the relaxation in the solid already takes place in discrete regions organized similarly to the melt and whose dimensions are large compared to the molecular correlation dimensions involved in the molecular motions responsible for the relaxation. It should be noted, however, that this result could possibly be appropriate to higher temperatures where the correlation distances involved in the molecular motions may be relatively short. At lower temperatures, it has been observed in some polymers[5] that thermal treatment and, in the case of PEO, crystallinity variations with molecular weight influence the location of the loss regions on the frequency axis as well as its strength. If we identify the discrete amorphous regions as interlammelar material our results show that at higher temperatures the chain lengths involved in the molecular motions are shorter than typical interlamellar chain lengths.

Nomenclature

ϵ'	dielectric constant
ϵ''	dielectric loss
ω	angular frequency
ϵ_R	low-frequency dielectric constant
ϵ_u	high-frequency dielectric constant
m	Fuoss–Kirkwood parameter defined by eq 3
$\bar{\beta}$	Cole–Cole parameter
T	temperature

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Irradiation of Linear Polyethylene. Partitioning between Sol and Gel[1]

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ABSTRACT: Molecular weight fractions of linear polyethylene were irradiated at 133°, in the completely molten and highly crystalline states, for the purposes of assessing the importance of chain-scission processes and establishing the critical conditions for gelation. The partitioning between sol and gel in either state was found to adhere to the theory for the intermolecular cross-linking of monodisperse species for dosages just beyond the gel point. Deviations from theory occurred as the dosage was increased further, but at high dosages the fraction of gel formed was found to be in the range 0.98–1.00. It was concluded that main-chain scission, at these temperatures, is not a significant process. High molecular weight samples, in the completely molten state, obeyed the Flory–Stockmayer condition for critical gelation. However, as the molecular weight was reduced below about 1×10^5, the critical dosage required for gelation systematically became less than that required by theory. These results are attributed to the influence of the vinyl end groups. This postulate is confirmed by the behavior of the hydrogenated samples. The lower molecular weight, highly crystalline samples display still greater deviations from theory. The results for the higher molecular weight crystalline samples are equivocal because of the difficulty of preparing very sharp fractions and maintaining a constant level of crystallinity.

The two major chemical events that can occur when polymers in general and linear polyethylene in particular are subject to the action of high-energy ionizing radiation are gel formation and main-chain scission. Although the radiation chemistry of polyethylene has been extensively studied,[2,3] the relative importance of chain-scission processes has not as yet been established nor has a quantitative analysis of the critical gelation conditions been given. For example, Alexander and Toms[4] and Shumacher[5] have concluded that main-chain scission is negligible. On the other hand, Charlesby and Pinner[6] have reached contrary conclusions. More recently, Kang, Saitô, and Dole[7] have also concluded that chain scission is a major consequence of irradiation. There are several important and fundamental reasons for the difficulties and contrary conclusions that have been reached. Foremost among these is the fact that all the investigations reported heretofore have been conducted with unfractionated polymers. The most commonly studied unfractionated linear polyethylene samples are notorious in possessing very broad molecular weight distributions. On the other hand, all the theories utilized in analyzing the experimental data, including the more sophisticated ones, require a very precise analytical specification of the molecular weight distribution.[6,8–10] This, of course, cannot be provided, and various approximations have to be invoked. Alternatively, if a careful study is made of the limiting gel fraction that is obtained at high irradiation dose, an assessment can be made of the relative importance of chain scission. Unfortunately, since the usual materials studied possess a relatively low ratio of number- to weight-average molecular weight, this necessitates high irradiation dosages and an inherent difficulty in establishing the asymptotic limit. These difficulties can obviously be alleviated by studying molecular weight fractions.

