

## Effect of Styrene Grafting on Diffusion and Solubility of Gases in Polyethylene

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### Synopsis

Diffusion and solubility coefficient data of gases for styrene-grafted high-density polyethylene obtained by  $\gamma$ -irradiation are reported. Diffusion coefficients were determined by the time lag method. Solubility coefficients were determined by a new, more accurate static method. Densities and volume fractions of grafted polystyrene were calculated from the observed values of extent of grafting and density of the graft copolymer films. The solubility coefficients obey simple additivity in terms of volume fraction of side-chain polystyrene and amorphous polyethylene. However, behavior of the diffusion coefficients is more complex. Inasmuch as diffusion is a kinetic process, it is influenced by morphology. The experimental results reported here, together with x-ray diffraction and DSC data, provide a basis for discussing the morphology of the graft copolymers.

### INTRODUCTION

A large number of graft copolymers prepared by irradiation have been developed and many of their physical and chemical properties examined. In general, their properties depend mainly on the number of graft sites and the length of the side chain. Huang et al.<sup>1,2</sup> attempted to correlate permeability data with structural changes induced by the graft copolymerization and obtained valuable information on the morphology of graft copolymer. In this study, we have regarded the graft copolymer as the two polymer components and investigated the question of additivity of their contributions to diffusion and solubility coefficients. The results are discussed in terms of the morphologic changes induced in polyethylene by graft copolymerization revealed by x-ray diffraction and DSC data.

### EXPERIMENTAL

#### Materials

Strips of Mitsui Chemical Co. high-density polyethylene film (density = 0.955 g/cm<sup>3</sup>; molecular weight =  $1.2 \times 10^5$ ; amorphous content  $\alpha = 0.29$ ) were extracted with benzene using a Soxhlet extractor for 12 hr to remove antioxidant and then dried under reduced pressure. Styrene was purified in the usual way and vacuum distilled before use. Styrene grafting was carried out

TABLE I  
Density of Polystyrene in Grafted Film Extracted by Benzene

$G^a$	$d(\text{obs.})^b$	$d_{pst}(\text{calc.})^c$
0.0 (polyethylene)	0.955	
0.0032	0.957	—
0.090	0.961	1.034
0.177	0.968	1.049
0.335	0.978	1.045
0.599	0.986	1.043

<sup>a</sup> Graft yield.

<sup>b</sup> Observed density of grafted film.

<sup>c</sup> Calculated density of polystyrene in grafted film.

by a simultaneous irradiation method (0.14 Mrad/hr by  $\gamma$ -ray from a  $^{60}\text{Co}$  source at room temperature) and a several-grafting-yield sample was attained by varying the irradiation times. Following irradiation, the grafted film samples were soaked in methyl alcohol for several hours and then dried under vacuum and weighed. Other samples were prepared after several measurements were completed; the remaining portion of the grafted samples was extracted with benzene in the Soxhlet extractor to remove the styrene homopolymer for approximately 10 hr to obtain a constant weight and then dried under vacuum.

The extent of grafting was determined as usual from eq. (1):

$$G = \frac{W_f - W_i}{W_i} \quad (1)$$

where  $W_i$  and  $W_f$  are the initial and final weights of the film, respectively. However, for discussing changes in physical properties, the volume fraction (or weight fraction) composition is more useful. If the density of the graft polymer is an additive property of the components, it can be represented by eq. (2):

$$d = v_a d_a + v_b d_b \quad (2)$$

Here, the graft yield is related to the density by

$$v_a = d_b / (d_b + G d_a) \quad (3)$$

where  $d_a, d_b$  and  $v_a, v_b$  are densities and volume fraction of polyethylene and polystyrene, respectively. Therefore, by measuring the density and graft yield of the grafted polymer, it is possible to calculate the density and volume fraction of polystyrene in the grafted films:

$$d_{pst} = d_b = d_a d G / [d_a (1 + G) - d] \quad (4)$$

$$V_{pst} = v_b = d_a G / (d_b + d_a G) \quad (5)$$

As shown in Table I, the density of grafted polystyrene was obtained as  $1.045 \pm 0.005$  based on calculation by eq. (4) from graft yield and film density which was measured by means of a density gradient column with an error of 0.2%. This value agreed with the density of 1.05 for pure polystyrene film.<sup>3</sup> The volume fraction of each sample was determined from eq. (5) by employ-

TABLE II  
Composition of Grafted Films Used

Irradiation dose, Mrad	$G^a$	$V_{pst}^b$	$V_{pst}^c$	$W_{pst}^d$
		Before Extraction		
0.576	0.100	0.082	0.231	0.091
0.846	0.203	0.155	0.378	0.169
0.962	0.426	0.273	0.561	0.299
2.45	0.885	0.444	0.726	0.470
		After Extraction		
0.576	0.090	0.076	0.212	0.082
0.846	0.172	0.133	0.340	0.147
0.962	0.381	0.256	0.533	0.276
2.45	0.596	0.348	0.629	0.373

<sup>a</sup> Graft yield.

