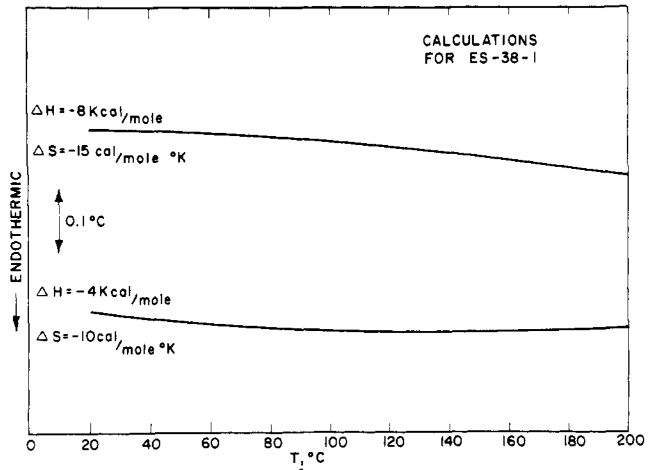

Figure 9. Calculated DSC curves for equilibrium-controlled dissociation of hydrogen bonds.

Science Foundation for support of this research through Grants GK-4554 and GH-31747.

Appendix I

Derivation of DSC Response for Equilibrium-Controlled Dissociation. For simplicity, only a single donor-acceptor reaction is considered:

$$\mathrm{D} + \mathrm{A} \rightleftharpoons \mathrm{D}\cdots\mathrm{A} \qquad (1)$$

D is the donor, A the acceptor, and D····A the hydrogen-bonded complex. We may then write

$$K = [\mathrm{D_b}]/([\mathrm{D_f}][\mathrm{A_f}]) \qquad (2)$$

where the subscripts b and f refer to bonded and free groups and the brackets to concentrations. K is the equilibrium constant, whose temperature dependence is given by

$$K = \exp(-\Delta H/RT + \Delta S/R) \qquad (3)$$

where ΔH and ΔS are the enthalpy and entropy changes associated with hydrogen-bond formation.

To predict the DSC curve we need the temperature derivative of $[\mathrm{D_b}]$, which may be found by combining eq 2 and 3 and differentiating. The result is

$$\frac{\mathrm{d}[\mathrm{D_b}]}{\mathrm{d}T} = \frac{-\Delta H}{RT^2}\left[K^{-1} - \frac{c_1K^{-1} + K^{-2}}{(K^{-2} + 2c_1K^{-1} + c_2)^{1/2}}\right] \qquad (4)$$

c_1 is the sum of the total acceptor and donor concentrations and c_2 their difference squared. The actual deflection on the DSC chart is the heat input rate, $\mathrm{d}Q/\mathrm{d}t$, given by

$$\mathrm{d}Q/\mathrm{d}t = (w/\rho Eb)(\Delta H)(\mathrm{d}[\mathrm{D_b}]/\mathrm{d}T)(\mathrm{d}T/\mathrm{d}t) \qquad (5)$$

w is the sample weight, ρ the sample density, E the instrument calibration factor, b the ordinate scale factor and $\mathrm{d}T/\mathrm{d}t$ the heating rate.

A Study of Radiation-Induced Grafting by Differential Scanning Calorimetry

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ABSTRACT: The melting behavior of styrene-grafted low-density polyethylene film was studied by differential scanning calorimetry (DSC). Styrene was randomly grafted to the polyethylene film by γ radiation at a dose rate of 0.23 Mrad/hr. The apparent graft (total polystyrene content) in the samples ranged from 5 to 200%. Several DSC runs were made for each sample. Grafting was found to lower both the melting point and the heat of fusion during the first DSC determination. For subsequent DSC runs, the melting point depression remained constant while the heat of fusion increased to the original value and became independent of grafting. Accordingly, the heat of fusion determined in the second DSC run was used to calculate the apparent graft of the samples. The lowering of the heat of fusion observed in the first DSC run was explained by a graft-induced strain on the surface of the crystals, which was later relieved by melting and recrystallization. This explanation was substantiated by a correlation between the heat of fusion from the first DSC run and the degree of covalent grafting.

The grafting of side chains to a polymer backbone has a pronounced effect on its physical and mechanical properties. Although this technique has been widely used to modify polymer properties, there are relatively few studies which deal with the influence of the side chains on the melting of the grafted polymer.

This paper is concerned with the melting behavior of styrene-grafted low-density polyethylene film where the grafting is initiated by γ radiation. The objective is to quantitatively isolate the effect of covalent grafting on the melting of polyethylene which contains both grafted and microdispersed styrene homopolymer.[1] The melting point and the heat of fusion were determined by differential scanning calorimetry (DSC) and discussed in reference to previously studied copolymer systems.