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TABLE I
CHARACTERIZATION OF MOLECULAR WEIGHT FRACTIONS

Sample	M_η	M_n	ΔH^*, cal/g	ρ (at 25°)
1	2,800			
2	7,400			
3	17,800	17,400		
4	26,000		62.6	0.9859
5	30,000	29,300	58.3	0.9821
5a (hydrogenated)	30,000	29,300	62.5	0.9821
6	46,000	44,000	57.8	0.9832
7	50,000	43,600	59.9	0.9809
7a (hydrogenated)	50,000	43,600	58.6	0.9842
8	77,000	75,500	53.1	0.9764
9	122,000	94,000	54.9	0.9762
10 highly crystalline	243,000		55.3	0.9783
10a quenched	243,000		39.1	
10b quenched	243,000		34.5	0.9413
11 highly crystalline	370,000	168,000	52.0	0.9727
11a quenched	370,000	168,000	32.8	0.9378

In experiments of this type, it is important to recognize and clearly specify the independent variables that are involved.[11–13] Among others, these variables include the temperature, state (crystalline or amorphous), morphological properties, and molecular weight. For example, varying the temperature can also change the level of crystallinity, and these quantities can have different influences on the radiation chemistry. It is also well known that the level of crystallinity is very dependent on the molecular weight.[14–16] Thus, when the molecular weight is varied, one has to be concerned not only with this direct change but also with possible changes in the degree of crystallinity. The usual polyethylene studied, whether fractions or whole polymer, contains one vinyl end group per molecule. Although this functional group must be present in very small concentrations, it uniquely influences the radiation-induced chemical reactivity[12,17] as well as the gelation efficacy.[12,13] This latter point was established from a comparative study of normal and hydrogenated samples.[13]

In the present work, we have studied in detail, utilizing molecular weight fractions of both normal and hydrogenated samples, the course of partitioning between sol and gel and the molecular weight dependence of the critical dosage required for gelation. The purpose of this study was to assess the importance of chain-scission processes on the one hand, and on the other the applicability of the general theory of network formation to polyethylene. To clearly distinguish between the completely molten state and the crystalline state, the irradiations were conducted at 133°. It has already been established that for linear polyethylene the liquid state can be maintained at this temperature for the times required for irradiation. In addition, samples previously crystallized can also be kept in the highly crystalline state at this temperature.[11,12]

Experimental Section

Molecular weight fractions were obtained by conventional column-elution techniques that have been previously described.[14] Marlex-50 was used as the starting unfractionated polymer. Viscosity-average molecular weights were obtained from intrinsic viscosity measurements in decalin at 135° utilizing the relationship given by Chiang.[18] The number-average molecular weight was obtained from the vinyl end group concentration which was determined from the intensity of the infrared absorption band at 908 cm^{-1}. A more detailed description of this method will be presented shortly.[19] The properties of the fractions studied in this work are listed in Table I. The densities at 25° were determined by the density-gradient method.[20] The enthalpies of fusion, ΔH^*, were measured in a Perkin-Elmer differential calorimeter (DSC-1B) by methods previously described.[21,22] High levels of crystallinity (high densities) were obtained by isothermal crystallization at elevated temperatures for long periods of time.[14,16] Quenched samples, of much lower densities, were obtained by rapid cooling from the melt. The hydrogenation was carried out according to procedures previously described.[13] As is indicated by the data in Table I, the properties of the samples remain unaltered after hydrogenation.

X-Rays from a 3-MeV Van de Graaff generator provided the high-energy ionizing radiation. The dose rate at the sample was 3.40 Mrads/hr for molecular weights up to 200,000; above this molecular weight range a dose rate of 1.70 Mrads/hr was employed. The dose rate was established, and periodically checked, by the usual ferrous sulfate method. The polymer samples were in the form of 30-mg thin strips and were checked for oxidation before use by examination for the presence of any infrared absorption in the 1270- and 1725-cm^{-1} range. The samples were contained in Pyrex tubes and sealed under high vacuum. All the irradiations in the present work were carried out at 133 ± 0.2°. Upon completion of the irradiation, the samples were cooled to room temperature and opened to the atmosphere. The validity of this procedure, for the particular irradiation condition used here, will be discussed in detail below.