<sup>b</sup> Volume fraction of polystyrene to amorphous and crystalline portion of polyethylene.

<sup>c</sup> Volume fraction of polystyrene to only amorphous portion of polyethylene.

<sup>d</sup> Weight fraction of polystyrene.

ing the graft yield and  $d_{pst} = 1.05$ . As the dissolving of gas occurred only in amorphous region, the solubility coefficients must be represented by volume fraction of polystyrene to amorphous polyethylene,  $V'_{pst}$ , according to eq. (6):

$$V'_{pst} = \frac{V_{pst}}{1 + (1 - \alpha)V_{pst}} \quad (6)$$

where  $1 - \alpha$  is the crystallinity of the polyethylene. The heat of fusion of crystalline polyethylene,  $\Delta H$  (kcal/g), will be related to weight fraction of polystyrene as given by eq. (7):

$$W_{pst} = \frac{G}{1 + G} \quad (7)$$

The grafted films used are listed in Table II with their respective four quantities  $G$ ,  $V_{pst}$ ,  $V'_{pst}$ , and  $W_{pst}$ .

Five commercial gases were used in this study: helium, nitrogen, oxygen, argon, and carbon dioxide. No attempt was made to purify the gases before use.

### Measurements

The solubility coefficients were determined by the volume change method with an apparatus described previously,<sup>4</sup> which gave the sorption rate curves from the initial to the equilibrium state. The change of oil level based on the pressure decrease in a measuring cell was recorded continuously by a photo-cell or observed intermittently by a cathetometer. The solubility coefficients were calculated from the difference between the equilibrium sorption and the surface adsorption obtained from the sorption rate curves.

The short-range pressure change or time lag was measured by the thermistor gauge which was combined with a recorder and a bridge circuit. Each film was out-gassed at room temperature for periods of up to one day. The pressure in the low-pressure side of the cell was reduced to  $10^{-5}$  torr with an

oil diffusion pump. The leakage rate into the measuring system was no greater than  $10^{-3}$  torr per day. At about  $10^{-3}$  torr (checked by another vacuum gauge), the time lag was determined from the straight line. Diffusion runs of relatively short duration were performed until drift was eliminated. By observance of this procedure it was possible to repeat tests at any previously attained temperature and reproduce values of diffusion coefficients with accuracy consistent with anticipated limits. Long-period pressure change or permeability was obtained by observing an ordinary manometer with a cathetometer.

## RESULTS AND DISCUSSION

### Solubility Coefficients

Linear relations between the solubility coefficients and the volume fractions of polystyrene to amorphous polyethylene in grafted film which were free from styrene homopolymer were observed for both argon and carbon dioxide as shown in Figures 1 and 2, respectively. Since the solubility is the value of an equilibrium state, it is thought that simple additivity is valid, and the data presented here display straight lines against the volume fraction of side-chain polystyrene. However, as shown in the same figures, the system containing homopolymer does not exhibit a straight line, and solubility is less. It is, therefore, considered that grafted side chains and homopolymer contribute differently to the increase of solubility.

Since it is difficult to conceive a definite tendency from solubility coefficients which was obtained from the data of permeability and diffusion coefficient, they cannot be discussed here.

Because approximately the same tendency as obtained for argon is found

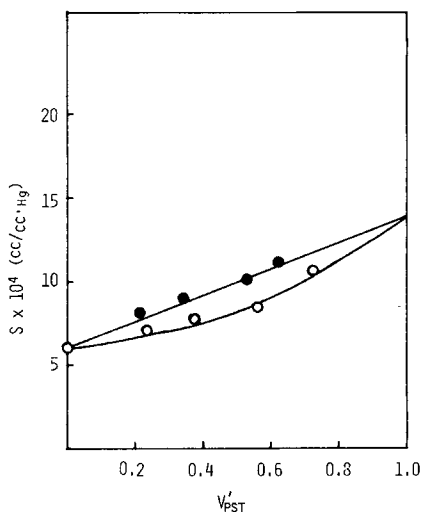


Fig. 1. Solubility coefficients for argon vs. volume fraction of polystyrene to amorphous polyethylene in grafted films at 30°C and 70 cm Hg equilibrium gas pressure: (O) before extraction; (●) after extraction.

