that samples crystallized in the manner described melt very sharply.[16]

range of partitioning between sol and gel. For the completely amorphous polymer

$$\rho_c = k_a R_c \qquad (3)$$

where k_a is the proportionality constant between dosage and fraction of units cross linked for the irradiation in the amorphous state at 133°. If separate proportionality constants, which are dependent on temperature, are assigned to the amorphous and crystalline phases then for the well-crystallized bulk polymer

$$\rho_c = kR_c = [(1 - \lambda)k_c + \lambda k_a]R_c \qquad (4)$$

where k_c is the proportionality constant for the cross linking of the completely crystalline polymer. For the specific case where $1 - \lambda = 0.83$ and the stipulation that the critical condition for gel formation $\rho_c = 1/y$ must be met in both cases we find that $k_a^{133} = 0.6 \times 10^{-4}$ while $k_c^{133} = 1.3 \times 10^{-4}$. These constants of course reflect the efficiencies of cross linking in the two states.

In Fig. 2 the weight fraction sol is plotted against the parameter σ for a fraction $M = 425,000$ at different temperatures and states of the system. The dashed line is the theoretical curve calculated according to eq. 2 assuming both perfect homogeneity in molecular weight and the random spatial distribution of cross links. The curve for the completely amorphous polymer (at 133°) deviates slightly from theory as expected, and demonstrates the overwhelming predominance of cross linking as the effect of irradiation since complete gel formation is obviously being attained. The curve for the well-crystallized bulk specimen irradiated at 25° is distinctly different. The different nature of the two curves must reflect more than just the higher efficiency of cross linking at the higher temperature. For a random cross-linking process this effect is automatically accounted for by plotting the fraction sol as a function of R/R_c. We also note that the level of crystallinity changes only slightly with temperature for this sample. Two possibilities suggest themselves to explain the protracted rate of gel formation at the lower temperature. One reason could be nonuniform cross linking at the lower temperature so that not all intermolecular cross links are effective in adding gel. The other possibility would be the occurrence of chain scission processes at the lower temperature. Curve A in Fig. 2 could be formally described in this manner[17] and despite the lower temperature the possibility should not be dismissed out of hand. If the formation of intermolecular cross links is retarded because of the immobility of the chain units in the crystalline region then it is possible for the initial ionization act to lead to chain scission. Curve B, for the poorly crystallized specimen, $1 - \lambda = 0.45$, irradiated at 122° is of a similar character to that for the well-crystallized sample irradiated at the same temperature.

If the experimental conditions for incipient gelation of these specimens are analyzed in a similar manner to that for the fraction $M_\eta = 1.82 \times 10^5$ then from the irradiation of the well-crystallized and partially crystallized samples at 122° we find that $k_a^{122} = 0.35 \times 10^{-4}$ and $k_c^{122} = 1.5 \times 10^{-4}$. The values obtained for k_c^{122} and k_c^{133} for the two different fractions are virtually identical. The value for k_a^{122} is still appreciably less
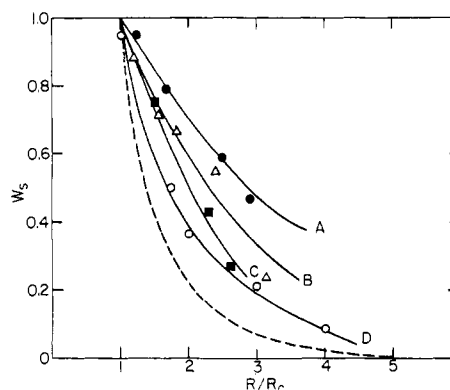
(17) A. Charlesby, J. Polymer Sci., 11, 513 (1953).

Fig. 2.—Plot of weight fraction sol, W_s, against R/R_c for molecular weight fraction $M_\eta = 4.25 \times 10^3$: dashed line, theoretical curve according to eq. 2; highly crystalline sample irradiated at 25° curve A, highly crystalline sample irradiated at 122° curve C, poorly crystallized sample irradiated at 122° curve B, completely amorphous polymer irradiated at 133° curve D.

than k_c^{122} but is somewhat less than k_a^{133}. This difference in the two values of k_a can be attributed either to experimental uncertainty or to small differences in chain disposition and mobility between the completely amorphous state and the amorphous regions in the partially crystalline polymer. If we make the further assumption that the value of k_a is essentially independent of temperature, then $k_c^{25} = 0.19 \times 10^{-4}$. Thus, there appears to be a tenfold reduction in the cross-linking efficiency of the crystalline polymer as the temperature is lowered.