In order to obtain the fractions of gel, weighed samples were placed in stainless-steel baskets and immersed in boiling xylene (139°) which contained about 0.1% antioxidant. Refluxing was continued for 24–48 hr, depending on the molecular weight. After refluxing, the samples in the baskets were dried *in vacuo* at 50° for at least 12 hr and then reweighed. A series of preliminary experiments indicated that this procedure yields a constant weight. The procedure just described gives the same results as the method previously used[12] wherein the sample was extracted with boiling xylene for 24 hr in a Soxhlet extractor. The former procedure was adopted in the present work solely as a matter of convenience. Dole and coworkers[7] have claimed that it is necessary to immerse the baskets in boiling xylene rather than using a Soxhlet extractor. They argue that using a Soxhlet extractor yields too high a gel content because the extraction temperature is only about 90°. We have carefully examined their claim and have found it to be correct when a conventional type of extractor is used. However, in the previous work reported from this laboratory,[12] we used a Soxhlet hot-liquid-jacketed extractor (Corning catalog No. 92150). Direct measurements demonstrate that the temperature of the liquid condensate in this extractor is 139°. The criticism directed at the previous work is therefore not justified.[7]

Results and Discussion

It has been established[3,7,23–26] that the fraction of gel that is obtained after the irradiation of polyethylene at low tem-

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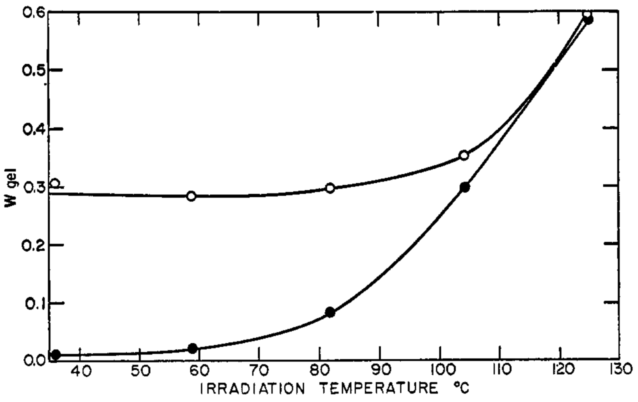

Figure 1. Plot of fraction of gel, w_g, against irradiation temperature for different postirradiation treatments: sample exposed to air for 3 days (●), sample heated for 2 hr at 140° immediately after irradiation (○). Radiation dose 1.25 Mrads, density 0.973 at 25°, sample 11.

peratures depends very markedly on the details of the postirradiation procedure that is adopted. These results have been attributed to the different reaction pathways which are available to the trapped free radicals which are generated. The main reactions are either chain scission, due to postirradiation oxidation, or further cross-linking due to radical reaction with the chain. The fraction of gel that is experimentally determined will be influenced in quite opposite ways by these two possibilities. A fundamental dilemma is therefore presented, since some kind of postirradiation treatment must obviously be introduced in order to determine the fraction of gel. Thus it is important that the procedures that are adopted are so chosen that they do not obscure the fundamental irradiation events and allow for an assessment of the true fraction of gel.

With the aforementioned concern in mind, we have investigated two distinctly different and contrasting modes of postirradiation treatment. In one of these, the sample was exposed to air, at room temperature, for 3 days before the extraction procedure was initiated. In the other, prior to extraction, the sample was heated *in vacuo* for 2 hr at 140° (above the melting temperature) immediately after irradiation and then cooled to room temperature and studied. These control experiments were performed with two different samples, prepared from the same fraction, but crystallized in different ways so that their densities at room temperature were 0.973 and 0.938, respectively. The results, for each of the samples, are given in Figures 1 and 2 as plots of the fraction of gel against the irradiation temperature for a fixed dosage. These plots clearly indicate that the two methods yield quite different results for irradiation temperatures below about 90°. The fraction of gel obtained from the samples exposed to air is drastically reduced in comparison with that obtained from the procedure involving heating *in vacuo*. The difference in the yield of fraction of gel, between the two methods, is greater for the sample of higher density, the one which is more crystalline. However, the disparity between the methods rapidly diminishes as the radiation temperature is increased. At 110°, for example, any differences have essentially disappeared. Thus, for the temperature of interest in the present experiments, 133°, the postirradiation treatment does not influence the fraction of gel that is obtained. As expected, it is also found that there is no influence of postirradiation treatment when the sample is irradiated in the completely molten state.