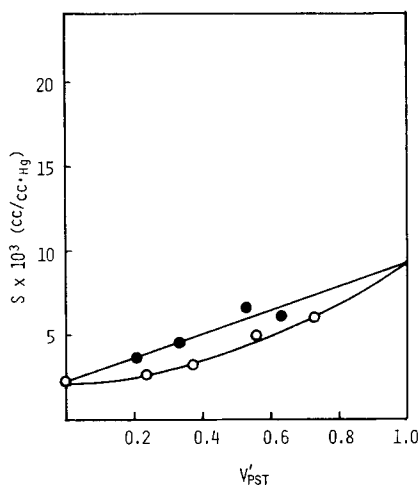


Fig. 2. Solubility coefficients for carbon dioxide vs. volume fraction of polystyrene to amorphous polyethylene in grafted film at 30°C and 70 cm Hg equilibrium gas pressure: (O, ●) same as Fig. 1.

for the solubility coefficients of nitrogen and oxygen, the latter are not separately illustrated graphically.

### Diffusion Coefficients

The relation of diffusion coefficients determined by the time lag and the volume fraction of polystyrene is plotted in Figure 3. For all gases, the diffusion coefficients initially decrease with increase in volume fraction of polystyrene and then increase above  $V_{pst} = 0.15$  and become maximum when  $V_{pst}$  is 0.30–0.35. They once again decrease and seem to approach the values of pure polystyrene. The reason why the diffusion coefficients present such complex phenomena is because the diffusion is a relaxation process. Since

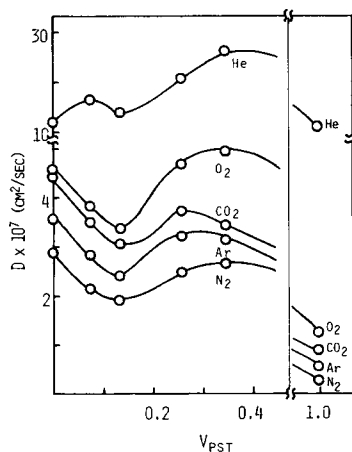


Fig. 3. Diffusion coefficients for gas vs. volume fraction of polystyrene to grafted film at 30°C (extracted by benzene).

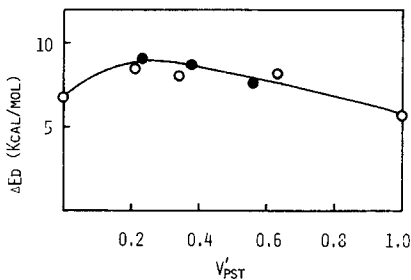


Fig. 4. Activation energy of diffusion for argon vs. volume fraction of polystyrene ( $15^\circ$  to  $40^\circ\text{C}$ ): (O) before extraction; (●) after extraction.

diffusion is a kinetic process, the grafted side chains interfere with the gas transport by reducing the volume available for the diffusion process. Beyond a certain grafting level, the increased presence of side chains such as polystyrene is probably sufficient to disrupt the spherulitic crystallite. This creates new areas for diffusion and results in the upswing of the diffusion coefficients. This can be seen also from the activation energy of diffusion which decreases with increasing graft concentration, except at low volume fraction, as shown in Figure 4.

It is thought that the behavior of the diffusion coefficients does not simply depend on volume fraction, but is greatly influenced by morphologic structure changes with grafting. In what follows, the contribution of the individual effects will be considered in some detail.

### Composite Effects

By assuming that the graft is a kind of mixture if there are no mutual interactions between both materials, the relation of physical properties ( $x_a, x_b$ ) and volume fraction ( $v_a, v_b$ ) of both materials is generally represented by eq. (8):

$$x^n = x_a^n v_a + x_b^n v_b \quad (1 \geq n \geq -1, n \neq 0). \quad (8)$$

With respect to the solubility coefficient in Figures 1 and 2,  $n = 1$  is assumed and the additivity seems to be valid. The slopes of the graph represent the difference of solubilities between polyethylene and polystyrene. From Fig-