The melting point depression has been utilized by previous workers for monitoring radiation damage in homopolymers.[2-5] However, the radiation dosages in all these studies were several orders of magnitudes higher than those used in the present work. These studies showed that

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(1) S. Machi and J. Silverman, *J. Polym. Sci., Part A-1*, **7**, 2737 (1969).

(2) M. Dole and W. H. Howard, *J. Phys. Chem.*, 61, 137 (1957).

(3) L. Mandelkern, D. E. Roberts, J. C. Halpin, and F. P. Price, *J. Amer. Chem. Soc.*, 82, 46 (1960).

(4) R. P. Kusy and D. T. Turner, *Macromolecules*, 4, 337 (1971).

(5) A. M. Rijke and L. Mandelkern, *J. Polym. Sci., Part B*, 7, 651 (1969).

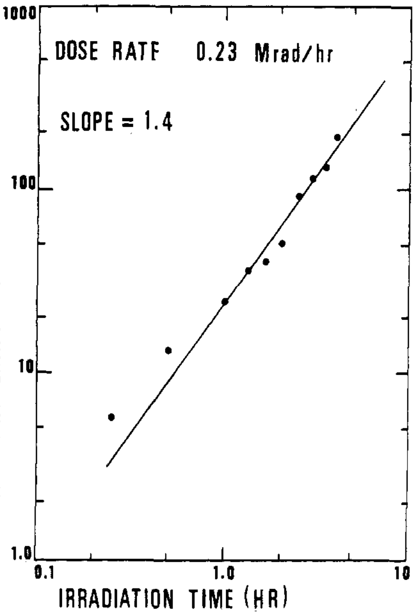

Figure 1. Degree of apparent graft *vs.* time at 20° and 0.23 Mrad/hr for polyethylene films in equilibrium with a solution of 30% styrene in methanol.

Flory's equation for the melting point depression of random copolymers[6,7] could in some cases be used to describe the variation in crystallinity due to the crosslinking of homopolymers. Other investigators[8,9] studied the effect of the methyl and ethyl branches on the melting point of linear polyethylene. Their findings showed that the magnitude of the effect depends on the nature, the amount and the distribution of the branches.

In the present work, the melting point and the heat of fusion data for grafted polyethylene films, and similar data obtained after the separation of the occluded styrene homopolymer from the films, were determined. The data were compared to Flory's theoretical treatment of random copolymers and the influence of the degree of branching and the length of the branches were examined. The results were comparable to those obtained in other systems.[8,9]

Experimental Section

Materials. Strips of additive free Du Pont low-density (0.918 g/cm^3) polyethylene film (10 × 60 × 0.063 mm) were used. Commercial grade styrene, a product of Polysciences Inc., was vacuum distilled and kept at 5° before use. Reagent grade methanol, a product of Merck & Co., was used without further purification

Preparation and Irradiation of Samples. Polyethylene samples of approximately 0.2 g were weighed accurately, then transferred to ampoules containing a solution of 30 vol % styrene in methanol. The methanol is used in order to reduce the equilibrium styrene concentration inside the film; the methanol diffusion into polyethylene was found to be negligible.[10] The ampoules were then degassed by four cycles of freezing and thawing under vacuum and subsequently sealed off at a pressure below 10^{-4} Torr. The sealed ampoules were exposed to γ radiation at 20° in the National Bureau of Standards ^{60}Co source in Washington, D. C. The dose rate was 0.23 Mrad/hr. Following irradiation, the grafted film samples were removed from the styrene solution and soaked in benzene for 3 days. The samples were then dried under vacuum and weighed. The increase in the film weight was determined to be the apparent graft since it includes both the covalently grafted polystyrene and the occluded homopolymer.[1] The thermal measurements were subsequently performed on these samples.

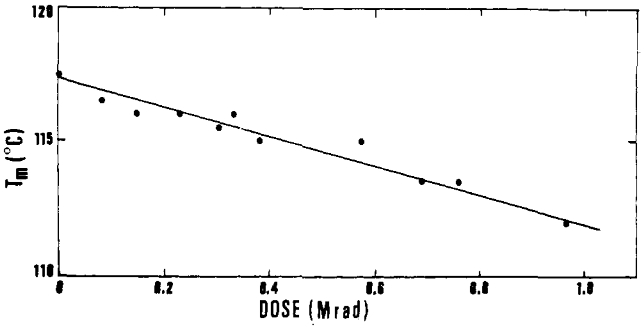

Figure 2. Melting point of grafted polyethylene as a function of dose from the second DSC run.