To pursue further the implications of this latter calculation it is desirable to determine the gel point and the nature of the partitioning between sol and gel at a series of temperatures between 25° and the melting temperature. However, it is clear that meaningful results can only be obtained by working with the same molecular weight fraction at all temperatures. However, the technical problems in collecting an adequate quantity of such samples are fairly prohibitive. As a consequence of this limitation, therefore, we have investigated the temperature dependence of the cross-linking efficiency by examining the partitioning between sol and gel as a function of temperature at a fixed irradiation dose rather than over an extended dosage range.

In Fig. 3 and 4 there are plotted some representative data for the weight fraction sol as a function of the temperature at which the irradiation was conducted for two molecular weight fractions. The dosage was held constant at each temperature and the samples represent different controlled crystallizations as well as the completely amorphous polymer for the higher molecular weight fraction. At low temperatures, for both molecular weight fractions, there is no significant difference in the amount of gel produced, at a constant dosage for the different levels of crystallinity. As the temperature is increased, however, a significantly large proportion of gel is produced from the more highly crystalline specimens. This effect begins to manifest itself at about 80–90° and at 130° it has become quite pronounced. A striking difference is observed at 130°, where comparison can also be made between the highly crystalline polymer and the completely amorphous one. In the latter case, at this temperature, only about
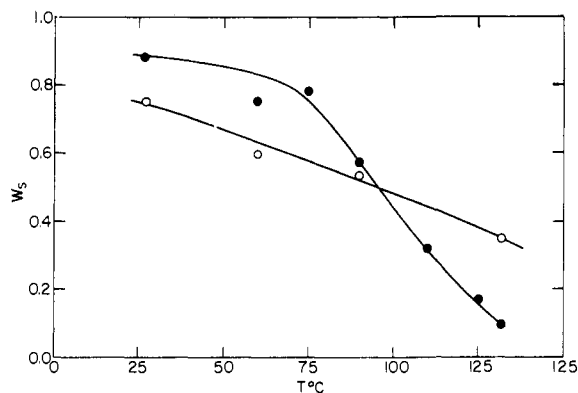
Fig. 3.—Plot of weight fraction sol, W_s, against temperature for molecular weight fraction $M_\eta = 2.07 \times 10^5$; radiation dose constant at 2.75 Mrads: highly crystalline sample ●; rapidly crystallized sample O.
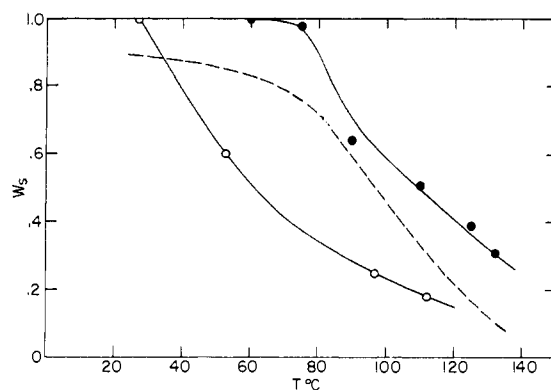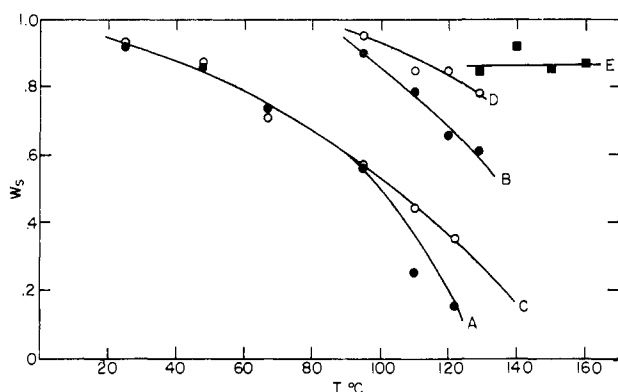