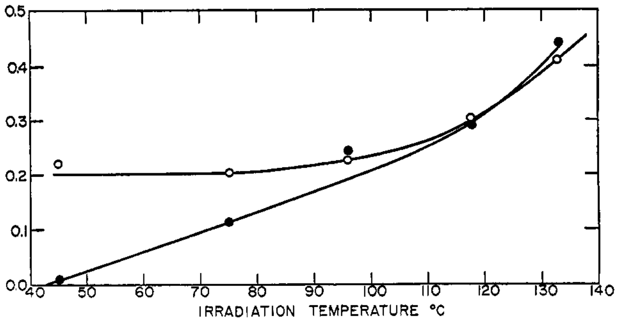

Figure 2. Plot of fraction of gel, w_g, against irradiation temperature for different postirradiation treatments: sample exposed to air for 3 days (●), samples heated for 2 hr at 140° immediately after irradiation (○). Radiation dose 1.47 Mrads, density 0.938 at 25°, sample 11a.

These conclusions are clearly not of general validity. For the lower temperatures of irradiation, the results will definitely depend on the postirradiation treatment. A fundamental problem is thus posed in obtaining a meaningful value for the fraction of gel under these conditions. Any interpretations and conclusions which are made under these circumstances must be tempered accordingly. The reason for the strong influence of temperature on the postirradiation treatment can be correlated with the α transition of linear polyethylene, which is located in the vicinity of 80–90°.[27,28] This transition is associated with the crystalline regions of the polymer and involves some type of molecular motion.[27,28] At temperatures below the transition, the relative immobility of the chain units in the crystalline state will allow the radicals to be trapped. The trapped radicals will thus be subject to further reactions which will depend upon the particular postirradiation pathway chosen. On the other hand, when the irradiation temperature is above the α transition, there is sufficient mobility so that the radicals can react *in situ*, and the results will thus be independent of the subsequent treatment adopted.

Having established, for the particular experimental conditions of concern here, that the partioning between sol and gel is independent of the postirradiation treatment, we can now examine the question of the magnitude and importance of chain-scission processes relative to intermolecular cross-linking. As has been indicated earlier, contradictory conclusions have been reached in the literature regarding this problem.

According to the general theory developed by Flory[8] and Stockmayer,[29] the critical condition for gel formation, when intermolecular cross-links are randomly introduced into a collection of long-chain molecules, is achieved when

$$\rho_c = 1/(\bar{y}_w - 1) \cong 1/\bar{y}_w \tag{1}$$

Here ρ_c is the fraction of units cross-linked and $\bar{y}_w$ is the weight-average degree of polymerization. Although the critical condition for gelation depends only on the initial weight-average molecular weight, the partitioning between sol and gel has been shown to be very sensitive to the initial molecular weight distribution.[8] For a very idealized system, homogeneous in molecular weight, the weight fraction of sol, w_s, varies with the fraction of units cross-linked according to[8]