Thermal Measurements. The melting point and the heat of fusion were determined for each copolymer sample using the DSC cell of a Du Pont, Model 900, thermal analyzer. Two runs were determined for each sample. The temperature of a 10-mg sample was first raised at the rate of 20°/min to 160°, then the sample was quenched in liquid nitrogen and a second run was made in a similar fashion. Subsequent runs were found to be identical with the second run.

The temperature at the maximum of the thermogram was taken as the melting point and the heat of fusion was calculated from the area under the thermogram.

It should be emphasized here that due to the rapid heating rate, the melting points obtained with this procedure are not the equilibrium melting points of the samples. However, because only relative changes in the melting points and the heats of fusion are desired, this variation is relatively unimportant.

Separation of the Occluded Homopolymer. After the DSC measurements were completed, the remaining portion of the copolymer samples were dissolved in xylene at 100°, precipitated slowly in an excess of methanol, then filtered. The precipitate was extracted with benzene to remove the styrene homopolymer, then dried under vacuum. The remaining precipitate, after the extraction, was taken as the polyethylene and the covalently grafted polystyrene.

Results

In order to minimize the effect of radiation damage to the semicrystalline polymer, the maximum dose used did not exceed 1 Mrad. To cover a large graft range within 1 Mrad, grafting at low monomer concentration in the film was utilized. This was found to create viscous conditions inside the film which partially inhibited the termination of the chain radicals and consequently higher yields were achieved. When grafting at high monomer concentration, steady-state prevails and the yield is proportional to time. However, in the present viscous system the yield was found from a previous kinetic investigation to be proportional to the 1.4th power of time.[10] Figure 1 shows a logarithmic plot of the apparent graft as a function of time. The data can be represented by a straight line with a slope of 1.4 as predicted. The scatter at low dose rates can be attributed to the lack of a precise control on the dosimetry which is relatively unimportant in this investigation. This plot, however, clearly shows the efficiency of grafting at low monomer concentration inside the polyethylene film. Within the short time of 4 hr, we were able to vary the grafting yield from about 5-200% while keeping the maximum dose below 1 Mrad.

Figure 2 shows the melting point data, as obtained from the DSC measurements, plotted as a function of the total dose. Irradiated but ungrafted polyethylene showed no detectable change in the melting point with dose indicating a negligible damage to the crystallinity of the polyethylene at the doses used in this work. These results are in

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(6) P. J. Flory, *J. Chem. Phys.*, 15, 684 (1947).
(7) P. J. Flory, *Trans. Faraday Soc.*, 51, 848 (1955).
(8) B. Ke, *J. Polym. Sci., Part A*, 61, 47 (1962).
(9) M. J. Richardson, P. J. Flory, and J. B. Jackson, *Polymer*, 4, 221 (1963).
(10) S. Machi, I. Kamel, and J. Silverman, *J. Polym. Sci., Part A-1*, 8, 3329 (1970).

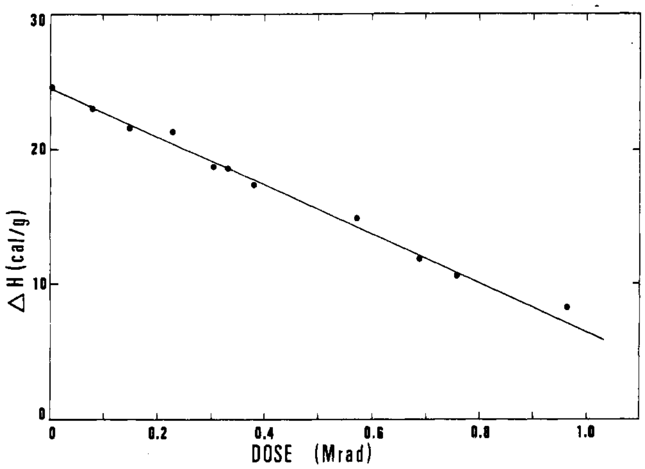

Figure 3. Heat of fusion of polyethylene-styrene copolymer as a function of dose from the second DSC run.