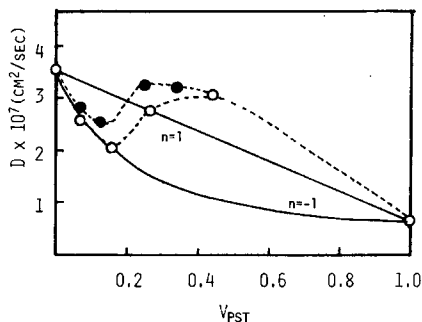


Fig. 5. Diffusion coefficients for argon vs. volume fraction of polystyrene at  $30^\circ\text{C}$ : (O) before extraction; (●) after extraction.

ure 5, the vibrational contributions to  $n = 1$  can be put into convenient forms with respect to the diffusion coefficients. On the other hand, the observed values of diffusion coefficients below 0.2 volume fraction are in accord with  $n = -1$  in eq. (8) and beyond this region deviate to the positive direction of  $n$ .

Initial decreases in the diffusion coefficients with volume fraction can be well explained in terms of  $n = 1$ . It is thought that above 0.2 volume fraction, diffusion coefficients are increased by another effect, such as disruption of the crystalline region. It is convenient to imagine that  $n = 1$  can be expected to hold as long as observed in Figure 5.

### Change of Free Volume

The initial decrease in the diffusion coefficient with volume fraction of grafted polymer could be also explained in terms of a decrease in the free volume or segmental mobility of the amorphous regions as expressed by the permeability coefficient by Huang et al.<sup>1,5</sup> The grafts fill in the regions between lamellae and in defects, thereby reducing the available free volume for diffusion. Crosslinking between lamellae by grafted side chains could also lead to a reduction in the diffusion coefficients. Equation (9) shows the relation of  $f_{am}(T)$ , the free volume of the amorphous region at temperature  $T$  °K, and  $D_T$ , the thermodynamic diffusion coefficient at the same temperature:

$$D_T = \alpha \exp \{-\beta/f_{am}(T)\} \quad (9)$$

where  $\alpha$  and  $\beta$  are considered to be positive constants for a given system.<sup>6</sup> Equation (9) is valid in the case of diffusion into the polymer of solvent vapor. However, the same concept is thought to hold for gases, too. It indicates that the free volume of the polymer network available for diffusion is decreasing as more styrene is grafted. The grafted polystyrene chains are formed from styrene monomer which has diffused into the amorphous regions of the polymer. When graft copolymerization takes place at the free-radical sites on the polyethylene backbone, the polystyrene attaches onto the polyethylene chains in the amorphous regions. In this way, the mobility of the polymer chains are reduced resulting in a lowering in the free volume.

It has been shown by Williams et al.<sup>7</sup> that the free volume of an amorphous polymer is given approximately by the relation

$$f_{am} = A + B(T - T_g) \quad (10)$$

where  $T_g$  is the glass transition temperature of the polymer and  $A$  and  $B$  are positive constants. The free volume of the crystalline polymer can then be obtained by multiplying the free volume of the completely amorphous polymer by the volume fraction of amorphous material in the polymer sample. In the absence of experimental data, the glass transition of the random copolymer will be calculated by the relationship quoted by Gordon and Taylor<sup>8</sup> as follows:

$$1/T_g = v_a/T_{g(a)} = v_b/T_{g(b)} \quad (11)$$

where  $T_{g(a)}$  and  $T_{g(b)}$  are the glass transition temperatures of component  $a$  and component  $b$ , respectively. It would be expected that at low levels of grafting, the grafted polystyrene chains would be relatively short and exhibit

approximately the nature of random copolymerization.<sup>9</sup> The glass transition temperature of the copolymer will increase with increasing polystyrene volume fraction according eq. (11). Using eq. (10), the increase in  $T_g$  decreases the free volume of the copolymer. Thus, it is explained qualitatively that at low levels of grafting, the reduction of the diffusion coefficients is due to the decrease in free volume.

Only helium shows an increase of the diffusion coefficients. It is necessary to consider the mutual interaction between the size of helium and the microbrownian motion of polymer segments to find a reason for this behavior. That is to say, as the graft polymer was added to the polyethylene chain, it is thought that the microbrownian motion of polymer segment was lowered and/or only a shorter wave vibration remained. Under these conditions, the diffusion of a relatively greater molecule is interfaced with, but a small molecule such as helium, unless the free volume is considerably decreased, is given a linear path and the diffusion coefficient increased. This consideration was revealed in Figure 3 as an early decreasing of the free volume. The larger the molecule is, the earlier and the more the diffusion coefficients decrease.