$$w_s = 1 - \rho(1 - w_s)^y \tag{2}$$

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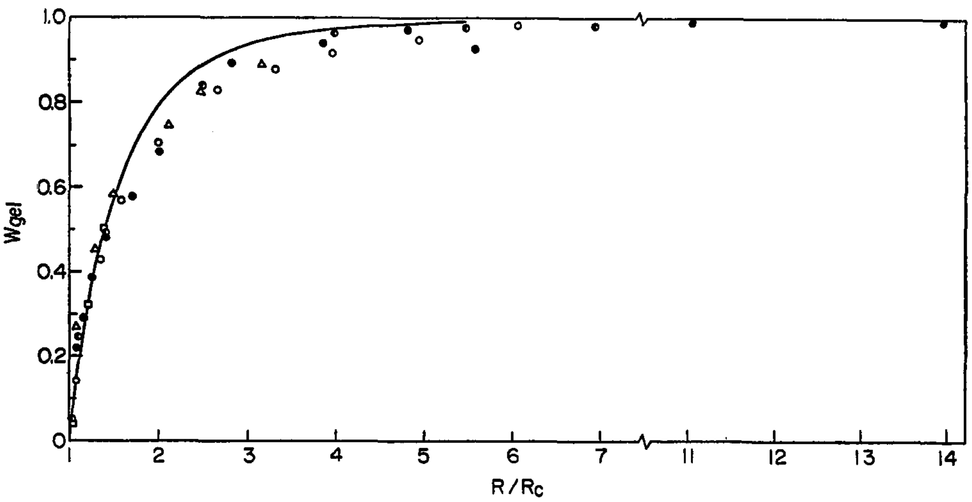

Figure 3. Plot of fraction of gel, w_g, against R/R_c for indicated molecular weight fractions of linear polyethylene irradiated in melt at 133°: M_η = ●, 122,000; ◐, 26,000; ○, 17,800; △, 7400; □, 2800.

which can be written to a good approximation as

$$-\ln w_s/(1 - w_s) = R/R_c \qquad (3)$$

Here a direct proportionality has been assumed between the radiation dose and the fraction of units cross-linked. Although eq 3 is valid only when the primary molecules are of exactly uniform molecular weight, it can serve as a very convenient frame of reference with which to analyze the partitioning between sol and gel for real fractions. It is also a convenient relation with which to compare the results in the two states, since differences in the inherent cross-linking efficiency are contained in the quantity R_c.

The results obtained for the molecular weight fractions studied here for irradiation at 133° in either the completely molten state or in the completely crystalline state are analyzed according to the procedure outlined. Appropriate plots are given in Figures 3 and 4 for each of the states. The solid line represents the theoretical curve of eq 3. The data for the crystalline state include two sets of complementary hydrogenated and nonhydrogenated samples. There are several major features which are common to both sets of irradiation conditions. For the initial radiation past the gel point, the results adhere quantitatively to the theoretical expectation for the intermolecular cross-linking of molecular weight fractions. Deviations from theory begin to appear when R/R_c is of the order of 1.5. The deviations are in such a direction that less gel is produced than would be theroetically expected. However, when the experiments are extended to higher radiation dosages, for R/R_c of the order of four or greater, the data again rejoin the theoretical curve. In this, the asymptotic region, the fraction of gel produced for all of the fractions, in either of the states, is in the range of 0.98–1.00. Hence, within this small experimental uncertainty we can conclude that there is no evidence for the manifestation of any random chain-scission processes. The data indicate quite clearly, however, that if the experimental determinations were limited to smaller values of R/R_c, of the order of four or less, then by incorrectly identifying the asymptotic radiation dose the conclusion could be reached that random chain-scission processes were playing an important role. However, even if this incorrect conclusion were reached, it would follow that less chain scission were taking place in the molten state as compared to the crystalline state at 133°.

When the plots of Figures 3 and 4 are examined in more detail, it is found that in the molten state the experimental results adhere initially to the theoretical expectations up to a weight fraction of gel $w_g \cong 0.6$. In the highly crystalline state the initial deviations for most of the fractions occur at a slightly lower value of w_g. One sample (M_η = 77,000, M_n = 75,700), which is a very sharp fraction and was only irradiated in the crystalline state, adheres almost exactly to theory over the complete dosage range. Polydispersity, even with molecular weight fractions, could be a major cause of the deviations which are observed, since the partitioning between sol and gel is very sensitive to the homogeneity of the sample.[8] The presence or absence of a vinyl end group does not appear to have any major influence in the present problem since, as can be seen in Figure 4, similar results are obtained when the hydrogenated and unhydrogenated samples are compared at the same value of R/R_c. Besides polydispersity, another possible cause for the deviations from random cross-linking theory when only the data presented in Figures 3 and 4 are considered, would be that chain-scission processes occur, but that subsequent recombination with the network takes place. This latter possibility would still allow for the experimental observation of complete gel formation.

