Melting and Glass Transition of Radiation-Induced Graft Polyethylene

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Synopsis

Melting and glass transition data are reported employing DSC for styrene-grafted high-density polyethylene obtained by γ radiation. Judging from the data of the melting point and the heat of fusion, the grafted polystyrene had no effect on the polyethylene crystallites, but the half-width of the thermogram was observed to increase slightly, showing an effect on the crystallite size distribution. As no effect was observed on the glass transition temperature by grafting, the amorphous region of the polyethylene apparently was not affected. It is suggested, therefore, that the free volume or segmental mobility will not be decreased by radiation-induced grafting. Very few but long grafted chains had negligible effect on the average polyethylene chain length available for segmental motion, and grafted polystyrene should be expected to differ little from the styrene homopolymer in thermal motions.

INTRODUCTION

It is well known that the physical and mechanical properties of a polymer are changed by radiation-induced grafting of side chains. The explanation of this fact is of interest in connection with a change of the polymer morphology. In styrene-grafted high-density polyethylene which consists of crystalline and amorphous phases, the influence of styrene side chains on the crystalline and amorphous regions must be discussed. By use of DSC, changes in the crystalline regions were studied from the melting behavior, and changes in amorphous regions were studied from the glass transition phenomena, respectively.

EXPERIMENTAL

Materials

The polyethylene film used in the grafting experiments was a high-density (0.955 g/cm^3) commerical product of Mitsui Chemical Co. designated Hizex #7000F. Styrene grafting was carried out by a simultaneous irradiation method (0.14 Mrad/hr by γ rays from a ^{60}Co source at room temperature). Details on sample preparation processes were described in a previous paper. The graft yield and the weight fraction of grafted polystyrene of each samples are listed in Table I, where the S series indicates the samples in which the polystyrene homopolymer

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part formed in the grafting process is extracted with benzene in a Soxhlet extractor.

Thermal Measurements

Thermal measurements were undertaken by using a Rigaku-Denki Model 8000 thermal analyzer. Two runs were operated for each sample on melting. The temperature of a sample weighing 10 mg was first increased at the rate of 20°C/min to 150°C and decreased at the rate of 5°C/min. A second run was made in a similar fashion. Subsequent runs were found to be identical with the second one. The maximum temperature of the thermogram was taken as the melting point, and the heat of fusion was calculated from the area under the thermogram curve. This procedure does not give the true melting point and true heat of fusion, especially for rapid heating rates; but because only relative changes in melting points and heat of fusion are desired, this variation is relatively unimportant.

A cooling unit filled with liquid nitrogen was attached to the DSC cell to determine the glass transition temperature of polyethylene. The temperature of a sample weighing 20 mg was first cooled down at a rate of 3°C/min from room temperature to −85°C to −95°C; then the temperature was raised at a rate of 20°C/min to 150°C, and then decreased at a rate of 5°C/min to room temperature. In the thermograms on the grafted copolymers, the inflection was defined and the crossing point of line A and line B was determined as the glass transition point T_g, as shown in Figure 1. It is difficult to assign the true glass transition point from the thermogram, but it is possible to obtain relative values.

RESULTS AND DISCUSSION

Melting Behavior

The relation between the melting points and crystallinity is expressed by Flory's equation.[2] The melting point depression obtained by us was much smaller than the results calculated by Flory's equation (Fig. 2).

The heats of fusion of the grafted samples were plotted as a function of the weight fraction of polystyrene in Figure 3. These values were obtained from the
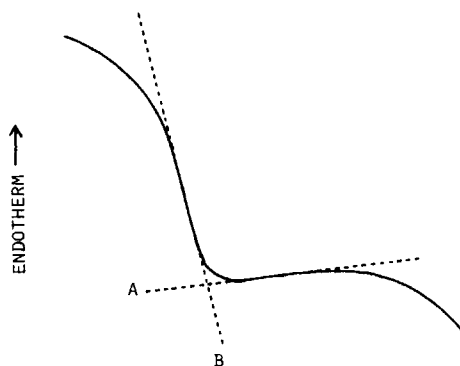

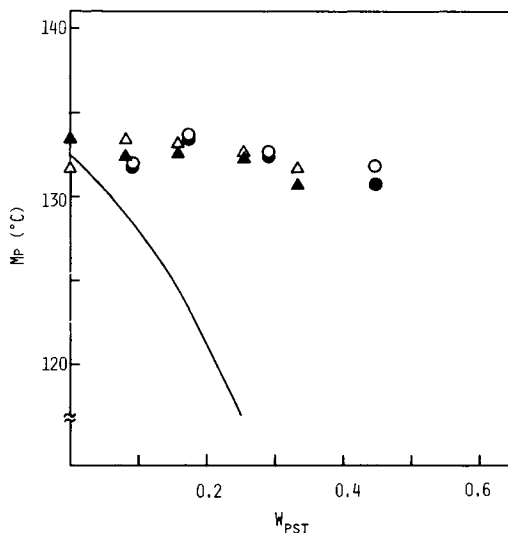Fig. 1. Thermogram near glass transition point.