### Disruption of Crystallites and Change of Crystallinity

As shown in Figure 3, diffusion coefficients increased when the volume fraction of polystyrene was about 0.2. With respect to a similar change in permeability coefficients, Myers et al.<sup>10</sup> and Huang et al.<sup>1</sup> explained the effect as the disruption of crystals during the progress of grafting. In order to investigate this relation, the sizes of crystallites were calculated by the Shener-Jones method of the half-intensity width of the x-ray diffraction pattern of the 110 diffraction spots. The result is shown in Figure 6. The sizes of the crystallites are at a minimum when the volume fraction of polystyrene is about 0.25. Comparing the increase in diffusion coefficients with this change in sizes, it is clear that the crystallites were disrupted.

According to Chen et al.,<sup>11</sup> under some graft condition, the higher the degree of crystallinity, the greater is the degree of grafting. That is because the radical which initiates the grafting is more stable in the crystallite. Since the styrene monomer cannot diffuse into crystallites, radicals produced in crystallites diffuse onto the surface of the crystallites. Since they act as initia-

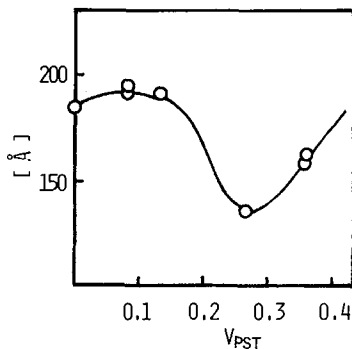


Fig. 6. Size of crystallite vs. volume fraction of polystyrene in grafted film extracted by benzene.



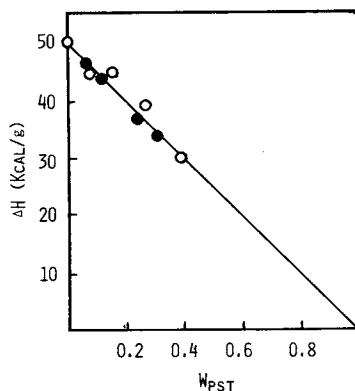


Fig. 7. Heat of fusion vs. weight fraction of polyethylene in grafted polymer: (○) before extraction; (●) after extraction.

tors, polymerization occurs locally around the crystallite, and then the crystallites are disrupted or strained.

On the other hand, the heat of fusion  $\Delta H$  of crystalline polyethylene in each grafted sample, calculated from the area under the thermogram of a DSC (Rigaku-Denki, Model 8001), was inversely proportional to the weight fraction of polyethylene, as shown in Figure 7. Assuming the heat of fusion of completely crystalline polyethylene is 69.0 cal/g,<sup>12</sup> the average value of  $\Delta H$  of the crystalline part in polyethylene of each grafted sample becomes  $69.15 \pm 1.60$  cal/g, and change in the degree of crystallinity by the grafting is not registered. The shape of the thermograms tended to flatten out to some extent for high polystyrene-containing samples, indicating a possible change in the size distribution of the crystallites by disruption or strain within crystallites.<sup>2</sup>

### Change in Distribution of Crystallite Size

The polyethylene used in this experiment is, of course, crystalline polymer, while polystyrene in the grafted polymer is an amorphous polymer. Polystyrene ductile film used as pure polystyrene was confirmed as almost amorphous by x-ray diffraction. The diffusion coefficient is, on the other hand, determined not by the amount of material. That is to say, assuming the film thickness to be constant, the diffusion coefficient is determined by the length of the diffusion path. When the sizes of the crystallites are sufficiently large, the diffusion path in the crystalline polymer becomes longer than in the polymer composed of only amorphous material, even if the macroscopic film thickness is the same. The diffusion coefficients in completely amorphous polyethylene must therefore be predicted.

Spheres of diameter  $w$  are assumed to represent spherulite crystallites; furthermore, it is assumed that high-density polyethylene is composed of closely packed crystallites of diameter  $w$ . At this packing fraction is 74%, it is a good approximation to compare it to the 71% of crystallinity of the polyethylene used in this study. As the penetrants move into amorphous regions among the crystallites, on the average, they detour at least one spherulite when they proceed two phases of crystallite as shown in Figure 8. We consider this de-