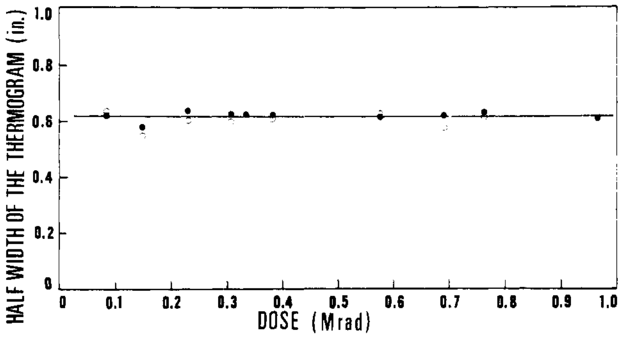

Figure 4. Half-width of the normalized DSC thermograms as a function of dose.

agreement with previous investigators.[2,4] Therefore, Figure 2 shows that the grafting of polystyrene will, in general, cause a depression in the melting temperature of polyethylene.

The heat of fusion of the samples are plotted in Figure 3 as a function of the radiation dose. These values are obtained from the second DSC determination after the samples were once heated and quenched. Here we do expect to see a decrease in the heat of fusion with dose since we are increasing the amorphous content of the sample by the grafted polystyrene.

One interesting observation on these thermograms is that although they vary in area according to the polystyrene content, their shape seems to be unchanged. If we consider the shape of the thermogram to be a rough measure of the crystal size distribution,[8] we can therefore suggest that radiation induced grafting occurs randomly in the material and is little affected by the crystal size. In an attempt to evaluate quantitatively the relative variation in the thermogram shape, the width of the normalized thermogram at half its peak height was measured and plotted as a function of dose in Figure 4. The values obtained were found to be constant over the entire graft range supporting the observed similarity of their shape. This observation, however, needs to be further confirmed at higher dose rates, where the initiation of graft sites is significantly higher than those obtained here, before any definite conclusions regarding their random formation can be reached.

The heat of fusion of a polymer sample, ΔH, can be calculated directly from the thermogram area, A

$$\Delta H(\text{cal/g}) = (A/m)K \qquad (1)$$

where m is the mass of the sample and K is a calibration constant for the instrument. Noting that the total mass of a grafted sample is the sum of the polyethylene (PE) mass, m_{PE}, and the polystyrene (PS) mass, m_{PS}, we can compare the heats of fusion of the ungrafted polyethylene to that of the grafted samples as follows

$$\Delta H_{PE}/\Delta H_{\text{sample}} = 1 + (m_{PS}/m_{PE}) \qquad (2)$$

If we now define the apparent graft yield in the sample, G_a, to be

$$G_a(\%) = (m_{PS}/m_{PE})100 \qquad (3)$$

we can calculate the graft yield from the thermograms of the sample and of pure polyethylene by combining eq 1, 2, and 3 to get

$$G_a(\%) = \{[(A/m)_{PE}/(A/m)_{\text{sample}}] - 1\}100 \qquad (4)$$

In arriving at eq 4 we made the critical assumption that the polystyrene chains grafted to the surface of the polyethylene crystals did not affect the heat of fusion of these crystals. Only by making this assumption is it possible to calculate the per cent graft from the decrease in the thermogram areas of the grafted samples. This decrease in area is solely due to the increased amorphous content of the grafted samples due to the incorporated polystyrene.

Figure 5 shows the apparent graft calculated by eq 4 using the thermogram data obtained from the second DSC determinations *vs.* the apparent graft values calculated directly from the weight gain of the samples (eq 5).

$$G_a(\%) = [(W - W_0)/W_0]100 \qquad (5)$$

where W_0 and W are the sample weights before and after grafting. It is apparent from Figure 5 that the grafting of polystyrene had no effect on the heat of fusion of the polyethylene crystals during the second DSC determination and hence we had a 1:1 correspondence between the apparent graft calculated from eq 4 and the actual increase in the film weight. In the first DSC determination, however, eq 4 gave lower graft values than those calculated from weight gain over the entire graft range. This finding indicates that the grafted chains substantially influenced the heat of fusion of the polyethylene crystals, but that this effect was eliminated when these crystals were melted and recrystallized.

Results of the covalent graft determinations are shown in Figure 6 as a function of the apparent graft in the samples. It is interesting to point out that the yield of the covalent graft, which was found to be 73% of the total polystyrene content of the film, is much higher than the yield obtained when grafting with undiluted styrene monomer. Machi and Silverman[11] reported a 48% yield for the covalent graft when grafting polyethylene with undiluted styrene under the same conditions of film thickness and dose rate used in the present work. The reason for favoring the formation of covalent graft over homopolymer is that at low monomer concentration there is a significant reduction in the homopolymer initiation rate while the initiation of grafted chains is unaffected. As a first approximation, the homopolymerization rate, R_h, can be assumed to follow a half-order dependence on the initiation rate, R_i. So $R_h \propto R_i^{1/2}$ or $R_h \propto C^{1/2}$, since $R_i = \phi IC$, where C is the concentration of monomer, I is the radiation dose rate, and ϕ is a proportionality constant.[12] The equilibrium

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(11) S. Machi and J. Silverman, Large Radiation Sources for Industrial Processes, International Atomic Energy Agency, Vienna, 1969, p 341.