Fig. 2. Melting point of grafted polyethylene vs. weight fraction of polystyrene: (O) first run; (●) second run before extraction; (△) first run; (▲) second run after extraction; (—) melting point evaluated by Flory's equation.

average values of second and subsequent runs. A first run was considered biased by previous thermal histories, but the second and subsequent runs were assumed to have a common history. It is apparent from Figure 3 that, since most points lie on a straight line, polystyrene has no effect on the heat of fusion of the polyethylene crystallites during the second and subsequent DSC determinations, whether containing homopolymer or not. Assuming that the heat of fusion of the crystalline part in ungrafted polyethylene[3] is 69.0 cal/g, those in grafted samples were calculated to be 68.75 ± 1.33 cal/g. In the previous paper,[1] we said that the degree of crystallinity was not affected by grafting processes with an average heat of fusion value of 69.15 ± 1.60 cal/g. In the present study we obtained the same results with an accuracy of ±1.33 cal/g. This result suggests
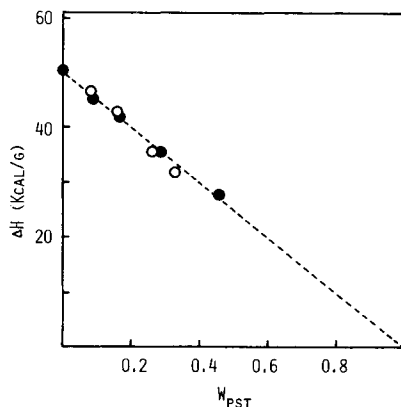

Fig. 3. Heat of fusion vs. weight fraction of polystyrene in grafted polymer: (O) before extraction; (●) after extraction.
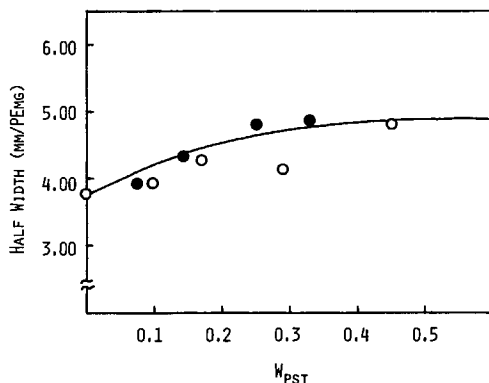
Fig. 4. Half-width of the normalized thermogram vs. weight fraction of polystylene: (O) before extraction; (●) after extraction.

that the presence of the grafted polystyrene has no effect on the crystallization of polyethylene.

Half-widths of the normalized thermogram (converted per 1 mg of polyethylene) were plotted as a function of weight fraction of polystyrene in Figure 4. If thermal effects by the radiation-induced graftings were present, they should be revealed in the first DSC determination, but these effects might have been eliminated when the crystals were melted and recrystallized. The values obtained were found to increase slightly with weight fraction of grafted polystyrene. If the half-widths of the thermogram can be considered to be a rough measure of the crystal size distribution,[4,5] it can be assumed that radiation-induced grafting diminishes.

Glass Transition

In Figure 5, the glass transition temperatures were plotted as a function of the weight fraction of polystyrene. The glass points of each sample remained almost
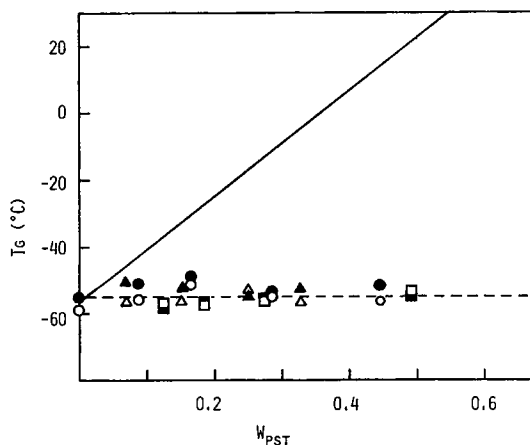

Fig. 5. Glass transition point of grafted polyethylene vs. weight fraction of polystyrene: (O) first run, (●) second run before extraction; (△) first run, (▲) second run after extraction; (□) first run, (■) second run of blend sample; (—) glass transition point evaluated by Gordon–Taylor's equation.