Fig. 4.—Plot of weight fraction sol, W_s, against temperature for molecular weight fraction $M_\eta = 4.25 \times 10^5$: curves A and B well-crystallized polymer, dosage 1.05 and 0.5 Mrads, respectively; curves C and D rapidly crystallized sample, dosage 1.05 and 0.5 Mrads, respectively; curve E, completely amorphous polymer, dosage 0.46 Mrad.
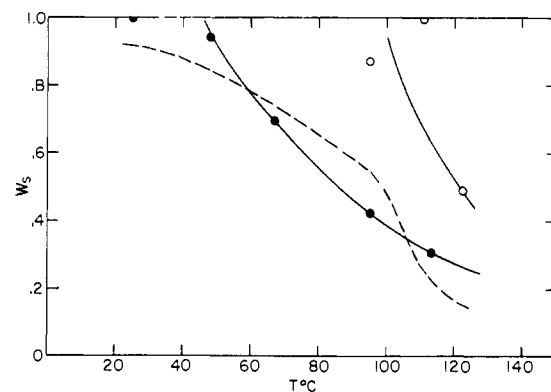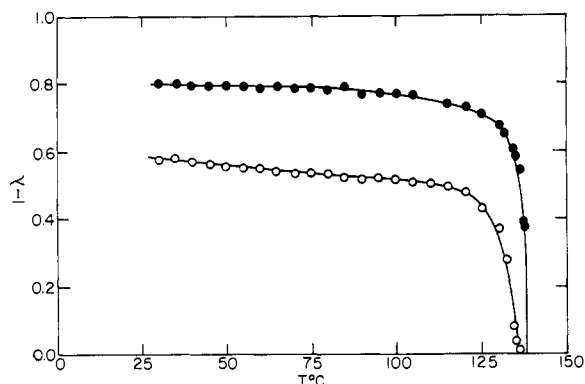

Fig. 5.—Plot of degree of crystallinity $1 - \lambda$ vs. temperature for molecular weight fraction $M_\eta = 4.25 \times 10^3$: sample initially isothermally crystallized at 130° ●; rapidly cooled sample O.

15% gel has been formed after 0.5 Mrad irradiation while for the highly crystalline specimen the gel content has reached 40%. We can also note in Fig. 4 that for the completely amorphous polymer the cross-linking efficiency is independent of temperature in the range studied.

These results at the higher temperature are in accord with the previous report[10] where the temperature was maintained constant and the radiation dose varied for both the highly crystalline and completely amor-

Fig. 6.—Plot of weight fraction sol, W_s, against temperature for crystals prepared from dilute solution for fraction $M_\eta = 2.07 \times 10^5$: dosage 2.75 Mrads ●; dosage 5.5 Mrads O; dashed line for well-crystallized bulk sample at 2.75 Mrads.

Fig. 7.—Plot of weight fraction sol, W_s, against temperature for crystals prepared from dilute solution for fraction $M_\eta = 4.25 \times 10^5$: dosage 2.1 Mrads ●, dosage 1.05 Mrads O; dashed line for well-crystallized bulk sample at 1.05 Mrads.

phous polymer. However, this greatly enhanced efficiency of cross linking in the crystalline state relative to the amorphous is not maintained as the temperature is lowered. Volume–temperature studies yield conclusive evidence that this drastic change in partitioning between sol and gel with changing temperature cannot be attributed to any significant variation in the relative proportion of the two states. This conclusion is demonstrated in Fig. 5, where the degree of crystallinity $1 - \lambda$ is plotted against the temperature. Over the temperature range of interest the change in the level of crystallinity is relatively small. Hence, the drastic change in cross-linking efficiency must be attributed to the crystalline state itself and result from some molecular changes within this state. These changes in the nature of the crystalline state are obviously not detected in the density–temperature measurements.

Before pursing the above points further it is pertinent to consider the partitioning between sol and gel of irradiated single crystals[18] formed upon the precipitation from dilute solution of the molecular weight fractions. The data for these systems are presented in Fig. 6 and 7. The dashed lines, given for comparative purposes, represent the data for the well-crystallized bulk polymer at all temperatures. These results are similar to the comparison previously reported by Salovey and Keller[19] for the room temperature irradia-

(18) A. Keller, Phil. Mag., 2, 1171 (1957).
(19) (a) R. Salovey and A. Keller, Bell System Tech. J., 15, 1397, 1409 (1961); (b) R. Salovey. J. Polymer Sci., 61, 463 (1962).
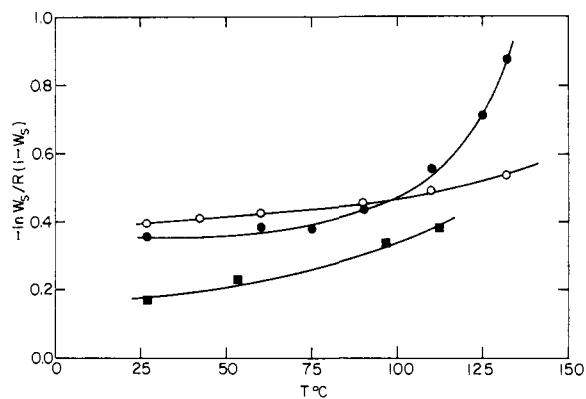
Fig. 8.—Plot of the quantity $-\ln W_s/R(1 - W_s)$ against temperature for a molecular weight fraction $M_\eta = 2.07 \times 10^5$: well-crystallized sample ●; rapidly cooled sample O, both at 2.75 Mrads. Crystal from dilute solution at 5.5 Mrads.