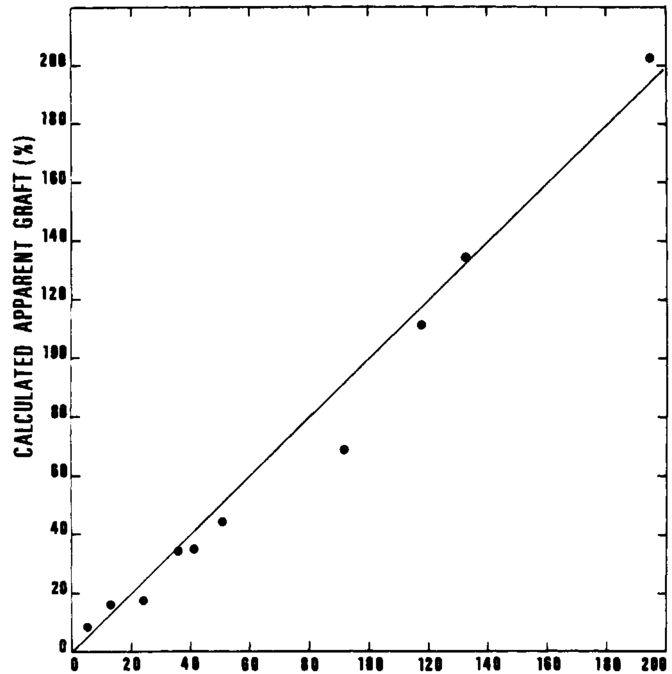

Figure 5. Apparent graft calculated by eq 4 using heat of fusion measurements from the second DSC run as a function of the total weight increase.

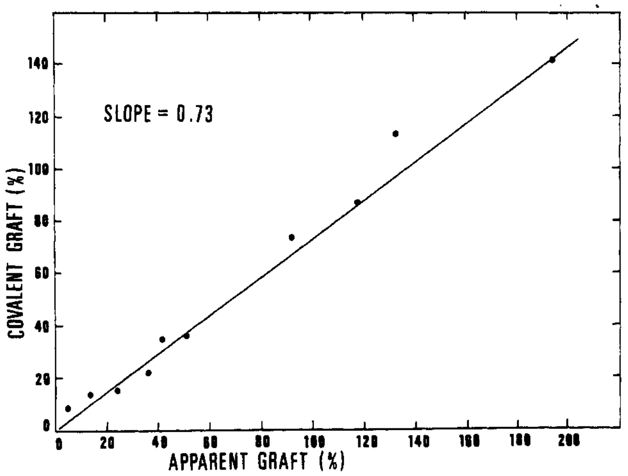

Figure 6. Yield of covalent graft in the copolymer *vs.* the total apparent graft. Grafting from solution of 30% styrene in methanol at 0.23 Mrad/hr and 20°.

concentrations of styrene inside a polyethylene film exposed to the undiluted monomer and to a 30% solution of styrene in methanol were found to be 15 and 6.2 wt %, respectively.[11] Therefore, the expected reduction in the homopolymerization rate, R_h, will be $(6.2/15)^{1/2}$, or 64% of the 52% yield obtained when grafting with pure styrene. This calculation predicts a homopolymerization content of about 33%, or a 67% covalent graft yield which is in good agreement with our experimental value of 73%.

An attempt was made in this investigation to test the possibility of relating the melting point depression of this copolymer to its crystallinity using a Flory-type equation.[7] It is understood that the present copolymer is far from the ideal one described by Flory in his derivation of this thermodynamic equation. However, a comparison with the ideal case will contribute to a better understanding of the present system. The low-density polyethylene used in this work has a crystallinity between 40 and 50%. If we consider the relative crystallinity of polyethylene before grafting, $X = 1$, we can relate the polyethylene melting point T_0, the copolymer melting point T and the relative crystallinity of the copolymer X by the relationship:[7]

$$(1/T) - (1/T_0) = -(R/\Delta H_u) \ln X \tag{6}$$

where R is the gas constant and ΔH_u is the enthalpy of fusion per mol of crystalline units. Since X is the ratio of the mole fraction of crystalline units in the copolymer to that of the polyethylene, we can describe it in terms of the heat of fusion data as follows