TABLE I
Styrene Content of Grafted Samples

Sample	Irradiation dose, Mrad	Graft yield	Weight fraction of polystyrene (W_{pst})
		Before Extraction	
PE	—	0	0
PS-10	0.576	0.100	0.091
PS-20	0.846	0.197	0.165
PS-40	0.962	0.409	0.165
PS-80	2.45	0.821	0.451
		After Extraction	
PS-S10	0.576	0.090	0.083
PS-S20	0.846	0.179	0.152
PS-S40	0.962	0.343	0.256
PS-S80	2.45	0.500	0.333

constant, about −54°C, with changes in polystyrene content. This is the same behavior with the melting points. The glass transition point of blends of polystyrene homopolymer prepared by irradiation of styrene monomer and polyethylene also exhibited the same behavior. The observed glass points deviated from the ones calculated by the Gordon–Taylor equation.[6] It is suggested, therefore, that the thermal properties of graft copolymer obtained by irradiation are not the same as those of random copolymers which can be calculated by this equation, but are the same as that of the macro blends. Further, if the graft copolymer had similar properties as the blends, two glass transition points of polyethylene and polystyrene should appear, respectively, but no polystyrene glass transition was observed in these thermograms for the grafts or blends. That is why the glass transition of polystyrene at 100°C occurs in the same temperature range as the melting peak of polyethylene crystallite and the energy associated with the heat of fusion is much greater than the heat of glass transition; therefore, the glass transition is completely masked in these thermograms.

Free Volume

On the basis of the above conclusions, an attempt was made to correlate the diffusion data with structural changes induced by graft copolymerization. It

TABLE II
Number and Length of Grafted Chain

Sample	Irradiation dose, Mrad	Number of chains per 10000 CH$_2$ units	Length of chain (number of styrene units)
PS-S10	0.576	0.50	2.4×10^2
PS-S20	0.846	0.75	3.1×10^2
PS-S40	0.962	0.84	5.5×10^2
PS-S80	2.45	2.1	3.2×10^2

was reported[7,8] that in the case of permeation experiments for small molecules into radiation-induced grafted polyethylene, the diffusion coefficients initially decrease with increase in volume fraction of polystyrene. This has been explained in terms of a decrease in free volume or segmental mobility by grafted side chains. It was shown by Williams et al.[9] that the free volume is given approximately by the relation

$$f_{am} = A + B(T - T_g) \tag{1}$$

where f_{am} is the free volume in an amorphous polymer and A and B are positive constants. According to eq. (1), the decrease in free volume in the copolymer will increase T_g. In the absence of experimental data on radiation-induced graft copolymer, the glass transition temperatures was calculated by the Gordon and Taylor equation, or eq. (2):

$$1/T_g = v_a/T_{g(a)} + v_b/T_{g(b)} \tag{2}$$

where $T_{g(a)}$ and $T_{g(b)}$ are the glass transition temperatures of component a and component b, respectively. However, according to our thermal measurements, T_g of polyethylene did not change with styrene contents, and, therefore, the above-mentioned interpretation does not hold. Consequently the decrease in the diffusion coefficient of small molecules cannot be explained by a decrease in free volume as has been accepted. Some other interpretation must be found.

Number and Length of Side Chains

The number of sites and the lengths of chains of graft copolymer will be calculated according to the literature.[10,11,12] Using a G value of 6 free radicals per 100 electron volts of absorbed energy, the number of radicals produced per 1 g polyethylene at the irradiation dose shown in Table I can be obtained. If all sites where radicals form can become grafting sites, the number of sites per 10000 CH_2 units is 0.5 to 2. From yield data, the number of styrene units in one polystyrene chain can be calculated. These values are listed in Table II. The production of free radicals by irradiation processes is a random process, but each radical will initiate a very long nonrandom polystyrene chain. Very few but long grafted chains had a negligible effect on the average polyethylene chain length available for crystallization and segmental motion, and the grafted polystyrene should be expected to differ little from the styrene homopolymer in thermal motion. That is to say, the graft copolymer obtained by irradiation is not considered a random copolymer. Flory's equation and the Gordon–Taylor equation, being valid in case of random copolymers, are not applicable to this system. Therefore, the number of branches seems to be the important factor affecting the depression of melting point and the rise of glass temperature of this graft copolymer.

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