Fig. 9.—Plot of the quantity $-\ln W_s/R(1 - W_s)$ against temperature for a molecular weight fraction $M_\eta = 4.25 \times 10^5$: well-crystallized sample ●; rapidly cooled sample O, both at 1.05 Mrads. Crystals from dilute solution at 2.1 Mrads.

tion of single crystals of whole polymer as compared to ordinary crystallized bulk polymer. However, gel is still formed relatively easily, indicative of intermolecular cross linking. The amount of gel formed also increases significantly with increasing temperature for this particular crystalline form.

A more direct comparison can be made of the relative cross-linking efficiencies of the different states and crystal forms by plotting the quantity $-\ln W_s/R(1 - W_s)$ against the temperature. This quantity should serve as a measure of the proportionality constant between cross-linking density and radiation dose and hence of the efficiency of cross linking.[20] The data for the fraction sol as a function of temperature are plotted in Fig. 8 and 9 according to this theoretical suggestion for two molecular weight fractions. At low temperatures the proportionality constant (and hence the cross-linking efficiency) is, within experimental error, essentially the same for the highly crystalline specimens and the samples of lower degrees of crystallinity. However, as the temperature is increased the proportionality factor for the highly crystalline specimens increases by a factor of two, while the degree of crystallinity decreases by only about 10%. Hence, in the highly crystalline state at temperatures greater than about 90° the cross-linking efficiency increases rather markedly with temperature while high levels of crystallinity are maintained. This is in agreement with the deductions made from the analyses of the data in Fig. 2. For the less crystalline samples only very slight increases are observed in the cross-linking efficiency with temperature in this interval. For the fraction $M = 425,000$, $1 - \lambda$ changes from 0.5 to 0.3 from 90 to 130°. The results for the latter type specimen are a manifestation of the lowered cross-linking efficiency of the noncrystalline regions and the increased concentration of such regions as the temperature is increased. Based on the results for the same fraction in the completely amorphous state over the temperature range 130–160° we can conclude that the cross-linking efficiency of the amorphous polymer is not only relatively low in this high temperature region but does not change significantly with temperature.
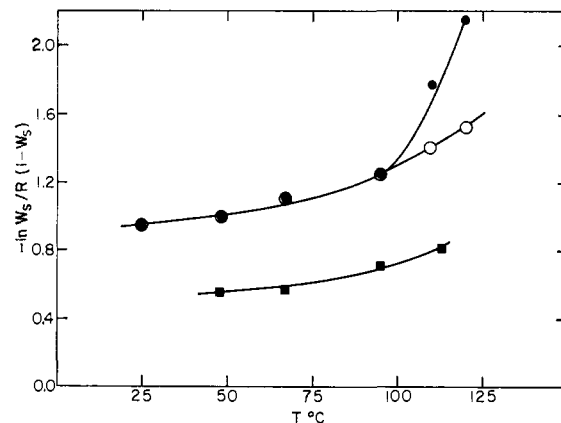
Also plotted in Fig. 8 and 9 are the data for the single crystal specimens at temperatures up to 110°. For both fractions the cross-linking efficiency is diminished by a factor of two when compared with the corresponding highly crystalline bulk specimens. The constants for the two molecular weight fractions are in the ratio of 2:1 which is also the ratio of the two molecular weights. It is known that at temperatures greater than about 120°, well-defined morphological changes occur in the single crystals.[21] Unfortunately, therefore an equitable comparison cannot be made between dilute solution formed crystals and well-crystallized bulk specimens irradiated at the higher temperatures. A few preliminary observations have indicated that at the higher temperatures the proportionality constants for the dilute solution crystals do not show a dramatic increase, but rather are qualitatively similar to those for the much less crystalline bulk specimens. These observations are in accord with the reduced thermodynamic stability characteristic of such crystals.[21b]

One of the major conclusions to be drawn from these experiments is the demonstration that for highly crystalline specimens, $1 - \lambda \geq 0.8$, prepared from pure polymers the cross-linking efficiency is greatly enhanced at temperatures exceeding 100°. We are therefore led to the deduction that a very high potential must exist for the formation of intermolecular cross links in such systems, which is realized from 100° to the melting temperature. Since we are dealing with such highly crystalline systems there must be a very high concentration of crystalline sequences in juxtaposition (or nearest neighbors) which are contributed by different molecules. This conclusion is still consistent, however, with the well-known lamellar morphology of crystallites in such systems.[22] For irradiation temperatures below the range of 90–100° this high potential is not realized, despite the slight increase in the level of crystallinity and the apparent absence of any thermodynamic discontinuity in the crystalline state. Hence, for the same chain configuration and disposition of chains within the crystallites the intermolecular cross-linking process has become severely reduced.