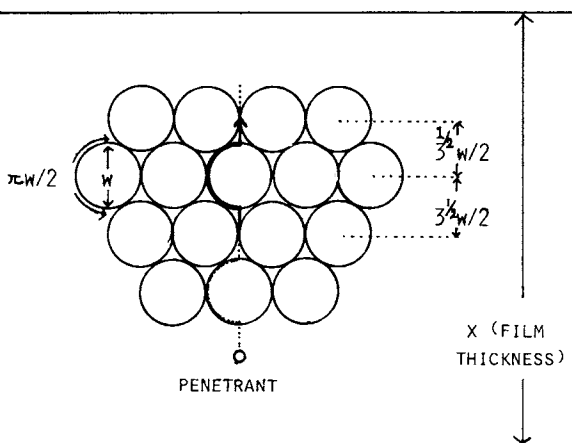


Fig. 8. Geometrical details of the diffusion path in the spherulite crystallite.

tour of one spherulite because the probability of taking a minimum distance is largest. According to this assumption, the distance between spherulite phases is  $(3^{1/2}/2)w$ . The increments of distance according to the detour by one spherulite phase is  $w(\pi/2 - 1)$  if the penetrant moves along the spherulite. Consequently, the effective thickness of the polyethylene film with apparent thickness  $x$ , becomes  $[1 + (\pi - 2)/2 \cdot 3^{1/2}]x$ . When the diffusion time  $t$  is a constant, the relation between the diffusion coefficients and diffusion path is  $x \propto (Dt)^{1/2}$ .<sup>13</sup> So the diffusion coefficient of completely amorphous polyethylene,  $D^*$ , becomes

$$D^* = D \left[ 1 + \frac{(\pi - 2)}{2 \cdot 3^{1/2}} \right]^2 x^2. \quad (12)$$

The actual value will be smaller than the one predicted from this equation, because the penetrants will take a linear course of the shortest distance possible as they move along spherulite. The values determined by applying this equation are shown in Figures 9 and 10. Where the polystyrene content becomes a large volume fraction, it is thought that  $n$  of eq. (8) becomes +1.

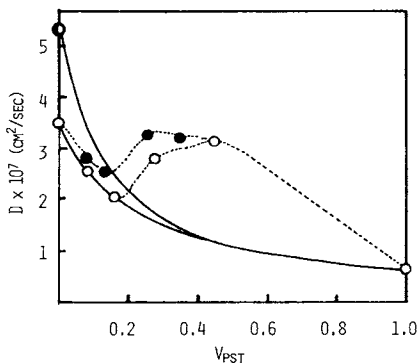


Fig. 9. Effect of composition heterogeneity for diffusion at  $n = -1$ : (O) before extraction; (●) after extraction; (●) predicted value of completely amorphous polyethylene.

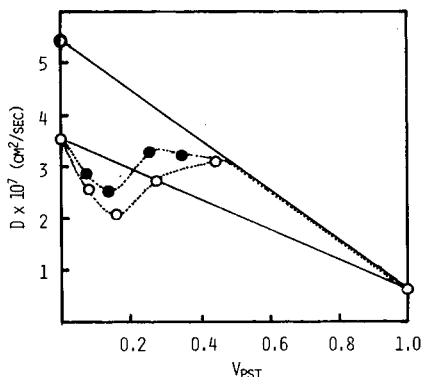


Fig. 10. Effect of composition heterogeneity for diffusion at  $n = 1$ : (O, ●, ◐) same as Fig. 8.

Figure 10 seems to fit better than Figure 9 as a prediction figure of the composite effect.

### Grafted Side Chains and Homopolymers

Kamel et al.<sup>14</sup> calculated that the grafted polystyrene is up to twice the weight of the low-density polyethylene sample, while the maximum concentration of chains is only 1/10,000  $\text{CH}_2$  units of polyethylene. This is a very low concentration of branch points; and if that is the case, the grafted styrene should be expected to differ little from the homopolymer by measuring the physical properties. However, the two polymers do not display the same behavior as far as transport phenomena properties are concerned; that is, in Figures 2 and 3, the two curves must be identical, but solubility coefficients (Figs. 2 and 3) and diffusion coefficients (Fig. 4) exhibit separate curves owing to presence or absence of homopolymer. However, the results of DSC give a linear line for both styrene polymers as shown in Figure 7.

On removing the homopolymer, the values of both solubility and diffusion coefficients become larger. This may depend on the difference between the side-chain polystyrene and the polystyrene homopolymer or on the change in the morphologic state of the amorphous portion of polyethylene after removing the homopolymer.

Closer examination of physical properties versus volume fraction of polystyrene on the systems containing and not containing homopolymer must be considered to obtain new information on the nature of grafting and on the amorphous portion in polyethylene.

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