With the data that have now been accumulated for molecular weight fractions of linear polyethylene,[12,13] one can

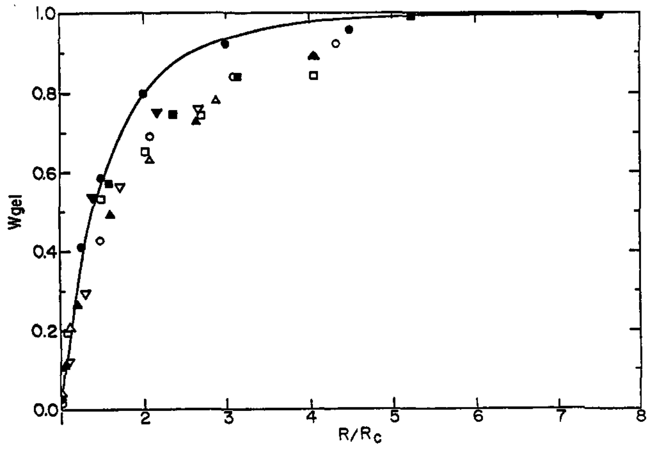

Figure 4. Plot of fraction of gel, w_g, against R/R_c for indicated molecular weight fractions of linear polyethylene irradiated in the crystalline state at 133°: M_η = ■, 122,000; ●, 77,000; ○, 46,000; □, 26,000; △, 30,000 (hydrogenated); ▲, 50,000 (hydrogenated); ▼, 30,000; ▽, 50,000.

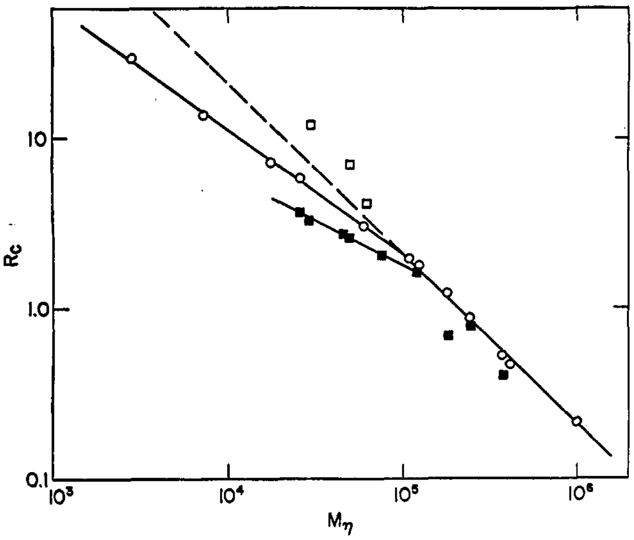

Figure 5. Double logarithmic plot of critical dosage for gelation against viscosity-average molecular weight. Irradiation in molten state at 133° (○) (□, hydrogenated); irradiation in crystalline state at 133° (■).

quantitatively assess the applicability of eq 1 to the critical condition for gelation. An appropriate representation of the data is given in Figure 5 as a plot of R_c against M_η, the viscosity-average molecular weight. The molecular weight fractions studied range from 3×10^3 to 1×10^6, and the irradiations were conducted at 133°. Although the vast majority of the samples are the usual linear polyethylene containing one vinyl end group per molecule, three of the samples, designated by the open squares, have been hydrogenated so that the vinyl end group is absent. In analyzing the data, we first consider the simplest situation, namely the irradiation of the completely molten polymer at 133°. These data are represented by the open circles of Figure 5. The seven samples of this group which are in the molecular weight range 1×10^5–1×10^6 accurately fall on the solid straight line which is drawn with a slope of −1. There is, therefore, substantial evidence that in this molecular weight range, in the completely molten state, the Flory–Stockmayer relation is rigidly obeyed. However, when the molecular weight is reduced below 1×10^5, systematic deviations from the linear relation which is applicable to the higher molecular weights are found. The critical dosage that is required for gelation is less than that predicted on the above basis. Hence, as the molecular weight is decreased and the concentration of vinyl end group increased, the intermolecular cross-linking process is enhanced. Under these conditions, the requirements underlying the Flory–Stockmayer theory are not fulfilled. In the higher molecular weight range, the end-group concentration is sufficiently reduced so that its reactivity is not an influential factor in the cross-linking process.