(20) In analyzing our data in this manner, the tacit assumptions are made that ρ is proportional to R and the empirical correction factor for fractions discussed in connection with the plot of Fig. 1 is independent of both the temperature and the state of the system.

(21) (a) W. O. Statton and P. Geil, J. Appl. Polymer Sci., 3, 357 (1960); (b) J. B. Jackson, P. J. Flory, and R. Chiang, Trans. Faraday Soc., 59, 1906 (1963).

(22) P. J. Flory, J. Am. Chem. Soc., 84, 2857 (1962).

A rational explanation of the above results can be obtained by noting that from other types of experiments the independent deduction has been made of the onset of some type of molecular motion within the crystalline region of polyethylene in the temperature interval of interest. Dynamic mechanical experiments on crystalline bulk polyethylene and on crystals from dilute solutions indicate a loss peak in the vicinity of 80–90°.[23–26] Hence, there is a mechanical energy absorption in this region which must be the result of some kind of molecular motion. In addition, Takayanagi[25,26] has reported that although the dimension of the b axis of the unit cell in polyethylene is essentially constant, a significant increase occurs in the a axis at 90°. Without concern at present for the detailed nature of the molecular motions involved, it is clear that at low temperatures (less than about 90°) the chain units in the crystalline sequences are relatively immobile and above this temperature some type of molecular motion exsits. Hence, although the high potential for intermolecular cross links still exists at the lower temperature the contact between units in neighboring chains is required in order to accomplish the cross-linking reaction. This contact should be difficult to achieve in a relatively immobile system. However, at temperatures corresponding to and greater than that for the onset of the molecular motions the inherent cross-linking efficiency should be easily realized. Although the cross-linking reaction is favored in the crystalline regions when sufficient chain mobility is made available, the possibility exists that subsequent to the initial ionization act chain scission processes could occur to a significant extent when the mobility is retarded. This would of course be observed at the lower temperatures in the crystalline state and would explain, in part at least, the differences between curves A and C in Fig. 2. The validity of this possibility must await further experimentation and the elucidation of the radiation mechanisms.

(23) D. E. Kline, J. A. Sauer, and A. E. Woodward, *J. Polymer Sci.*, **22**, 455 (1956).

(24) K. H. Hellwege, R. Kaiser, and K. Kuphal, *Kolloid-Z.*, **147**, 155 (1956); *ibid.*, **157**, 27 (1958).

(25) M. Takayanagi, *J. Polymer Sci.*, **46**, 531 (1960).

(26) M. Takayanagi, *Mem. Fac. Eng., Kyushu Univ.*, **23**, 41 (1963)

Another conclusion that can be made involves a comparison of the cross-linking efficiency between the highly ordered crystalline polymer and the random-coiled chains of the completely amorphous state. At temperatures where a direct comparison is possible the efficiency is approximately two to four times greater for the highly crystalline form. The results previously reported[10] for the irradiation of completely amorphous polymers at 133° wherein the gel point was found to be inversely proportional to the initial weight-average molecular weight and the nature of the subsequent partitioning between sol and gel where it is demonstrated that almost complete gel is formed as in curve D of Fig. 2 do not allow chain scission in the amorphous regions at these temperatures to be of serious consequence in this conclusion. The cross-linking efficiency of the amorphous regions is not seriously affected by temperature, indicating that sufficient mobility exists in this state to allow for the completion of the cross-linking reaction. Furthermore, it appears that intermolecular cross linking is inherently more conducive between two portions of polyethylene chains in the planar zigzag *trans* configuration, the ordered configuration, than in the random coil.

A qualitative explanation has been offered for the reduced cross-linking efficiency of crystals formed from dilute solution.[19] In essence, it has been postulated that in the resulting crystalline array a very high proportion of nearest-neighbor crystalline sequences must arise from the same molecule. That is, the chain molecule within the crystal is regularly folded. However, we note that although gel formation is retarded it is not suppressed. Intermolecular cross linking can be accomplished but higher dosages are required. The distinct possibility again exists that in this highly crystalline array, relatively immobile at the low temperature, chain scission processes can be affecting the interpretation of the fraction gel formed. Deduction in regard to the fine details of the chain arrangement within the crystallites cannot be made solely on the basis of the sol–gel analysis. More details of the radiation mechanisms are needed and, to establish these, cognizance must be taken of the independence of the temperature and the state of the system.