$$1/X = 1 + [(M_{PE}/M_{PS})(m_{PS}/m_{PE})] \tag{7}$$

where M_{PE} = the molecular weight of polyethylene repeat unit = 14 and M_{PS} = the molecular weight of polystyrene repeat unit = 104. From eq 2 we can substitute for the mass ratio (m_{PS}/m_{PE}) in eq 7 in terms of the heat of fusion to get

$$\begin{aligned} 1/X &= 1 + (M_{PE}/M_{PS})[(\Delta H_{PE}/\Delta H_{sample}) - 1] \\ 1/X &= 0.865 + (0.135/\Delta H_R) \end{aligned} \tag{8}$$

where $H_R = \Delta H_{PE}/\Delta H_{sample}$. Figure 7 shows a plot of $-\ln X$ [or $\ln (1/X)$] calculated by eq 8, using data from the second DSC determination, and plotted *vs.* $1/T$; the linearity of the plot indicates agreement with the form of Flory's equation (eq 6). The slope of this curve, however, is a factor of 10 lower than the value of $R/\Delta H_u$ predicted by Flory. In other words, the experimental results indicate that the change in the crystallinity of the copolymer is exaggerated. In reality the polystyrene chains exhibit a much lower level of interference with the recrystallization and melting of the polyethylene crystals than predicted from eq 6. This deviation from ideality can be accounted for by assuming: (1) the occluded ungrafted polystyrene, which is immiscible with polyethylene has little to do with the melting of the polyethylene crystals; (2) the covalently grafted polymer is composed of long chains and few

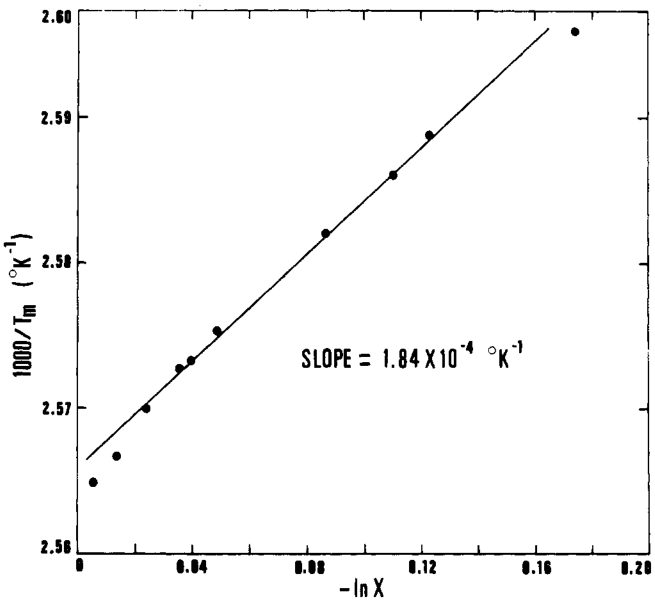

Figure 7. $1/T_m$ *vs.* $-\ln X$ calculated by eq 8 using the data from the second DSC run.

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(12) A. Chapiro, "Radiation Chemistry of Polymeric Systems," Interscience, New York, N. Y., 1962, pp 131 and 606.

grafted sites which again do not markedly interfere with the crystallization and the melting of the polyethylene.

Up to this point, we have utilized the melting points and the heat of fusion obtained from the second DSC determination only. This determination allows for the relaxation of the stresses on the surface of the grafted crystals by melting and recrystallization prior to the measurements. Since covalent grafting is expected to induce some strain on the surface of the polyethylene crystals, it is justifiable to try to correlate the thermodynamic measurements from the first DSC determination with the covalent graft in the sample.

This was accomplished by comparing the apparent graft yield calculated from eq 4, using the data from the first DSC determination, with the covalent graft content of the samples. This comparison is shown in Figure 8 and indicates, for this particular copolymer, almost 1:1 correspondence between the two quantities within the experimental error.