It has been reported previously that the critical dosages required for gelation (at 133°) for hydrogenated samples are the same in the completely molten and in the highly crystalline states.[13] This finding, with regard to the state of the polymer, is restricted to the presently available data, which are limited to the molecular weight range 3–6 × 10^4. If the presence of the vinyl end group is the only reason for the difference in cross-linking efficacy between the two states and for the deviation from the linear relation just described, it would be expected that the results for the hydrogenated samples (irrespective of state) should fall on the extension of the straight line of slope −1. As can be seen in Figure 5, the data points (open squares) display a tendency to lie slightly above the line. A portion of this discrepancy from expectation can be attributed to the usual experimental error in establishing the critical condition. In addition, if a small amount of oxidation took place during the hydrogenation reaction, a slightly greater critical dosage would be required.[30] In this molecular weight range, the hydrogenated samples do, however, show a significantly closer adherence to the Flory–Stockmayer condition than either the completely amorphous or highly crystalline conventional samples.

The results obtained for the highly crystalline, conventional-type molecular weight fractions are designated by solid squares in Figure 5. For the lower molecular weights it is quite clear that there are marked deviations from the extension of the straight line of slope −1. In this molecular weight range, the critical dosage required for gelation is substantially less than when the same molecular weight is in the completely molten state. These results could be caused by the higher effective concentrations of the vinyl group in the crystalline state, since the end groups are excluded from the crystalline lattice.

The results for molecular weights greater than 1×10^5 irradiated in the crystalline state are not as yet unequivocal. There are several inherent difficulties in studying the higher molecular weight crystalline polymer that hamper the interpretation. · One of the major problems is that above a molecular weight of about 7×10^4, the optimum level of crystallinity that can be attained monotonically decreases with increasing molecular weight.[14,15] Thus, it is difficult to compare samples having exactly the same level of crystallinity. Furthermore, it is more difficult to prepare very sharp fractions as the molecluar weight is increased. Hence, there will be a tendency for such samples to have a proportionately higher concentration of end groups than would be characteristic of a given weight-average molecular weight. Among the four high molecular weight samples studied, two adhere very closely to the straight line of slope −1. These particular results would thus agree with the conclusion made from the study of the lower molecular weight hydrogenated samples in that irrespective of the state of the polymer, the vinyl end group concentration is the determining factor for the differences in cross-linking efficiency. These particular two fractions are relatively sharp. The data in Table I indicate the ratio of weight- to number-average molecular weight to be of the order of 1.2–1.4 for both. The results for the other two fractions fall below the reference line and thus indicate a more effective cross-linking reaction than would be predicted solely from the weight-average molecular weight. In this sense they follow the pattern established for the lower molecular weights. The ratio of weight- to number-average molecular weight is about 2.2 for the highest molecular weight fraction in this group. The number-average molecular weight for the other sample, $M_n = 1.8 \times 10^5$, is not available. However, studies of the partitioning of this sample between sol and gel indicate that it is more polydisperse than the other fractions studied. We tentatively conclude, therefore, that the deviations of the higher molecular weight crystalline samples from the reference line of Figure 5 can be attributed to the vinyl end group concentration of these samples. If this conclusion is sustained by future work, then it becomes clear that the only reason for the difference in cross-linking

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(30) Studies with slightly oxidized, but not hydrogenated, samples indicate that the critical dosage required for gelation is somewhat increased.

efficiency in the different states above the α transition is the difference in the effective end group concentration.