It is interesting to note that Harrison and Baer[13-15] found no change in the heat of fusion of polyethylene single crystals treated with bromine or chlorine. They reasoned that the halogenation occurred only on the surface of the crystals with no apparent effect on the heat of fusion. The present copolymer is a little different than the one described by their experiments. At present, we are grafting a very long bulky molecule to the surface of a tightly packed polyethylene crystalline lamellae. Introducing such a long grafted chain into the interlamellar space of the film can induce a strain on the surface of the lamella which can only be relieved by melting and recrystallization. The size of the grafted styrene molecules in the small free volume surrounding the lamellae of the polyethylene film will give it a greater tendency to strain the crystals than the small Cl atoms grafted to the polyethylene single crystals by Harrison *et al.*

Discussion

The present results indicate that thermal measurements obtained by the DSC can be correlated to both the apparent graft and the covalent graft in the copolymer samples described above. This technique in addition to being fast and relatively simple requires only a small sample weight (2–10 mg). The technique is also relatively insensitive to measurement errors since only relative changes, rather than absolute values, are utilized. As illustrated by the present results, this method applies to the grafting of a noncrystallizable polymer onto the chains of a semicrystalline one. In the more general case, however, when both polymers are semicrystalline, the method can still be used if the difference in the melting points of the two polymeric components is large enough to produce two separate DSC melting peaks. The peak areas can then be individually measured to obtain the heat of fusion and to calculate the change in the crystallinity of each component.

The accuracy of this technique will suffer, however, when calculating the average graft in a large inhomogeneous sample because it is difficult to choose a representative DSC sample weighing 2–10 mg. Despite this limitation, the technique can be quite useful to the radiation chemist who usually employs lengthy extraction procedures to separate and determine the covalent graft in the irradiated monomer–polymer system. By correlating the first DSC run to the covalent graft, similar to the results shown in Figure 8, its future determination in that system will be reduced to a fast and simple routine.

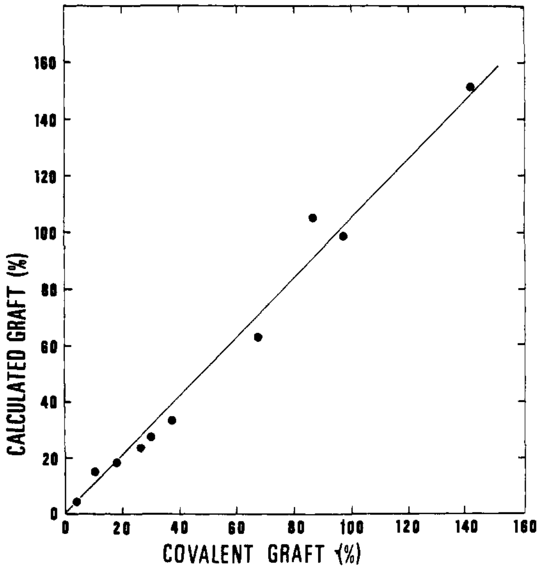

Figure 8. Apparent graft calculated from eq 4 using heat of fusion measurements from the first DSC run, and compared to the chemically separated covalent graft yield.

It is important at this point to discuss the explanation for the copolymer thermal behavior; an explanation that was based on the length and the number of graft sites. The radiation-induced grafting of styrene to polyethylene is relatively well documented in the literature. From previous investigations,[11,12,16] the estimated G value for radical production in polyethylene or long-chain alkanes is on the average of 6 radicals/100 eV of absorbed energy. Using this value, an estimate of the number of radicals produced in polyethylene can be calculated as follows

$$\text{total radicals produced/g of PE} = 6.24 \times 10^{19}\, GD \quad (9)$$

where G is the G value for radical production, D is the total dose in Mrads, and 6.24×10^{19} is a conversion factor. Calculating for the maximum dose used in this investigation ($D = 1$ Mrad, and using $G = 6$ radicals/100 eV) the maximum number of radicals is found from eq 9 to be 3.75×10^{18} radicals/g of PE. The maximum radical yield can also be calculated per repeat unit of polyethylene and is found to be about 1/10,000. If we assume that every radical produced in polyethylene forms a grafted chain, the maximum yield of grafted chains will be one chain for every 10,000 CH_2 units. This is a very low concentration of branch points and should not be expected to interfere with the recrystallization of the polyethylene chains in accordance with the experimental findings of previous investigators.[8,9] The length of the grafted chains, L_c, can be calculated from the yield of the covalent graft, m_{PS}/m_{PE}, and the number of grafted chains, N_c, as follows

$$L_c(\text{styrene units}) = (m_{PS}/m_{PE})(N_A/M_{PS}N_C) \quad (10)$$

where M_{PS} is the molecular weight of the polystyrene repeat unit and N_A is Avogadro's number. Using the experimental value of 1.42 g of PS/g of PE for the covalent graft at the highest radiation dose, $M_{PS} = 104$, $N_A = 6 \times 10^{23}$,

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(13) I. R. Harrison and E. Baer, *Anal. Calorimetry*, **2**, 27 (1970).

(14) I. R. Harrison and E. Baer, *J. Polym. Sci., Part A-2*, **9**, 1305 (1971).

(15) I. R. Harrison and E. Baer, *J. Polym. Sci., Part B*, **9**, 843 (1971).

(16) T. Gäumann and J. Hoigné, Ed., "Aspects of Hydrocarbon Radiolysis," Academic Press, London, 1968, p 26.

and N_c = 3.75 × 10^{18} chains/g of PE; the grafted chains were calculated from equation 10 to be an average of 2000 styrene units in length. So we are indeed talking about very few but long grafted chains which should have a negligible effect on the average polyethylene chain length available for crystallization. Hence the second thermogram provides a good estimate of the apparent graft in the sample.

If we assume that grafting a long polystyrene chain on the surface of a formed polyethylene lamella will strain the crystal, the heat of fusion of the grafted sample will be lower than the ungrafted polyethylene. After recrystallization, the long grafted branches will be excluded from the crystalline region and newly formed crystals will not have the surface strain they experienced before. Therefore, one would expect the heat of fusion determined from the first DSC run to be proportional to the covalent graft. However, the heat of fusion from the second DSC run, after the exclusion of the grafted chains from the crystalline region, will have decreasing values depending on the effect of branching on the average length of the polyethylene chains available for crystallization. If the concentration of branches is very low, as was the case in this research, the second DSC run should be expected to yield heat of fusion values, per gram of polyethylene, close to those obtained from the ungrafted samples.

The deviation of the present results from those predicted by Flory's equation requires some clarification. First of all Flory's model of a copolymer[17] is a completely random one composed mainly of one type of monomer units capable of crystallization and of a second type of monomer units which do not crystallize. Although the production of free radicals by radiation is a random process, these radicals migrate to the surface of the crystals[18] in order to interact with the styrene monomer. In addition, each one of these radicals will initiate a very long nonrandom polystyrene chain. In other words, this system is not a random copolymer. The grafted polystyrene is up to twice the weight of the original polyethylene sample, while the maximum concentration of chains is only 1/10,000 CH_2 units. It is mainly due to this nonrandomness that the depression of the copolymer melting point calculated by Flory's equation was much greater than the measured experimental values. Accordingly, Flory's equation is not applicable to the present system and can only be used in a qualitative manner. It is interesting to note, however, that the deviation of the present results from Flory's equation indicates that the number of branches rather than the mole fraction of the crystalline units seems to be the important factor affecting the depression of the melting point of this copolymer.

Acknowledgments. We gratefully acknowledge the National Science Foundation Departmental Development Grant and the Division of Isotope Development of the U. S. Atomic Energy Commission for the support of this research, the use of the γ radiation facility at the National Bureau of Standards, and the experimental assistance of Mr. M. Needleman.

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(17) L. Mandelkern, "Crystallization of Polymers," McGraw-Hill, New York, N. Y., 1964, p 74.

(18) T. Kawai, A. Keller, A. Charlesby, and M. G. Ormerod, *Phil. Mag.*, **10**, 779 (1964); **12**, 657 (1965).

Comparison of the Effects of Polydispersity on the Rayleigh Line Width as Determined by Homodyning and Heterodyning Spectrometry

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Received August 3, 1972

ABSTRACT: Numerical calculations have been made of the spectrum of the Rayleigh line in light scattered from dilute solutions of random-coil polymers having the Schulz distribution of molecular weights; the resulting spectra are comparable to heterodyning experiments. These calculated spectra have been convolved to give results comparable to homodyning experiments. As shown by Reed, the Rayleigh spectral width from heterodyning measurements can be used to calculate an average diffusion constant which is close to the diffusion constant of the species having molecular weight equal to the z-average molecular weight. Homodyning spectra are somewhat more than twice as broad as corresponding heterodyning spectra. Analogous numerical calculations are given for the autocorrelation function of the photocurrent for both homodyning and heterodyning experiments.

With the increasing use of Rayleigh line spectrometry for measuring diffusion coefficients of macromolecules in dilute solution, considerable attention has been given to the effects of polydispersity on such measurements. In principle, it is possible to determine the distribution function of molecular weights from the Rayleigh line spectrum, and mathematical techniques for doing this have been devised. However, extremely accurate spectral measurements are required for successful application of these methods, and determination of a molecular weight distribution using only experimental Rayleigh line data has not yet been demonstrated.

Although it is difficult to determine the distribution function of molecular weights from the Rayleigh line spectrum, it is relatively easy to determine the effect of polydispersity by calculating the spectra which would be observed using known distribution functions. Such calculations show how the shape and breadth of the spectrum depend on the distribution function and its characteristic parameters, typically an average molecular weight and a