Further work in the high molecular weight range, utilizing samples possessing extremely narrow molecular weight distributions, is clearly necessary in order to substantiate these conclusions. Only when the results of these experiments are available can an unequivocal answer be obtained as to whether there is any direct influence of the drastically different molecular conformations in the two states on the cross-linking process. The results for the lower molecular weight hydrogenated samples argue against any direct influence of conformation at these temperatures. This conclusion is in accord with the results obtained for the irradiation of poly(*trans*-1,4-isoprene) in the crystalline state at 20° and in the completely molten state at 100°.[31]

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Molecular Weight Distribution of Polyethylene Produced by Ziegler–Natta Catalysts

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ABSTRACT: The unusually broad molecular weight distribution observed in the Ziegler–Natta polymerization of ethylene is explained by considering the diffusion of monomer and the movement of catalytic sites in a growing polymer particle. An analysis of appropriate mathematical models for various intervals of polymerization indicates that broad molecular weight distributions ($\overline{M}_w/\overline{M}_n > 2$) may be obtained for values of Thiele parameters (based on the size of the polymer particle) greater than about 6. The use of additives which decrease the polymerization rate appears to be a promising method for reducing $\overline{M}_w/\overline{M}_n$. Better solvents and a programmed pressure cycle during polymerization may also be helpful. The anomalies reported in the rates and orders of reaction in literature have been traced to the experimental conditions and are explained in the light of the proposed diffusion analysis.

The polymerization of unsaturated monomers using heterogeneous catalysts has been actively researched in recent years, producing a variety of patented catalysts, most of which contain a transition metal halide (typically $TiCl_4$ or α-$TiCl_3$) and an organometallic compound (generally an alkyl halide or trihalide of aluminum) in various combinations and proportions.[1] This type of catalyst is frequently referred to as a Ziegler–Natta catalyst and has the distinct advantage of being able to polymerize ethylene into a high-molecular-weight, high-density material at low pressures (typically, 1–5 atm). The polyethylene produced by these catalysts is highly linear, having less than 1 side chain per 200 carbon atoms in the backbone chain, and, as a consequence, it possesses better physical and mechanical characteristics (compared to the high-pressure product).[2] However, the polymer has an unusually broad molecular weight distribution[3–5] which adversely effects properties like resistance to environmental stress cracking and crazing.[2] A broad molecular weight distribution also results in melt-processing difficulties. Solid-state properties usually correlate with $\overline{M}_n$, but melt viscosity varies as some power of $\overline{M}_w$. A "high-*M* tail" to the distribution thus makes a disproportionate contribution to viscous drag, power costs, etc. It is therefore of interest to be able to understand the cause of this broad molecular weight distribution and devise techniques for narrowing it.

In the case of homogeneous free-radical or ionic polymerizations, where the mechanism of polymerization is well understood, the molecular weight distribution of polymer can be derived either from the polymerization kinetics or from simple probability arguments. The width of the instantaneous molecular weight distribution, as measured by the ratio of the weight-average to the number-average molecular weight, lies in the range 1.5–2.0,[6] depending upon the predominant mode of termination. Chain-transfer reactions may lead to a value slightly greater than two, but in all cases, the molecular weight distributions are relatively narrow. The distributions derived theoretically are generally in good agreement with the experimental results.

For Ziegler–Natta polymerizations, however, the molecular weight distributions are much broader ($\overline{M}_w/\overline{M}_n$ generally lies between 4 and 40), and the reasons for this are not well understood.[7] For polyethylene, two empirically derived distribution functions have been proposed, both of them having two parameters. The distribution function derived by Tung[3] has the integral form given by

$$I(M) = 1 - \exp(-aM^b) \tag{1}$$

where a and b are empirical parameters and $I(M)$ is the weight fraction of all species having molecular weight less than M. The other distribution function, suggested by Wesslau,[4] is given by

$$I(M) = \frac{1}{\beta\pi^{1/2}}\int_0^M \left(\frac{1}{M}\right) \exp[(-1/\beta^2)(\ln M/M_0)^2]\mathrm{d}M \tag{2}$$

where β and M_0 are the parameters. Equation 2 represents

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